

**REPORT OF THE
MARINE CHEMISTRY WORKING GROUP**

**Dublin, Ireland
8–12 March 1999**

This report is not to be quoted without prior consultation with the General Secretary. The document is a report of an expert group under the auspices of the International Council for the Exploration of the Sea and does not necessarily represent the views of the Council.

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

Palægade 2–4 DK–1261 Copenhagen K Denmark

TABLE OF CONTENTS

Section	Page
1 OPENING OF THE MEETING	1
2 ADOPTION OF THE AGENDA.....	1
3 REPORT OF THE 86TH ICES STATUTORY MEETING	2
4 REPORTS ON RELATED ACTIVITIES	5
4.1 OSPAR and HELCOM.....	5
4.2 Intergovernmental Oceanographic Commission (IOC)	5
4.3 QUASIMEME	5
4.4 Any Other Activities.....	6
5 REPORTS ON PROJECTS AND ACTIVITIES IN ICES MEMBER COUNTRIES.....	6
6 REQUESTS FROM ACME AND REGULATORY COMMISSIONS.....	6
7 PLENARY PRESENTATIONS	6
7.1 EU SMT Project 'Quality Assurance of Sampling and Sample Handling' (QUASH)	6
7.2 Organic Compounds as Tracers	6
7.3 MATT Project under the EU-FAIR Programme.....	7
7.4 The Arctic Dilemma	8
8 SUB-GROUP ACTIVITIES AND DISCUSSIONS.....	8
8.1 Topics Requested by ACME	8
8.1.1 Review and endorse the updated list of chemical compounds that can be monitored on a routine basis (ICES C.Res.1998/12:31 a)	8
8.1.2 Review a note on how to identify topics under 'New contaminants and their relevance to the marine environment' and how this can be implemented (ICES C.Res.1998/2:31 b).....	10
8.1.3 Review information on contaminant concentrations in biological media as environmental indicators (ICES C.Res.1998/2:31)	11
8.1.4 Review information on QA systems used in laboratories involved in marine monitoring and report the outcome (ICES C. Res.1998/2:31 d)	12
8.1.5 Review progress on supplementary work to the Icelandic cod study (ICES C. Res.1998/2:31 e)	13
8.1.6 Review and report on information on estuarine transport of trace metals (ICES C.Res.1998/2:31 f).....	13
8.1.7 Review a note on tributyltin in the marine environment, with a view to submitting to ACME (ICES C.Res.1998/2:31 g).....	14
8.1.8 Review and report on the progress of the joint study on PCBs in fish-eating mammals (ICES C.Res.1998/2:31 h)	14
8.1.9 Review and report on progress in the collaborative work on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) (ICES C.Res.1998/2:31 i)	15
8.1.10 Review the note on synthetic musk compounds in the marine environment, with a view to submitting to ACME (ICES C.Res.1998/2:31 j)	15
8.1.11 Review and report information on modelling PCB bioaccumulation in the Seine estuary (ICES C.Res.1998/2:31 k).....	16
8.1.12 Review an updated paper on polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) (ICES C.Res.1998/2:31 l).....	16
8.1.13 Collate and critically review available data on the two main analytical techniques to measure PAH metabolites with the aim of establishing how robust each technique is with respect to its application to general monitoring and site-specific monitoring and develop a strategy to calibrate results obtained by both techniques, including the conduct of intercalibration exercises (ICES C.Res.1998/2:31 m)	17
8.1.14 Review progress on the application of high temperature techniques for the determination of total nitrogen in sea water (ICES C.Res.1998/2:31 n).....	17
8.1.15 Review and report on information on strategies for monitoring inputs of nutrients to the coastal zone (ICES C.Res.1998/2:31 o).....	18
8.1.16 Review information on the experience of the use of automated <i>in situ</i> chemical oceanographic systems for the observation of chemical variables (ICES C.Res.1998/2:31 p).....	19
8.1.17 Review the report on particulate organic carbon (POC) in anoxic waters (ICES C.Res.1998/2:31 q).....	20
8.1.18 In consultation with the ICES Oceanographic Data Centre and WGMDM, develop guidelines for the use of appropriate units for reporting data on nutrients and oxygen in sea water (ICES C.Res.1998/2:31 r).....	20

Section	Page
8.1.19 Review preliminary guidelines concerning QA of nutrients, chlorophyll and oxygen data (also including CTD measurements) (ICES C.Res.1998/2.31 s).....	20
8.1.20 Finalise the discussion on a standard chlorophyll a technique for use within ICES programmes, and prepare a report for ACME, in collaboration with WGPE, on the quality assurance of chlorophyll <i>a</i> (ICES C.Res.1998/2.31 t).....	20
8.1.21 Take note of the report from SGQAC (ICES C.Res.1998/2:31 v).....	21
8.2 Any Other Business Raised by the Subgroups.....	21
8.2.1 Organics Sub-Group	21
8.2.2 Chemical Oceanography Sub-Group	22
8.2.3 Trace Metals Sub-Group.....	22
9 PLENARY DISCUSSION OF SUB-GROUP WORK	22
10 ANY OTHER BUSINESS	23
11 RECOMMENDATIONS AND ACTION LIST	23
12 DATE AND VENUE OF THE NEXT MEETING	23
13 CLOSURE OF THE MEETING.....	23
ANNEX 1: LIST OF PARTICIPANTS	24
ANNEX 2: AGENDA	28
ANNEX 3: QUASIMEME TABLES.....	31
ANNEX 4: 'NEW' CONTAMINANTS AND THEIR RELEVANCE TO THE MARINE ENVIRONMENT	36
ANNEX 5: INFORMATION ON GERMAN SEABIRD EGG STUDIES (TRACE METALS)	38
ANNEX 6: MARINE INSTITUTE MED/BIOTA ICES REPORTING DATABASE AND QC DATABASE.....	49
ANNEX 7: THE ENVIRONMENTAL DISTRIBUTION AND EFFECTS OF TRIBUTYL TIN- AN UPDATE TO 1999.....	52
ANNEX 8: MONO- AND NON-ORTHO CHLORINATED BIPHENYLS IN MARINE MAMMALS OF THE NORTHERN ATLANTIC OCEAN AND THE BALTIC SEA: A LITERATURE SEARCH IN AQUATIC SCIENCES AND FISHERIES ABSTRACT (ASFA) FOR THE PERIOD SINCE 1990.....	59
ANNEX 9: POLYCYCLIC MUSK FRAGRANCES IN THE AQUATIC ENVIRONMENT	65
ANNEX 10: DRAFT GUIDELINES FOR QUALITY CONTROL AND METADATA SUPPORT OF DISCRETE HYDROGRAPHICAL DATA IN MARINE ENVIRONMENTAL MONITORING PROGRAMMES	77
ANNEX 11: OVERVIEW AND RECOMMENDATIONS FOR THE DETERMINATION OF CHLOROPHYLL <i>a</i> BY SPECTROSCOPIC METHODS	85
ANNEX 12: ACTION LIST	93
ANNEX 13: RECOMMENDATIONS	95

1 OPENING OF THE MEETING

The Chair, Dr B. Pedersen, opened the meeting of the Marine Chemistry Working Group (MCWG) at 10.00 hrs on 8 March 1999. Mr David de G. Griffith welcomed MCWG on behalf of the Marine Institute's Fishery Research Centre.

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

2 ADOPTION OF THE AGENDA

The terms of reference for this meeting of the Marine Chemistry Working Group [ICES C.Res.1998/2:31] were to:

- a) review and endorse the updated list of contaminants which can be monitored on a routine basis;
- b) review a note on how to identify topics under 'New contaminants and their relevance to the marine environment' and plan how this can be implemented;
- c) review information on contaminant concentrations in biological media as environmental indicators and report on the outcome;
- d) review information on QA systems used in a laboratory involved in marine monitoring and report on the outcome;
- e) review progress on supplementary work to the Icelandic cod liver study;
- f) review and report on information on estuarine transport of trace metals;
- g) review a note on tributyltin in the marine environment, with the view to submitting it to ACME;
- h) review and report on the progress of the joint study on PCBs in fish-eating mammals;
- i) review and report on progress in the collaborative work on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe);
- j) review the note on synthetic musk compounds in the marine environment, with a view to submitting it to ACME;
- k) review and report on information on modelling PCB bioaccumulation in the Seine estuary;
- l) review an updated paper on polybrominated diethylethers (PBDEs) and polybrominated biphenyls (PBBs) with a view to submitting it to ACME;
- m) collate and critically review available data on the two main analytical techniques to measure PAH metabolites with the aim of establishing how robust each technique is with respect to its application to general monitoring and site-specific monitoring and develop a strategy to calibrate results obtained by both techniques, including the conduct of intercalibration exercises;
- n) review progress on the application of high temperature techniques for the determination of total nitrogen in sea water;
- o) review and report on information on strategies for monitoring inputs of nutrients to the coastal zone;
- p) review information on the experience of the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables;
- q) review the report on particulate organic carbon (POC) in oxidizing waters;
- r) in consultation with the ICES Oceanographic Data Centre and WGMDM, develop guidelines for the use of appropriate units for reporting data on nutrients and oxygen in sea water;
- s) review preliminary guidelines concerning QA of nutrients, chlorophyll and oxygen data (also including CTD measurements);
- t) finalise the discussion on a standard chlorophyll *a* technique for use within ICES programmes, and prepare a report for ACME, in collaboration with WGPE on the quality assurance of chlorophyll *a*;
- u) contribute to the ICES strategic planning process through assisting the Marine Habitat Committee in the following tasks:
 - i. formulating tactics to achieve the six objectives adopted by the Committee,
 - ii. suggesting and/or developing activities and products to fulfil the objectives,
 - iii. estimating the resources required for each activity according to categories that will be supplied,
- v) take note of the report from SGQAC.

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

The annotated agenda is provided in Annex 2.

The work outlined in the agenda was carried out in three Sub-Groups. The members and guest participants were grouped as follows:

Chemical Oceanography Sub-Group (COSG): S. Carlberg (Chair), A. Aminot, L. Føyn, M. Krysell, K. Nagel, J. Ólafsson, O. Vagn Olsen.

Trace Metals Sub-Group (TMSG): G. Asmund (Chair), M. Bloxham, J.F. Chiffolleau, B. Pedersen, P. Woitke, M. Leermaker, V. Besada, C. Duffy.

Organics Sub-Group (OSG): J. de Boer (Chair), J. Klungsøyr, E. Andruliewicz, A.J. Biscaya, M. Cleemann, E.H.G. Evers, M. Haarich, B. Jansson, M. Lebeuf, E. McGovern, T. Nunes, P. Roose, D. Wells, A. Abarnou, A. Talvari, J. Suijlen, C. Allchin, A. Rowe, B. Mc Hugh, P. Behan, J. Tronczynski.

3 REPORT OF THE 86TH ICES STATUTORY MEETING

The Chair informed the participants that all of the tasks requested for consideration by MCWG at the 1998 ICES Annual Science Conference (86th Statutory Meeting) had been incorporated into the draft agenda.

MCWG was asked to contribute to the ICES strategic planning process through assisting the Marine Habitat Committee in the following tasks (ICES C.Res.1998/2.31 u):

- i. formulating tactics to achieve the six objectives adopted by the Committee;
- ii. suggesting and/or developing activities and products to fulfil the objectives;
- iii. estimating the resources required for each activity according to categories that will be supplied.

This task was dealt with under this agenda point.

Stig Carlberg (Chair of ACME) first presented the process of the ICES strategic planning, and the result so far, to the MCWG. He also explained the draft objectives of the Marine Habitat Committee, as agreed at the ICES Annual Science Conference in 1998, and emphasized how he thought some of the objectives relate to current and possible future work of MCWG.

MCWG discussions on the ICES strategic planning focused especially on the following items:

- 1) How can we maintain and enhance access to high quality expertise on marine habitat quality relevant to societal development?
- 2) Availability of resources, to work for ICES (MCWG). How have we solved it in the past? Suggestions for the future.
- 3) How does the existing (for this year and the coming year) work program of MCWG fit into the six objectives of the Marine Habitat Committee? Products that we can fill in? Are there any items that do not fit these objectives?

Several views and ideas were exchanged and they are summarised in the following paragraphs.

Ad 1.

The general view was that the scientific expertise of the MCWG can only be maintained through the active participation and contribution of research scientists to the work of this group as well as through the professional commitment and personal involvement of its members.

It is rewarding for the MCWG members to get a feedback, recognition and encouragement from elsewhere in the ICES system that what has been produced by the MCWG is useful for its parent committee, other working groups or, through the Advisory Committees, for ICES member countries or partner organisations. This will contribute to maintain and further enhance production of the high quality expertise of MCWG.

But more important is that the MCWG members feel that their time spent on participation in a Working Group is of direct use to themselves as scientists and to their institutes.

MCWG members feel that ICES fulfills these requirements since:

- 1) The parent committee remit is wide enough to allow WGs to propose work items which are interesting enough to keep members attending the WG meetings as well as serving the needs of ICES.
- 2) In contrast to many international scientific conferences the WG provides a forum that is non-competitive and instead concentrates on two-way communication between members. This fact promotes intersessional cooperation between individual members or groups of members and effective exchange of relevant scientific information between ICES countries.
- 3) The MCWG provides an international forum of experts on marine environment monitoring, on marine habitat quality related to the anthropogenic contamination of the marine environment, and other related topics that is unique to members of the MCWG, which means that they do not have to duplicate their work in other fora.
- 4) The MCWG covers not only the (narrow) field of analysis but the whole spectrum from sampling programmes and sampling techniques to validation and interpretation of data.

Some ideas for improvements were also suggested.

A more effective direct support from ICES to the WGs would improve the possibilities to maintain and further enhance the production of the high quality expertise of MCWG. In this respect, the identification and allocation of necessary resources should be undertaken. This includes, for instance, the development and support of a networking system for more efficient access to the information and communication processes between relevant environmental fora, organisations, programs, activities and MCWG. Intersessional activity of acting chairs, including official representation and participation at scientific symposia and meetings should be supported. A better communication system should be established between the ICES Scientific Committee and its WG experts. Participation to MCWG activities of members from USA and Canada is valued and should be further encouraged.

It is also recommended that processing of manuscripts for publication in the *ICES Cooperative Research Report* series is accelerated and that the reports are made available via the Internet to widen their distribution and impact.

Some of the work of the various ICES working groups could also be made available through the Internet.

The international community of ICES as well as the working group participants would all benefit from this. The report of the results of the last ICES intercomparison exercise on trace metal in seawater in 1996 is not yet published even though it was submitted to ICES some time ago. This causes inconvenience for the participants, who have no official information on their performance which they can refer to, e.g., in their own publications. It can also result in a decrease in motivation to participate in future exercises. A similar delay was seen for the publication of the report on the ICES/IOC/OSPAR interlaboratory study on CBs in marine media.

In order to maintain a critical mass of MCWG the recognition of national commitments is needed. This can be achieved by a continuous process of a positive feed-back on national and institutional levels from the ICES/WGs. The Member Countries have a need for advice and/or recommendations made by the working groups, which could be implemented in their own national strategies, e.g., for monitoring. The national members of the WGs also play an important role in improving feedback.

Ad 2.

The second discussion concerned the item on 'Availability of resources'. MCWG noted the well known fact that WG members on the environmental side of ICES often have to carry out their intersessional work for their WG in their spare time rather than during official office time. This is in contrast to the fisheries side where WG members, particularly in assessment WGs, can use their regular work as input to the WG. Several countries have a very limited budget for environmental work and cannot find the necessary resources to send (or even appoint) an expert to a meeting. It was suggested by some of the participants, that holding the MCWG meetings regularly at ICES Headquarters in Copenhagen (e.g., every second or third year) could increase the participation from several countries.

It was also suggested that ICES could play a more active role in supporting applications for research projects and that the new ICES strategic plan could be used to support the relevance of a project if this falls within the six objectives of the Marine Habitat Committee.

The discussion then focused on increasing resources in general for ICES. MCWG agreed that there is a need to make ICES more visible and better known both nationally and internationally. A continuous process of positive feedback on national and institutional levels from the ICES/WGs would support this work and help ICES to maintain its image as an important centre for marine sciences.

This should also allow a better and more effective link to societal needs and demands concerning marine habitat quality in Member Countries and respective national priorities.

Ad 3.

The third discussion on the strategic planning concerned the draft objectives of MHC. MCWG welcomed in general the idea of having approved objectives and also supported these draft objectives. The role and contribution of MCWG appears to be important in the achievement of these objectives. How the working programme of the MCWG can be adapted to meet the objectives was especially discussed. Some comments to and suggestions for additions of objectives were also made. The transfer of knowledge between participating countries is considered to be very important. It is suggested that this should be added as a new objective of MHC.

The Chemical Oceanography Sub-Group (COSG), found, however, that in the strategy document there was no definition of the word 'habitat'. If the word is interpreted in a wider context, the proposed six objectives are acceptable to the COSG; but in the absence of any clarification of 'habitat', the COSG was not able to make detailed comments on the objectives. The COSG discussion concerning the working programme for COSG in relation to the MHC objectives is reported in Section 8.2, below.

The two other Sub-Groups mainly considered objectives 1, 4 and 6 in the identification of activities and work products of MCWG supporting their fulfilment:

Objective 1: Development of a toolbox to assess marine habitat quality.

Objective 4: Development of knowledge on the effects of anthropogenic contaminants on habitat and depending living resources.

Objective 6: Enhancement of the knowledge on monitoring methodology in relation to the well-being of marine habitats.

A special comment was made about objective 4, where it was felt that there is a discrepancy between the objective and the subsequent text, as the objective only mentions *the effects* of anthropogenic contaminants but not the *presence, behaviour and fate* which is described in the subsequent text. The comment was also made that the current state of knowledge is not sufficient to describe the behaviour and fate even of the 'old' anthropogenic contaminants.

Objective 6 was regarded as especially important for the MCWG as it focuses on monitoring methods. The importance of improvement in sampling and sample handling, prioritisation of new anthropogenic contaminants and analytical methods, developing new techniques of quality assurance to be applied by all the Member Countries, and the establishment of a specimen bank for retrospective monitoring studies should be stressed.

Some examples were given on how the work programme of the MCWG conformed to the suggested MHC objectives in the past or in the present (see below).

MCWG contributes to selecting 'contaminant indicators' by:

- preparation of the extensive overviews on contaminants (e.g., PBBs and PBDEs, musk compounds);
- information on environmental levels and trends;
- identifying 'new' contaminants;
- proposing contaminants for monitoring programs and evaluating feasibility (e.g., choice of seven CB congeners).

MCWG contributes to the development of knowledge on the effects of anthropogenic contaminants by:

- discussion and improvement of selective analytical methods of toxic compounds (e.g., planar CBs) and their metabolites (e.g., PAHs);

- overviews on exposure to antifouling booster biocides and contaminants (e.g., TBT, DNA-adducts of PAHs, etc.);
- promoting biological effects studies (e.g., imposex).

MCWG contributes directly to the enhancement of knowledge of marine monitoring methodology by:

- organising intercomparison studies;
- preparation of guidelines on contaminants analysis;
- identification of background levels.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR and HELCOM

There was no official request from OSPAR or HELCOM.

4.2 Intergovernmental Oceanographic Commission (IOC)

During the MCWG meeting in 1998 different initiatives to improve the contacts between ICES MCWG and the IOC were discussed, as there was a general feeling that the two organizations have several areas of interest in common. It was decided that all members should try to seek information about the IOC and report back at the next MCWG meeting. The GIMPE/MARPOLMON (Marine Pollution Research and Monitoring) seemed to be particularly interesting. The objectives of GIPME are described in the 1998 MCWG report.

Since the 1998 meeting, some of the members of the MCWG have tried to seek contact with the IOC, but without any great success. It was decided that MCWG should continue to work on improving contact with the IOC and B. Pedersen, as the Chair of MCWG, should contact the new Executive Secretary of IOC to discuss the possibilities of inviting a person from IOC to give a presentation of the work of IOC at the next MCWG meeting.

4.3 QUASIMEME

Dr D. Wells briefly informed about the progress of QUASIMEME. It is now six years since the launch of QUASIMEME in 1993. It has meanwhile gone from an EU pilot project to a Laboratory Quality Assurance Performance programme supported by its participating members. More than 100 laboratories worldwide have joined the scheme. ICES is represented on the Advisory Board, along with representatives from OSPAR and HELCOM. The active feedback from the participants and the Advisory Board is a key issue in the development and improvement of the programme.

The main areas of change in the 1998/1999 QUASIMEME programme are:

- the conduct of Training Workshops;
- launch of a Windows-based data transfer system;
- an extended development programme including links between biological effects and the EU BEQUALM project;
- improved test material.

The development exercises have been designed to provide a series of laboratory studies followed by a workshop to evaluate the exercise, provide training and plan for subsequent studies.

There have been three workshops during 1998/1999 covering the following areas:

- Organotin, a workshop held at the IVM, Free University, Amsterdam;
- PAH metabolites, a joint workshop with the IVM, Free University, Amsterdam and the Rogaland Research Institute, Norway, in the EU Standards, Measurements and Testing Project (see also agenda item 5.1.7);
- Chlorobornanes (CHBs, chlorinated camphenes or toxaphene) and their measurements in biota, held at the University of Basel

- The window-based data transfer system has made it possible to provide each participant with a database with their own performance which can be displayed, printed or passed to a third party as a part of their quality assurance of the environmental monitoring data.
- New development programmes include, e.g., marine snails for the determination of imposex, a progression of the organotin programme, and chlorophyll in solution and on filter papers. Both the chlorophyll programme as well as the imposex programme will be continued, the latter in cooperation with the new EU project BEQUALM which will be involved in establishing methods for the quality assurance of a wide range of biological effects methods.

For details about the QUASIMEME II Project, visit the web site of QUASIMEME, at the address <http://www.quasimeme.marlab.ac.uk/>.

4.4 Any Other Activities

Nothing was reported under this agenda item.

5 REPORTS ON PROJECTS AND ACTIVITIES IN ICES MEMBER COUNTRIES

Nothing was reported under this agenda item.

6 REQUESTS FROM ACME AND REGULATORY COMMISSIONS

All requests from ACME were included in the agenda.

7 PLENARY PRESENTATIONS

7.1 EU SMT Project ‘Quality Assurance of Sampling and Sample Handling’ (QUASH)

The status of the QUASH project was presented by the co-ordinators of the project, see below. The aim of the project is to establish validated methods for sample handling and pretreatment, and to improve the analytical results by identifying and reducing errors due to sampling and sample handling. The programme consists of six work packages (WP):

- 1) sampling and preservation of nutrients in sea water [Coordinator: Mr Stig Carlberg, Mr Mikael Krysell (SMHI, Sweden)];
- 2) monitoring contaminants in biota: lipid and water as cofactors [Coordinator: Dr Jacob de Boer (RIVO-DLO, NL)];
- 3) sampling of biological tissues [Coordinator: Dr Britta Pedersen (NERI, DK)];
- 4) sample handling and cofactors in relation to normalization procedures for sediments [Coordinator: Crete)];
- 5) preparation of test material, laboratory and field performance studies [Coordinator: (IVM, NL)];
- 6) laboratory and field performance studies [Coordinator: Dr David Wells (Aberdeen, UK)].

Interlaboratory studies focusing on sampling and sample handling of sea water, biota and sediments have been carried out in all of the QUASH work packages and practical workshops have been held to discuss the results from these exercises. A second phase of interlaboratory studies for the biota and sediment handling work packages is presently running. The outcome of these exercises will, e.g., provide us with outstanding and long-awaited contributions to the discussions on normalization of concentrations in sediment samples, as well as giving practical experience in several normalization techniques including sieving.

A great deal of work on QUASH has been done at the international level, but there have also been a number of initiatives at the national level in a number of Member Countries.

A remaining workshop will be held in October 1999 in the Netherlands where the QUASH project will be reviewed and information on all the work packages including workshop reports will be presented.

7.2 Organic Compounds as Tracers

Jo Suijlen from RIKZ in the Netherlands was invited in order to give a presentation on the potentials of fluorescent organic compounds as river water tracers. These compounds are carried along by rivers as natural contaminants. To

date, only a few have been identified (rhodamine B, sulpho rhodamine B and probably the fluorescent brightener DAS1). The HPLC-fluorometry-based method used is sufficiently sensitive to detect non-volatile, polar (fluorescent) compounds in natural samples from the North Sea and the North Atlantic using a sample volume of maximum 1 litre. A detection limit of about 0.2 pg/l (4×10^{-16} M) can be obtained for the rhodamines. The Rhine River is by far the largest source of these compounds to the open sea area. Since all detected compounds are photolytic, the observed concentrations have to be corrected for the decay due to photolysis. This is possible as several photolytic tracers are also present in the natural environment. The correction can be based on the measurement of the ratios of concentrations and of reaction rates.

Preliminary results, based on one set of samples taken during the EU-MAST XTRANS project, have shown that the percentage of Rhine water in Skagerrak samples appears to be about 2.5 %–3.5 %. The percentage of Rhine water between the North Cape and Bear Island is around 1 %. Also, the transport times of Rhine water have been estimated on the same set of results. This is possible due to the photolysis. The transport time of Rhine water to the Skagerrak is estimated to be about 150–200 days, to near the North Cape at about 2 years. Because of these potentials of the fluorescent compounds, they are well suited for the calibration and validation of flow models, which are the basis for water quality models.

During the XTRANS project, it appeared that the data on photolysis reaction rates already published in the literature cannot generally be applied to photodegradation problems in the marine environment. The reason for this is, e.g., that results obtained at the frequently used 254 nm line are completely useless for the prediction of photolysis in the aquatic environment. Most of the reported half-lives obtained by the irradiation of solutions in daylight give, in general, an incorrect impression of the persistence. One of the most-used fluorescent brighteners (DAS1) has been shown to have a half-life of about 5 hours on a sunny day, 21 June in Switzerland (J.B. Kramer *et al.*, 1996, Environ. Sci. Technol. 2227–2234). However, based on observations in the XTRANS samples of the Rhine plume up to Bergen, Norway, it has been demonstrated that the half-life of DAS1 in the sea is between 30 and 80 days. The fluorescent brighteners mentioned here are very persistent when they are released into the sea, as the attenuation of the photolytic active excitation wavelengths (320–380 nm) in the water column is very large.

For more information on this subject, see J.M. Suijlen and J.J. Buyse, 1994. Limnology and Oceanography, 1411–1423, where the basics of the method have been published.

7.3 MATT Project under the EU-FAIR Programme

B. Mc Hugh, J. de Boer, and J. Klungsøyr presented information on the MATT project under the EU-FAIR programme.

The European Research Project MATT (Investigation into the Monitoring, Analysis and Toxicity of Toxaphene) started in 1997 and has the main objective of providing information on toxicological risks to the consumer of toxaphene residues in fish from European waters. The means of achieving this objective are subdivided as follows:

- a study on the improvement of analytical methods for the determination of toxaphene in marine foodstuffs;
- a baseline survey on toxaphene concentrations in fish from European waters;
- studies on the carcinogenicity of toxaphene extracts from fish.

The analytical block consists of three main studies:

- a series of stepwise-designed interlaboratory studies;
- a study on gas chromatographic (GC) separation;
- a study on GC injection techniques.

The results of these three studies were presented here. The studies initially focused on the three congeners (CHBs) Parlar 26 [B12012-202] (2), 50 [B12012-212] and 62 [B30030-122], but at a later stage Nos. 40 [B12012-112], 41 [B21020-122] and 44 [B20030-122] were added, because they were reported to be the six most persistent toxaphene congeners. Total toxaphene analyses were not carried out.

The results of the interlaboratory study reflect, on one hand, the difficulties that particularly the inexperienced laboratories had in setting up a reliable toxaphene analysis, which shows the degree of difficulty of this analysis. On the other hand, the results show that a CV value of approximately 20 % is about the best that can be obtained at present, even for more experienced laboratories. This value is in agreement with results obtained in other

interlaboratory studies, such as a recent study organised by QUASIMEME in which CV values of 16 %–39 % were obtained for CHBs 26, 50 and 62 in cleaned marine mammal and fish extracts.

The multidimensional GC (MDGC) study showed that for CHB 26 it is very difficult to obtain a good separation from other CHBs. By using a 50 m × 0.15 mm CP Sil 8 column as a first column, it was possible to obtain complete separation for CHBs 50 and 62. This result was actually better than those of earlier MDGC experiments in which 25 m columns were used as a first column. However, for CHB 26 no real improvement was obtained. This means that the determination of CHB 26 in particular is very difficult, as also a good fractionation of this congener on a silica column is difficult to achieve. It is expected that for CHBs 40, 41 and 44 further separation problems will be encountered when using single-column capillary GC. Other columns are not of much help. On a CP Sil 19 column, CHBs 41 and 44 co-elute, as do CHBs 40 and 50.

The injection study showed that with on-column injection smaller RSDs were obtained. However, these experiments were carried out with standard solutions. The injection of sample extracts may, of course, produce different results with on-column injection due to contamination of the first part of the column. In that respect, pressure-pulsed splitless injection may be a good alternative.

The toxicological studies are being carried out at present. Initial results of *in vitro* studies indicated a relatively high inhibition of gap-junction intracellular communication by technical toxaphene, which may be an indication of tumour promotion. Other toxicological results and results of the baseline study are expected to be available by the end of 1999.

7.4 The Arctic Dilemma

Gert Asmund showed a video from Greenland entitled, 'The Arctic dilemma'. The video was based on the results of the Arctic Monitoring and Assessment Programme (AMAP), which several of the MCWG members have contributed to. The video highlighted the problem with long-range transport of several contaminants from the more industrialised areas to the pristine area of the Arctic and their effects on humans.

Several contaminants are biomagnified through the food chain. The highest concentrations are found in the top predators, e.g., seals and fish, which are important foods for the indigenous people. As a result, increased concentrations of many contaminants have been found in the blood samples of these people, concentrations that in many cases were very high. This is alarming and further investigations are now taking place to investigate eventual effects on humans of these high concentrations.

8 SUB-GROUP ACTIVITIES AND DISCUSSIONS

For the sake of clarity, the outcome of the discussions on topics requested by ACME will be presented in Section 8.1. Then, additional items discussed in the Sub-Groups will be dealt with in Section 8.2 below. ICES C.Res.1998/2.31 u) was already dealt with in agenda item 3.

8.1 Topics Requested by ACME

8.1.1 Review and endorse the updated list of chemical compounds that can be monitored on a routine basis (ICES C.Res.1998/12:31 a)

The overall performance in the QUASIMEME programme for a given parameter was used as an indicator of the ability of laboratories to perform routine monitoring. A tabular presentation prepared by D. Wells outlined the performance of laboratories as a whole group (see the tables in Annex 3). The tables provide a summary of the results from ten exercises carried out over a period of 2½ years (June 1996–December 1998) for determinands analysed in the QUASIMEME 2 Programme (CBs, organochlorine pesticides (OCPs), and metals in biota; metals, PCBs, OCPs, and PAHs in sediments; and trace metals and nutrients in sea water).

It must be realised that results from all laboratories are included, not specifically OSPAR laboratories or groups of laboratories representing the ICES community, for which comparable material is not presently available.

In the QUASIMEME 2 scheme, analytical performance is evaluated using individual laboratory Z scores. For a particular contaminant/medium combination in an intercomparison exercise, these are defined as

$$Z = \frac{\bar{c} - \bar{c}}{k}$$

where \bar{c} is the laboratory mean contaminant concentration, \bar{c} is an assigned value, usually given by the mean for a group of reference laboratories, and k is an externally defined total allowable error for laboratory bias, taking a value of 12.5 % (6 % for nutrients) and increasing to 50 % towards the limit of detection.

A global target of $|Z| < 2$ is used to characterize 'satisfactory' analytical performance by a laboratory. The criterion for satisfactory group performance for a contaminant/medium combination is that at least 75 % of the laboratories have attained a satisfactory analytical performance.

Specific comments to the Nutrients Exercises

During the period mentioned above, a total of ten intercomparison samples for oceanic waters and eleven samples for estuarine waters, covering a range of concentrations, were distributed for the analysis of dissolved ammonia, nitrite, phosphate, silicate, total nitrogen, total phosphorus, and total oxidized nitrogen (nitrate + nitrite). For either type of water, up to 40–50 laboratories returned results. The overall assessment of these groups of laboratories can be taken as an indication of their capacity to monitor nutrients.

The group success indicator shows the number of intercomparison rounds where the performance of the group as a whole was satisfactory; this number can be 10 or 11 at the most for the two types of water, respectively. When comparing the laboratories' results from 1997 and 1998, it appears that some determinands that did not give rise to fully satisfactory performance in 1997 actually attained satisfactory performance in 1998. This was true for ammonia and phosphate. Some improvement is also shown for Total-N. For Total-P some laboratories still encounter problems and the overall group performance is not entirely satisfactory.

Specific comments to the trace elements results

The Trace Metals Sub-Group used this information to update the tables presented in the 1998 MCWG report in which the minimum trace metal concentrations in sediments and biota for which more than 60 % of the laboratories achieved scores $|Z| < 2$ were presented (see Table 1, below).

Table 1. Lowest concentrations of trace elements in sediments and biota which can be monitored on a routine basis by the majority of laboratories (outcome of ten QUASIMEME LPS carried out June 1996–December 1998).

Trace element	Sediments (dry weight)	Biota (wet weight)
Zn	75 mg/kg	≤ 4.6 mg/kg
Cd	340 µg/kg	Fish tissue 5 µg/kg
Pb	40 mg/kg	Problems for the majority of the labs, even at 1 mg/kg
Cu	17 mg/kg	≤ 0.3 mg/kg
Cr	28 mg/kg	Problems for the majority of the labs, even at 2 mg/kg
Ni	23 mg/kg	For cod liver and muscle, 0.1 mg/kg
As	6 mg/kg	≤ 1.3 mg/kg
Hg	120 µg/kg	≤ 28 µg/kg
Al	Value not available*	
Mn	≤ 750 mg/kg	
Fe	≤ 2.8%	
Li	≤ 35 mg/kg	
Sc	≤ 7.6 mg/kg	

*'≤' means that only a less than concentration can be given and not a minimum concentration which the majority of the laboratories is able to analyse. A minimum concentration could not be calculated from the results of the QUASIMEME LPS, as the concentrations of the samples used were not low enough.

*Method dependent. Some laboratories do not use hydrofluoric acid for complete dissolution of the sample. There is generally no detection limit problem for aluminium.

General comments to Tables in Annex 3

The tables presented in Annex 3 give an idea of the overall performance of the laboratories as a whole group. From the tables it is clear that not all laboratories are able to meet the criteria of $|Z| < 2$ for various parameters, this is particularly true for OCPs. Laboratory performance with respect to nutrients can, however, be regarded as more encouraging, as it must be realised that a situation where all laboratories simultaneously show good performance is unlikely to occur.

This also shows that laboratories used in international marine monitoring programmes should be carefully selected and should always submit QA information together with their data. It is important to keep track of the long-term performance of the laboratories, and it is urged that long-term proficiency testing schemes be followed.

It was recommended that the tables are updated each year, and that they show only data from the three most recent years. Efforts will be made to prepare a similar table next year based on a smaller selection of laboratories, in particular, those reporting to ICES and OSPAR.

It was also recommended that updating the list of reference materials presented at the MCWG meeting in 1998 should remain on the agenda for the 2000 meeting. E. McGovern volunteered to update the list before the meeting.

8.1.2 Review a note on how to identify topics under ‘New contaminants and their relevance to the marine environment’ and how this can be implemented (ICES C.Res.1998/2.31 b)

At the 1998 MCWG meeting, Prof. Bo Jansson agreed to prepare an overview of ‘New contaminants and their relevance to the marine environment’. During the intersessional period he realized that a lot of activities have already been undertaken in this field. He informed the members of the Sub-Group that he would give an overview of the current activities rather than construct a list himself. See also Annex 4, where a short summary of Bo Jansson’s presentation, ‘New contaminants and their relevance to the marine environment’, is given. During his presentation, he discussed the priorities set by marine conventions, international monitoring programmes, and risk assessment programmes such as the OSPAR DYNAMEC group, UNEP POPs, and the EU risk assessment of existing substances (see also Annex 4). He further discussed the alarm signals in the marine environment (compounds being found far from sources or at increasing levels, observed effects) and some recently found compounds. Finally, he identified the role the MCWG can play in this field, namely to monitor if measures have the intended effect, to look for ‘new’ substances, support those who set priorities and support risk assessors with exposure data.

In the ensuing discussion, several comments were made concerning the screening for new contaminants. It was remarked that a set of guidelines on how to proceed with this type of work would be helpful and that this type of work should be coordinated as much as possible by a central organization such as the marine conventions. The work is also quite different from monitoring, as for a first approach an estimate of the concentrations within one order of magnitude can be sufficient. The importance of linking ‘new’ contaminants with their sources was also emphasized. Frequently, the chemical industry will not reveal its sources or diffuse sources might be involved. The lack of information from the industry is also one of the complaints of the INPUT group of OSPAR. It was, however, made clear that for risk assessment purposes, the chemical industry does reveal its production figures although this information is generally kept a secret. The group further discussed the OSPAR 1998/14/1 list of candidate substances that was made available for the meeting. Apparently, not all the compounds on the list are toxic or persistent. This emphasizes the importance of prioritization procedures. It was remarked that biological effects are an important factor in risk assessment, together with exposure levels. However, in many cases the toxicology of the compounds in question is not well enough established for a proper evaluation, although routine toxicological tests are generally part of the evaluation processes. The Swedish government has proposed, based on the precautionary principle, that within ten years products in Sweden should not contain persistent compounds without taking toxicity into account. With regard to the alarm systems that were given in the presentation, it was mentioned that the presence of a compound far away from its source illustrated the importance of Arctic research. Looking for increasing concentrations may often prove difficult or even impossible. Specimen banks are useful in this respect and should be encouraged by ICES. The group further discussed a number of initiatives that are currently under way. In Germany, a non-target screening for new contaminants is being undertaken and Peter Woitke has agreed to provide the group with an update of this for the next meeting. In Japan another approach is used. Apparently, when a laboratory develops a method it is distributed to the others who are then encouraged to analyse a limited number of samples. In this way an extensive list of compounds has been set up and should be investigated. This approach was suggested to be applicable for this group, as it is similar to exercises undertaken in the past.

The group in any case recognized the importance of looking for new substances and recommended that it should be one of the objectives of ICES. A clear distinction should be made between this type of work and routine monitoring. Some room should be created in monitoring programmes to look for new contaminants. The work should be defined as a survey or screening instead of monitoring for new compounds. This is considered to be an important part of risk assessment. MCWG can play an important role in this field. It could, for instance, act as a forum to distribute data on 'new' compounds or evaluate the lists of new contaminants that have currently been produced. MCWG should continue to study new contaminants and to produce useful background information on new contaminants for OSPAR and HELCOM.

8.1.3 Review information on contaminant concentrations in biological media as environmental indicators (ICES C.Res.1998/2.31)

At the MCWG meeting in 1998, the Trace Metals Sub-Group had initiated work on the use of biological media as environmental indicators of contaminant concentrations, as they felt that this subject was highly relevant in many ICES Member Countries. This is supported by the fact that the use of indicators is an important part of the Marine Habitat Committee's objective 1 (Development of a toolbox to assess marine habitat quality). A productive discussion on the topic was undertaken, although no working paper was presented at the meeting. The advantages and disadvantages of various types of biological media were discussed using examples presented by the group members. A summary of the discussions is given below.

Contaminant concentrations in biota as environmental indicators

(1) Seabird eggs

At the MCWG meeting in Stockholm in 1998, Anders Bignert gave a presentation on the Swedish seabird egg monitoring programme, which indicates that seabird eggs are an appropriate matrix for assessing temporal trends of mercury and organochlorines, but not for some of the other metals, e.g., Cd. Careful selection of the right species is, however, required, due to the migratory nature of some species. Black guillemot eggs are used in the Swedish monitoring programmes as well as in the Arctic monitoring programme (AMAP), whereas in the German monitoring programme, herring gull, oyster catcher and common tern eggs are used. The latter was presented by Peter Woitke at this year's meeting. He gave an overview of the German studies on seabird eggs as a monitoring matrix. Extensive study programmes have been carried out in Germany since 1975, mainly by the research group at the Institut für Vogelforschung, An der Vogelwarte 21, 26386 Wilhelmshaven, Germany.

The work has demonstrated temporal trends, spatial trends, and differences between species.

Clearly seabird eggs have proven useful for environmental monitoring also in Germany. The overview presented by Peter Woitke is attached as Annex 5, and contains detailed references to the published results of the German seabird egg studies.

(2) Shellfish

Due to their sessile nature, shellfish have historically been considered to be good environmental indicators of trace metal concentrations. However, the discussions indicated that although this is generally true, care should be taken when using these organisms.

In colder waters, e.g., off the Greenland coast, it has been shown that although *Mytilus edulis* reflects stable environmental conditions (concentrations) as well as increases in trace metal levels, e.g., for Pb, this species does not reflect the subsequent return to background levels, measured by chemical analysis of the water in which the shellfish are growing. This is most probably due to the storage of metals such as Cd, Zn, and Pb as metallothionein in metal-binding complexes, which are not excreted. Because the population in such climates has a very slow turnover, the same cohort of shellfish may be analysed each year for many years and therefore does not reflect the return to normal background levels.

This scenario would not occur in more temperate waters because new cohorts of adults of the correct sample size will occur every 2–3 years. For example, oysters from along the French coast were considered to generally reflect both an increase as well as a decrease in the metal concentrations in the environment. It was reported that the levels of Cd had decreased from 170 to 40 mg/kg over a ten-year period in a contaminated area.

In a Spanish study, concentrations in shellfish were considered to be a good indicator of Hg contamination in the environment in spite of the slow elimination of this element from the organism. It was reported that high levels of Hg were found in the shellfish in the vicinity of a chlor-alkali plant over ten years, indicating a contamination problem due to the plant. However, after changes in the process at the plant, a steady decrease in Hg concentrations was observed over the following three years.

(3) Fish

The choice of fish is important due to the mobile and migratory nature of fish. Fish liver and bone were considered to reflect Pb contamination in the environment, as was Hg in fish muscle. However, monitoring of Hg in flounder muscle in the Sound at a site of known Hg contamination had shown that the Hg concentration varied from year to year even though a slow overall decrease had taken place during the past 15 years. It was thought unlikely to be attributable to analytical variations, but reflected some unknown natural variation (e.g., temperature, salinity, tidal variations, nutrient levels) but this was difficult to prove. The group concluded that generally concentrations in biological media could be good environmental indicators, especially if the natural variations in the environment are well understood.

(4) Seaweed

The group also realised/agreed that metal concentrations in seaweed are a good environmental indicator of Pb and Zn, and probably several other elements. However, the use of this type of biota has often been overlooked in many monitoring programmes in the past.

The group also discussed the importance of determining the environmental background levels of trace metals. The analysis of samples from 'pristine' sites could be useful in this respect, as was the use of historical specimens, e.g., bird feathers and eggshells. The development of an international specimen bank was discussed as an alternative for the future.

The group also highlighted the need for supporting chemical oceanographic data in order to improve our possibilities to use metal concentrations in biota as indicators. The importance of comparing the concentrations in biota with historical data, trace metal concentrations in sediments and sea water was also stressed, as they also contribute to a better assessment of the data.

The Sub-Group decided to continue the work intersessionally. All members of the Trace Metals Sub-Group should send examples similar to those given above on the use of metal concentrations in biota as indicators for contamination, to Martin Bloxham. He will then collate the data and prepare a note on the topic for the next MCWG meeting. Martin Bloxham was asked specifically to try to seek information on British seabird egg studies and also if there is any information on seabird egg monitoring studies in Ireland.

8.1.4 Review information on QA systems used in laboratories involved in marine monitoring and report the outcome (ICES C. Res.1998/2:31 d)

Peter Wotke had prepared a discussion paper for this agenda point which was available at the meeting. The paper, presented by Peter Wotke for the Trace Metal Sub-Group, was based on experience with the QA system used in the German Marine Monitoring Programme (GMMP).

Due to the involvement of over twenty laboratories in the German monitoring programmes, a national coordination of the procedures for the QA of data is required, in order to be able to compare the data with some confidence. The QA procedure used is based on three main parts:

- 1) validation of analytical methods;
- 2) internal quality control (including the use of CRMs or in-house reference materials and the plotting of QC charts);
- 3) participation in interlaboratory performance studies.

Several views and ideas were exchanged which are summarised below.

There was general agreement that the three main parts of the German QA procedures were also the basic requirements for the QA procedures in most laboratories.

It was, however, pointed out that the use of CRMs does not always give adequate information on the ability of the laboratories to measure real samples. The reported standard deviation on CRMs is always much smaller than the observed relative errors in intercomparison exercises. The CRMs used must match the samples with respect to sample matrix and contaminant levels in order to be informative. Gert Asmund presented some graphs showing the relative error in intercomparison exercises expressed as a function of the trace element concentrations in the samples which emphasize this. The graphs showed that there could be high relative errors for some elements, below a certain concentration. It was suggested that more realistic limits of quantification can be derived using graphs of this type, as well as a more correct estimate of the uncertainty of the analytical method at a given concentration.

The reporting of QA data together with monitoring data has been the subject of ongoing discussion in the MCWG. The discussion focused on the differences in QA information produced by laboratories for their national programmes and that QA information normally sent by them to ICES. More QA data are usually reported for national programmes than are required by ICES, including different CRMs, QC charts, and the results of laboratory performance studies. It was deemed useful that the laboratories include a definition of their detection limits in their national comments to OSPAR. A standardisation of rounding-off values is also needed.

The procedures used in different countries varies, however, e.g., due to the fact that some national laboratories report directly to ICES according to the format used by ICES, whereas others report to a national data centre.

Martin Bloxham described the method used by Ireland, involving the use of an Access database for entering the monitoring data and a linked Access database for the QA data. Each sample in the monitoring database is linked to the QA database through an identifying code. This method also provides a rapid means of transferring data to the ICES database. It was stressed that there is a need to update the reporting format for QA data used by ICES if the QA data are to be used in the assessment of monitoring data. This was already an issue at the 1998 MCWG meeting in Stockholm and MCWG proposed that a method like that described by M. Bloxham should be used. This method is described in Annex 6.

It was also stressed that guidelines on how QA data are to be used in the assessment of monitoring data need to be established. Reference was made to an approach to quality assessment recommended in a recent publication by Dobson *et al.* (J. Environ. Monit., 1999, 1: 91–95).

A QA evaluation of monitoring data, e.g., in OSPAR, should not take place at the last moment, but should be ready before the data evaluation takes place. Finally, it was emphasised that the data transfer may also be a source of error. The data transfer procedures should be checked and should in fact have their own QA procedure.

The information available concerning this agenda item, together with interpretation of the Chemical Oceanography Sub-Group on this task, was such that the COSG decided not to treat this agenda point separately. Instead the Sub-Group decided that as certain parts could be treated together with agenda item 8 where information was available, this was the best way of bringing the subject forward during the meeting.

As more information will almost certainly become available during 1999, the group concluded that this agenda item should stay on the working schedule for next year. J. Klungsøyr, P. Roose, P. Woitke, and M. Cleemann volunteered to prepare a discussion paper for the 2000 MCWG meeting on the subject of QA.

8.1.5 Review progress on supplementary work to the Icelandic cod study (ICES C. Res.1998/2:31 e)

A study on the relations between cod length, size, fat and water content of the liver, and the trace element and/or major element concentrations in cod liver was presented by Guðjon Audusson at the MCWG meeting last year in Stockholm. This study was on Icelandic cod, and is now being published in the Icelandic journal 'Rit Fiskideildar' in English.

Cod liver data in the ICES database from the Baltic Sea, the Kattegat, Skaggeirak, the North Sea, and the Norwegian Sea have been treated intersessionally the same way as the Icelandic cod data (for details, see last year's report) to investigate whether the relations found for the Icelandic cod have a more general applicability. It was found that this was generally the case, although there were some deviating results in the Baltic cod data sets.

It was recommended that a small Sub-Group, consisting of Jørgen Nørrevang Jensen (ICES Environmental Data Scientist), G. Audusson, and G. Asmund, continue to work on this subject intersessionally with a final view to publishing the data in the open literature. This, however, requires that permission from the countries that have supplied the data to ICES is obtained.

Action: Jørgen Nørrevang Jensen (ICES), G. Audusson, and G. Asmund volunteered to write a paper on these findings.

8.1.6 Review and report on information on estuarine transport of trace metals (ICES C.Res.1998/2:31 f)

J.F. Chiffoleau presented a working paper to the Trace Metals Sub-Group, which is an overview on the occurrence, behaviour and fluxes of trace metals in estuaries. The topic has been of interest to the MCWG for many years and is still highly relevant for ICES as it forms an integral part of objective 4 of the Marine Habitat Committee. A better understanding of the behaviour of trace metals in estuaries is a prerequisite for the correct estimation of net riverine trace metal fluxes to coastal zones and the work is therefore highly relevant for the Commissions, e.g., the OSPAR INPUT group. It was stressed that the subject is closely related to the work carried out in the Chemical Oceanography Sub-Group.

Relevant information regarding the distribution of trace metals in different model estuaries, their chemical speciation, laboratory experiments, thermodynamic calculations as well as the work done on chemical and hydrosedimentary modelling was summarised in the review note. MCWG encouraged J.F. Chiffoleau to continue the work and the members of the Trace Metals Sub-Group will make an effort to send relevant information collected intersessionally to J.F. Chiffoleau, who will present a summary at the next meeting.

It was proposed that a specialist in this field should be invited to next year's MCWG meeting.

- 1) M. Leermakers will send information to J.F. Chiffoleau and other members of the group will enquire whether relevant information exists in their countries.
- 2) J.F. Chiffoleau should continue this work and present the results to the Sub-Group next year.
- 3) B. Pedersen should invite a speaker who is an expert on this subject to next year's meeting.

8.1.7 Review a note on tributyltin in the marine environment, with a view to submitting to ACME (ICES C.Res.1998/2:31 g)

A review note entitled 'The Environmental Distribution and Effects of Tributyltin—an Update to 1998' by Robin Law and Erik Evers was prepared with particular emphasis on aspects related to the continued use of tributyltin antifouling paints on large sea-going vessels. The note, summarising the current knowledge of the fate, distribution, and effects of tributyltin in open-sea areas, shipping lanes, and close to ports and harbours, was presented by Erik Evers to the Organics and Trace Metals Sub-Groups.

It was concluded that reduced TBT concentrations have been observed in coastal areas and marinas frequented by small craft but not in sites affected by inputs from large vessels. Similarly, although some affected dogwhelk populations have recovered since the partial ban on TBT was enacted, effects can still be observed in populations close to harbours receiving large vessels. Recent studies along major shipping routes, however, indicate that water concentrations of TBT in the vicinity of large vessel traffic are still elevated relative to those in the open sea. The cessation in the decline of TBT concentrations in water in many areas, its continued impact on distant, non-target organisms, and the persistence of butyltins in sediments and associated problems for the disposal of dredged sediments all provide support for an extension to the partial ban on TBT to include its use in antifouling paints for vessels larger than 25 m in length. It was recommended that tri-, di-, and monobutyltin concentrations should be clearly reported in the correct units, for example, based on the tin atom.

MCWG agreed with these general conclusions. The comments provided to the authors were mainly on the incorporation of more detailed information and the addition of data on TBT concentrations in tissues of fish. It was recommended that the final version incorporating all the comments be added as an annex to the 1999 ACME report. It is appended to this report as Annex 7.

New or additional information should be sent to R. Law and E. Evers by 10 April 1999.

8.1.8 Review and report on the progress of the joint study on PCBs in fish-eating mammals (ICES C.Res.1998/2:31 h)

There was no progress reported on the joint study for the past year.

With respect to PCBs in mammals, a report on the outcome of a literature search for information on mono- and non-*ortho* substituted CBs in marine mammals of the North Atlantic Ocean and the Baltic Sea available from the ASFA

(Aquatic Sciences and Fisheries Abstract) database for the period since 1990 was presented under this agenda item (action of the Sub-Group referring to agenda 8.1.7 of MCWG 1998), and is attached to this report at Annex 8. The report supplies complementary information to Annex 10 of the 1998 ACME report on 'Concentrations and relevant effects of mono- and non-*ortho* chlorobiphenyls in marine mammals' that has been forwarded to the OSPAR working group SIME (SIME 99/4/5) by ICES in February 1999.

8.1.9 Review and report on progress in the collaborative work on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) (ICES C.Res.1998/2:31 i)

A group of laboratories within the MCWG implemented the analysis of TCPM and TCPMe and in 1998 presented results of analyses of sediments, fish, shellfish, and marine mammals from the North Sea and the Gulf of St. Lawrence. As the ratios of TCPM and TCPMe were different in fish of different origin, it was decided to conduct an interlaboratory study in order to validate the comparability of the data.

Since last year, one sample of cod liver and one sample of sediment, made available through QUASIMEME, have been sent to each laboratory within the collaborative group. Results on cod liver have, to date, been received from four laboratories, in Canada, Germany, Belgium, and the Netherlands, of which one had great difficulties with the detection limits. The results from the remaining three laboratories were reasonably comparable. No results have been received on sediments thus far.

Falandysz *et al.* (1999) recently published that the ratio of TCPM to TCPMe in fish varies. Thus, as for the results obtained by the MCWG, no clear relationship could be obtained. Still, the collaborative group wanted to continue their work and the interlaboratory study.

It was decided that:

a) The interlaboratory study will proceed as follows:

- results on cod liver and sediment samples should, if possible, be submitted from laboratories that have not responded yet;
- sediment samples already sent out should be analysed. (All collaborating laboratories please send in results!) It was stressed that no new samples would be sent out to a laboratory that had not responded earlier.
- another round on two new fish samples will be performed. The fish samples will be made available by QUASIMEME. It was agreed that in case participants would not be able to produce results for these samples before 1 January 2000, they would have to pay the costs of these materials to QUASIMEME.

b) a paper on the occurrence of TCPM and TCPMe in fish will be elaborated (Michel Lebeuf).

8.1.10 Review the note on synthetic musk compounds in the marine environment, with a view to submitting to ACME (ICES C.Res.1998/2:31 j)

A review paper on 'Polycyclic Musk Fragrances in the Aquatic Environment' by Gerhard Rimkus was presented by Jacob de Boer. This group of substances is replacing the nitromusks as fragrances in perfumes, cosmetics and laundry detergents. The major emission pathway is therefore via sewage treatment plants and thus the highest concentrations are found downstream from such installations. The database for concentrations in the marine environment is so far very limited. The concentrations in sea water from the German Bight were measured in 1990 and 1995 (somewhat higher values for 1995) for the two most common polycyclic musks (HHCB and AHTN). A few marine organisms, blue mussels and shrimps, have been investigated and levels up to 0.37 mg HHCB/kg lipid weight and 0.06 mg AHTN/kg lipid weight were measured. The nitromusks were present at similar levels. The bioaccumulation of polycyclic musks in fish is lower than could be expected from their K_{ow} values, probably due to metabolic breakdown. In spite of this, considerable concentrations of these substances can be found in fish from freshwater environments. The extent of distribution in the marine environment is difficult to judge until further data become available.

The comments on this review paper from the Organics Sub-Group of MCWG included the following:

- this paper represents a very good overview of the present knowledge of the environmental distribution of these substances;
- direct exposure of humans may be more important than indirect via fish consumption;
- more information on ecotoxicological properties of these substances is needed;

- there may be a risk for contamination of samples in the laboratory;
- there are some new data on levels in freshwater environments in The Netherlands.

It was recommended that the report be forwarded to ACME for information with the view that it should be appended to the ACME report after contact with the author regarding a few minor changes. The report should also be added as Annex 9 to the MCWG report.

8.1.11 Review and report information on modelling PCB bioaccumulation in the Seine estuary (ICES C.Res.1998/2:31 k)

A. Abarnou reported on progress in a bioaccumulation study of PCBs in the Seine Estuary, which is part of a larger multidisciplinary research project (Programme Scientifique Seine Aval) that started in 1995. A presentation was given for information only and no review was carried out.

The study is part of a water management programme on the recovery of the water quality of the Seine estuary. The bioaccumulation models are needed in order to be able to predict the effectiveness of measures, regulations, and remedial actions by authorities on water contamination.

After a short introduction on the hydrology of the Seine estuary, a description of the modelled trophic food web was presented. The model is based on the bioenergetic equilibrium model of organic chemical accumulation in aquatic food webs (Thomann *et al.*, 1992) and has been adapted for the Seine estuary. The food web consisted of the following classes of organisms: the sea bass *Dicentrarchus labrax* at the top, the goby, *Pomatoschistus microps*, and suprabenthic species *Neomysis integer*, *Palaemon longirostris*, *Crangon crangon* and the main zoobenthic species (*Eurytemora* sp.) which feeds on phytoplankton and detritic material. The calculated concentrations of PCB 153 in sea bass were in good agreement with the observed concentrations under steady-state conditions. Uptake of PCBs through the food chain was shown to be much more important than the direct uptake from the water phase. The influence on PCB concentrations in sea water, temperature, variability in phytoplankton growth during the different seasons, and differences between sexes, e.g., due to spawning, could also be studied with the dynamic model developed at IFREMER. The modelling work showed that a reduction in the PCB concentrations in detritus would have a larger impact on the decrease in the PCB concentrations in sea bass muscle than a decrease in the PCB concentrations in phytoplankton and that the biotransformation of PAHs results in a negligible accumulation of PAHs in sea bass compared to PCBs. This highlights the importance that such processes are taken into account in models as well. Some members of the group argued that other factors, such as the variations in diet composition and the contribution of sediment-bound PCBs, should be incorporated in the model also.

Reference

Thomann, R.V., and Connolly, J.P. 1984. Model of PCB in the lake Michigan lake trout food chain. Environ. Sci. Technol., 18(1): 65–71.

8.1.12 Review an updated paper on polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) (ICES C.Res.1998/2:31 l)

A paper entitled 'Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs)' by Jacob de Boer, Karin de Boer, and Jan P. Boon was presented by Jacob de Boer.

The paper is a draft of a chapter to be included in a new volume of 'The Handbook of Environmental Chemistry' series and was presented with a view to being passed to ACME for information. The paper presents a review of the current state of knowledge of the two groups of compounds under the following headings:

- Chemical and physical properties
- Production and use
- Consumption
- Combustion and recycling
- Alternatives
- Analytical methods
- Emission, transformation and distribution
- Environmental levels

- Toxicology

Particular emphasis was placed on the occurrence of PBDEs in sperm whale blubber, which is seen to be indicative of contamination of the deep oceans, the normal feeding grounds of the sperm whale. Also noted were the very high levels in cormorants—a piscivorous bird. *In vitro* studies have indicated that PBDEs are stable to attack by hepatic microsomes. Concern exists over the rapidly increasing levels of PBDEs in human milk samples from Sweden, which demonstrated that levels are currently doubling every five years.

This paper prompted much discussion in an area of increasing activity. A number of technical questions remain over the analytical methodology, particularly of decabromodiphenyl ether. More information is needed on the behaviour of decabromodiphenyl ether in the environment, because this is the major compound currently produced, whereas mainly tetra and penta BDEs are found in environmental samples.

It was recommended that, after some minor changes to the text, the paper be submitted to ACME.

8.1.13 Collate and critically review available data on the two main analytical techniques to measure PAH metabolites with the aim of establishing how robust each technique is with respect to its application to general monitoring and site-specific monitoring and develop a strategy to calibrate results obtained by both techniques, including the conduct of intercalibration exercises
(ICES C.Res.1998/2:31 m)

(This is a request from WGBEC to resolve questions concerning the best techniques for measuring PAH metabolites and the level of comparability among the laboratories in the application of these techniques.)

MCWG was requested by WGBEC to collate and critically review data on the two main analytical techniques for measuring PAH metabolites with respect to their application to general monitoring and to develop a strategy to calibrate the results by both techniques.

MCWG acknowledged the need for this information on a prolonged scale, however, intersessional activity is needed to fulfill this task.

The Organics Sub-Group noted that there is an ongoing EU project on the 'Preparation and certification of fish bile reference materials for exposure monitoring of PAHs in the aquatic environment EU SMT 4-CT98-2250'. The project is coordinated by Dr Freek Ariese at IVM, Amsterdam and his co-partners Dr Jonny Beyer of RF Rogaland Research, Norway and Dr David Wells, FRS, Marine Laboratory, Aberdeen. The project involves some 15 institutes in Europe and the USA that will be developing and refining their analytical methodologies within the framework of interlaboratory studies conducted by QUASIMEME.

Dr Wells agreed to make the information on the progress, results, and conclusions of the project available to the Chair of WGBEC, with a copy of the letter to the Chair of MCWG, subject to the agreement of the other partners of the EU project and the EU S, M & T officer. Members of other institutes active in the field of PAH metabolite measurement who are interested in participating in the interlaboratory studies should, in the first instance, contact Dr Wells at FRS. Where sufficient materials are available, they would be distributed to participants free of charge provided that results were returned within the agreed deadlines of the project. Invitation to the Project Workshops would also be possible, depending on the overall numbers, at the participant's own expense.

Further information on the progress of this project will be brought to the MCWG annual meeting in 2000.

8.1.14 Review progress on the application of high temperature techniques for the determination of total nitrogen in sea water (ICES C.Res.1998/2.31 n)

A paper describing a comparison between the standard wet oxidation method and a High Temperature Catalytic Oxidation method (HTCO) for the determination of Total Dissolved Nitrogen (TDN) was discussed by the COSG. The paper was based on data produced by U. Westernstroer and Dr G. Kattner (Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven (AWI) and K. Nagel (Institut für Ostseeforschung, Rostock-Warnemünde (IOW)).

Several views and ideas were exchanged and they can be summarised as follows.

The wet digestion method published by Koroleff is the generally accepted method for the determination of TDN in natural seawater samples. Although this method has been used for several years by a large number of laboratories, intercomparison exercises have revealed significantly higher differences between laboratories than those found for some other nutrient determinations (e.g., nitrite, nitrate, silicate). The reasons for this have not been analysed in detail until now.

Determination of TDN by HTCO methods was first introduced some 20 years ago and several modifications of the basic method have been described in the meantime. An advantage of the HTCO method is that it can be performed automatically without time- or manpower-consuming pretreatment of the sample. It is also claimed that HTCO methods are more effective in the analysis of TDN than the wet digestion method, because nearly all inorganic and organic forms of nitrogen-containing compounds are quantitatively determined. As the HTCO method requires a highly sophisticated instrument, its use until now has been limited to a relatively small number of laboratories. Furthermore, there are some doubts as to whether all commercially available systems fulfill the requirements for an accurate analysis of natural seawater samples.

The performance of the two methods has been compared by analysing a set of more than 300 samples taken from different regions of the Baltic Sea and at different times of the year. The samples differ significantly in the ratio between inorganic and organic nitrogen compounds and also in the composition of DOM, as some are of marine origin and some are from terrestrial sources. It was found that the mean TDN concentration in this set of samples obtained by the HTCO method is about 1.1 µmol/l higher than the concentration found by wet digestion. However, for a number of samples, differences of up to 10 µmol/l between the methods were found.

No systematic error was found that could explain the differences as they were not strictly correlated with any other parameter. It has been demonstrated, however, that nitrate can be overestimated by the HTCO method by 10 %–15%. Different ratios between the inorganic and organic nitrogen compounds, as well as differences in the chemical composition of DOM in the samples are therefore suggested to cause the differences between the results obtained by the two methods, even though this could not be proved from the investigation described here. It has therefore not been possible to decide which method is ‘more correct’ in the analysis of natural marine samples.

As more information will almost certainly become available during the coming years, the COSG concluded that this agenda item should stay on the working schedule for next year.

The instrumental developments and any new results obtained by HTCO methods for samples collected from different natural marine sources should especially be followed.

Mikael Krysell and Stig Carlberg volunteered to prepare a discussion paper on this topic for the next meeting.

8.1.15 Review and report on information on strategies for monitoring inputs of nutrients to the coastal zone (ICES C.Res.1998/2.31 o)

Alain Aminot had prepared a paper in advance of the meeting as background information for the discussions in the group.

The question of monitoring inputs of nutrients to the coastal zone is driven by the increasing problems of eutrophication and is linked to the assessment of the efficacy of measures taken to reduce inputs from continental sources.

The problem can also be expressed in terms of *gross* and *net fluxes*. The gross flux is the sum of all inputs at the downstream limit of a river; the net flux is the amount that actually reaches the coastal zone. Several questions can be raised, such as: Is there a clear definition of the coastal zone? Can the net flux be easily determined? Is there a satisfactory evaluation of the gross flux? Which forms of each nutrient have to be measured?

Nutrients (N, P, Si) present in various forms in fresh water can be converted from one form to another in the intermediate mixing zone between fresh and coastal waters. Many processes can be responsible for these changes, for instance: sedimentation-resuspension, adsorption-desorption, assimilation, mineralisation, nitrification, denitrification. Several of these processes can proceed simultaneously or successively (in space and/or time), while some of them are exclusive (oxygen-dependent processes, for instance).

Many examples, from the literature and from the studies undertaken by MCWG members, show that the morphology of the area under consideration (estuaries, lagoons, deltas) and local hydrographic conditions (tide, wind, currents, stratification, upwelling, etc.) are important factors that affect the overall behaviour of nutrients. While macrotidal

estuaries often exhibit conservative behaviour for dissolved inorganic nitrogen, river-lagoon systems in small-tide areas are extremely reactive and complex regarding nutrient fluxes. Inputs can be pulsed or severely influenced by seawater inflow, depending on the location of the boundary selected to determine the fluxes.

From the above considerations, it seems that there will be no unique, simple approach for monitoring nutrient fluxes from estuarine environments. As a consequence, it would seem unrealistic to build a general strategy for monitoring nutrient inputs to the coastal waters. The gross inputs from the river are, at least, what should be well determined.

In estuaries where the behaviour of a nutrient has been shown to be conservative, monitoring this nutrient in the terrestrial sources will give the required answer. The nutrient in the estuary has simply to be monitored from time to time to confirm the conservative conditions, since frequent sampling at many stations within the estuary will bring no additional information.

Where (or when) a nutrient is not conservative (but the deviation is not severe), net fluxes may be determined using the nutrient-salinity relationships. By extrapolating from the high-salinity part of the curve to salinity = zero, a net concentration for fresh water is obtained. Multiplying this value by the corresponding water flow gives the net flux. However, a satisfactory determination of the flux will probably require many cruises each year, with many sampling stations.

In general, more complex situations will be encountered. In these cases, high spatial and temporal resolution would be necessary to achieve input determination. However, this would require an unrealistic amount of resources for monitoring such areas.

It is therefore suggested that ecological modelling can advantageously replace heavy monitoring programmes. However, models should be refined enough to take into account all the major processes that may affect nutrient concentrations. Such sophisticated models are being developed in many countries, but mostly still for research programmes. Improvement of their performance and their user-friendliness, as well as their dissemination to the monitoring community, should be strongly encouraged. Indeed, these models can be useful tools for predicting potential eutrophication problems and for computing fluxes through any selected boundary. Once a model is calibrated using a high-resolution study, validation will only require low-resolution monitoring.

The COSG decided to pursue work on this item and, to this end, proposed a joint session with the WGSSO next year to discuss the use of chemical data in numerical modelling and possible implications for future work in modelling and in field sampling programmes.

8.1.16 Review information on the experience of the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables (ICES C.Res.1998/2.31 p)

There was no written contribution to this item on the agenda and therefore it was only briefly discussed.

Automated *in situ* chemical oceanographic systems for the observation of chemical variables are used to some extent. Continuous monitoring can be divided into two types: one which is based on on-line transmission of data via a direct link or via satellite and one where the observed data are contained in the instrumentation and retrieved at a special signal or when the instrumentation is visited for service purposes. There are buoys designed to contain instrumentation in addition to salinity, temperature and turbidity sensors, among others, also devices for measuring the most common nutrients (NO₂, NO₃, PO₄, Si). On the market there are available specially designed autoanalysers that can be deployed in underwater compartments connected to buoys or on the working deck of fixed platforms. These autoanalysers work according to the same principles as laboratory autoanalysers. The main disadvantage of this kind of instrumentation is that even if they have containers for the various chemicals large enough for several months of operation, the chemicals themselves degrade so that they have to be renewed once a month. This means that the operational costs of this type of chemical monitoring could be substantial.

UV sensors that can be used for *in situ* measurements are under development for some nutrients. They are, however, sensitive to changes in salinity and are also affected by fouling and thereby disturbance in the light penetration to the sensors.

It is difficult to combine automated deep-water monitoring of chemical variables with the need to access the data on-line. The reason is that the anchoring systems do not allow for cable transmission of data from the chemical unit to the transmitting surface buoy. This means that sensors deployed for on-line monitoring are limited to the surface layers.

Buoys that are deployed in shallow and nearshore waters, where the operational costs can be kept at a reasonable level, can be valuable tools in monitoring daily inputs and fluctuations (for example, in river mouths or fjord entrances). As these types of platforms most often serve navigational or meteorological purposes, the share of the costs between several purposes may allow for an introduction of additional analytical instrumentation for chemical measurements.

As more information will most certainly become available during the coming years, the group decided to continue to follow the subject.

8.1.17 Review the report on particulate organic carbon (POC) in anoxic waters (ICES C.Res.1998/2.31 q)

In 1993 a large inflow of saline water occurred that terminated the stagnation period in the central basins of the Baltic Sea. As the stagnation period had lasted for more than 10 years, concentrations of H₂S had increased in the deep water during that period. Although several other data had been collected in the area through different monitoring programmes, the data available for POC or other organic compounds are very limited from that area.

However, IOW (Germany) and during certain periods also SMHI (Sweden) have collected data for these parameters on a routine basis since the mid-1990s. The redox state has fluctuated throughout the years (oxic conditions in the winter and anoxic conditions in autumn) during the observation period. Therefore, no data are available for stable anoxic conditions. Nevertheless, existing data show a tendency toward an increase in the concentrations of POC, DOC, and the C/N ratios in the anoxic water layers. A statistical verification of the observed tendency is, however, not possible at present, due to the limited number of data and the high variability of the redox state. The investigations are planned to continue, but it is, at the moment, not possible to envisage when sufficient data from more stable anoxic conditions in the Baltic Sea deep water will become available. The results are so far promising and, as the topic is of great interest, the group decided to continue to revisit this topic regularly, as a better knowledge will improve our possibilities to give advice on the future strategy for the monitoring of organic carbon and nitrogen in anoxic waters.

8.1.18 In consultation with the ICES Oceanographic Data Centre and WGMDM, develop guidelines for the use of appropriate units for reporting data on nutrients and oxygen in sea water (ICES C.Res.1998/2.31 r)

At the MCWG meeting in 1998, the use of appropriate units for hydrographic parameters was outlined in some detail by the Chemical Oceanography Sub-Group (COSG). The task given for the 1999 meeting was to establish more practical guidelines for the appropriate use of units, and to give advice on the supporting information (meta data) needed to convert between different applied units (e.g., from the per litre basis to per kilogram). During the meeting, the Sub-Group concluded that the most appropriate way of addressing this task would be to combine these guidelines with the guidelines developed under agenda item 8.1.19 (ICES C.Res.1998/2.31 s). The Sub-Group thus revised that paper, not only with the task given under agenda item 8.3.8 in mind, but also considering whether any extra information would be needed to cover the task concerning units, given under this agenda item. The amended suggested guidelines are given as Annex 10 to this report.

8.1.19 Review preliminary guidelines concerning QA of nutrients, chlorophyll and oxygen data (also including CTD measurements) (ICES C.Res.1998/2.31 s)

The working material for this task consisted of the paper 'Guidelines for quality control and meta data support of discrete hydrographical data in marine environmental monitoring programmes', written by Mikael Krysell. The Sub-Group considered the paper and thought that it was generally useful and should be able to fulfill the task given. The draft paper was revised after some comments were given by the participants in the Chemical Oceanography Sub-Group. As mentioned above, the revision also focused on fulfilling the task given under agenda item 8.1.18 (ICES C.Res.1998/2.31 r). After revision, the Sub-Group decided to accept the paper (Annex 10 to this report) and also to forward it to the ICES WGMDM for comments on Annex 1 (of the paper), containing a list of suggested quality flags, as it appears that WGMDM might have useful views on the more practical aspects of quality flagging. After the comments by the WGMDM have been taken into consideration, the Sub-Group suggested that the paper be forwarded to the ICES Oceanographer.

8.1.20 Finalise the discussion on a standard chlorophyll a technique for use within ICES programmes, and prepare a report for ACME, in collaboration with WGPE, on the quality assurance of chlorophyll a (ICES C.Res.1998/2.31 t)

In 1998, the Sub-Group reviewed a paper produced by A. Aminot on quality assurance aspects in the determination of chlorophyll *a* in sea water. Since the Working Group on Phytoplankton Ecology (WGPE) undertook a similar task,

merging the two papers was thought to be very constructive. Meanwhile, the ACME recommended preparation of a method for the determination of chlorophyll *a* that would become the recommended method for the ICES countries and published in the ICES TIMES series. The Chair of the Chemical Oceanography Sub-Group of MCWG (Stig Carlberg) contacted the Chair of the WGPE and the task was given to A. Aminot (MCWG) and Francisco Rey (WGPE) to lead the work. F. Rey prepared a draft version of the paper to be reviewed by the MCWG. Alain Aminot had already made some comments in advance of the MCWG meeting directly to F. Rey.

The COSG of MCWG made several comments that have been compiled with some detail and will be passed within a few days after the MCWG meeting to the WGPE, which meets in early April 1999. A. Aminot will continue to act as the contact person with WGPE until the paper is finalised.

In the light of this development, COSG agreed that the paper on chlorophyll determination that A. Aminot had prepared for the meeting in 1998 should be included as Annex 11 to the MCWG report this year with a view to publishing it in the ACME report.

8.1.21 Take note of the report from SGQAC (ICES C.Res.1998/2:31 v)

The Chair of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), Mikael Krysell, presented the Sub-Group with four technical notes from the latest SGQAC meeting for comments and revision. The four technical notes have been developed as quality assurance guidelines for certain hydrographic parameters (dissolved oxygen, hydrogen sulphide, pH and alkalinity), and are aimed for inclusion in the existing HELCOM monitoring (COMBINE) QA guidelines. These four notes will be combined with similar papers covering the QA of temperature and salinity measurements to form a QA note on hydrography. However, the parts covering temperature and salinity have not yet reached a state where they can be presented for revision.

The Sub-Group found the four existing parts useful, and gave comments and suggestions for revisions directly to the SGQAC Chair. The Chair promised to update the notes after the meeting according to the comments given. The Sub-Group then recommended that the revised technical notes should be published in the COMBINE QA guidelines of HELCOM.

The Trace Metals Sub-Group was informed about the main topics of the meeting of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea held at ICES Headquarters in February this year. These included:

- the current status of the Guidelines on Quality Assurance in the COMBINE Programme of HELCOM (the COMBINE Manual can now be found at the web address: <http://www.helcom.fi/manual2/contents.html>);
- the outcome of two regional QUASH workshops within the framework of WP1 (Sampling and sampling handling for the determination of nutrients in sea water) held in Göteborg and Hamburg in October 1998;
- the review of draft technical notes for inclusion in the guidelines (organochlorine compounds in sea water, PAHs in sea water and biota, measurement uncertainty, hydrochemical parameters).

A Workshop on QA Procedures in the COMBINE Programme of HELCOM was announced by SGQAC and will be held at the Finnish Institute of Marine Research in Helsinki from 21–23 October 1999.

8.2 Any Other Business Raised by the Subgroups

Among others, the Sub-Groups need to appoint a Chair to deal with matters which may arise intersessionally and who can chair the Sub-Group next year.

8.2.1 Organics Sub-Group

a) Toxaphene

Further discussions took place on the technical aspects of toxaphene analysis following the plenary presentation on progress in the MATT programme. The requirement to ensure that toxaphene components are separated from chlordane compounds as well as from chlorobiphenyl residues prior to gas chromatography was emphasised.

b) New contaminants

It was suggested that it is necessary to bring the work of MCWG on 'new' contaminants to the more direct attention of OSPAR. It was stressed that the participating countries here play an important role as they, as well as ICES especially through the work of ACME, can make new information on 'new' contaminants available at the OSPAR meetings. However, it was also felt that the more recent arrangements for information to be presented to OSPAR via SIME were effective.

c) Election of Chair

By unanimous acclamation, J. de Boer was re-elected Chair for a further year.

8.2.2 Chemical Oceanography Sub-Group

a) The 'Home' for the Chemical Oceanography Sub-Group

Chemical oceanography has a long tradition within ICES, dating back to the very beginning of ICES as an organisation. Chemistry laid the ground for salinity determinations and the Martin Knudsen tables and Copenhagen Standard Sea Water opened for a standardisation of hydrographic work.

Chemical oceanography is in essence the use of chemical data to describe processes in the water masses, whether for characterisation of water masses or the conditions for biological production (primary production). Most of the chemical data that are used for the description of water mass dynamics and primary production modelling are data that can be sampled and analysed on a routine basis, preferably on-board a research vessel, with a sampling density allowing for the above-mentioned descriptions.

In the new Committee structure of ICES, both physical and biological oceanography are dealt with by the Oceanography Committee (OCC). There are a number of working groups dealing with the various oceanographic matters reporting directly to the OCC. Chemical oceanography is not a part of this, although chemical data such as on nutrients are used frequently, for example, in the work of the Working Group on Shelf Seas Oceanography (WGSSO) of the OCC.

The present structure, whereby chemical oceanography is handled within a Sub-Group of the MCWG reporting directly to the Marine Habitat Committee (MHC), does not allow for the handling of these type of problems within the OCC. The COSG therefore suggests that this is taken into account in the continuing reorganisation of the ICES Committee parentage of working groups.

b) Work Programme for COSG

The COSG suggests that the following items be included on the agenda for the MCWG meeting in 2000:

- 1) review and endorse the updated list of contaminants which can be monitored on a routine basis;
- 2) review information on QA systems used in laboratories involved in marine monitoring and report the outcome;
- 3) review progress on the application of high temperature techniques for the determination of total nitrogen in sea water;
- 4) review information on experience in the use of automated in situ chemical oceanographic systems for the observation of chemical variables;
- 5) review a comparison of spectrophotometric and volumetric alternatives for quantification in the Winkler method for the determination of dissolved oxygen in sea water and report on the outcome;
- 6) review the use of chemical data in numerical modelling and the possible implications for future work in modelling and in field sampling programmes (requires joint session with WGSSO).

c) Election of Chair

The COSG unanimously re-elected Stig Carlberg as Chair for the intersessional period.

8.2.3 Trace Metals Sub-Group

Election of Chair

The Trace Metals Sub-Group unanimously re-elected Gert Asmund as Chair for the intersessional period.

9 PLENARY DISCUSSION OF SUB-GROUP WORK

Topics of more general interest for all three working groups were discussed currently during the meeting and all agenda items were finally discussed in plenary on the last day of the meeting.

10 ANY OTHER BUSINESS

Under this agenda point, MCWG conducted a general discussion on the following topic:

‘How can we attract our colleagues from Canada and the USA to attend MCWG meetings?’

Several views and ideas were exchanged. It was especially highlighted that a lot of projects the different members of the group presently participate in are oriented towards the EU, one reason being the rules of EU foundations. It was also suggested that previous members of MCWG should be contacted to get their views on how the situation can be improved. Lack of resources is known to be at least one reason for the lack of US/Canadian participation. MCWG finally suggested to meet more often on the American continent as one way of improving US/Canadian participation.

11 RECOMMENDATIONS AND ACTION LIST

The Action List and Recommendations are given in Annexes 12 and 13, respectively.

12 DATE AND VENUE OF THE NEXT MEETING

MCWG discussed the venue and dates of the next meeting. It was decided to plan the next meeting at ICES Headquarters in Copenhagen from 28 February to 3 March 2000.

13 CLOSURE OF THE MEETING

Staff members of the host institute joined the closing session of MCWG. On behalf of the MCWG, B. Pedersen, thanked them for their warm hospitality, their hard work and all the support and services they provided.

In addition, she thanked the Sub-Group Chairs for their efforts and support, and all participants for their hard work.

The Chair then closed the meeting at 14.00 hrs on 12 March 1999.

ANNEX 1: LIST OF PARTICIPANTS

Name	Address	Telephone	Telefax	E-Mail
Alain Abarnou	IFREMER Centre de Brest B.P. 70 29280 Plouzane France	+33298224357	+33.298224548	aabarnou@ifremer.fr
Colin Allchin	CEFAS Burnham Laboratory Remembrance Ave Burnham on Crouch Essex CMO 5HA UK	+ 44 1621 787200	+44 1621 784989	c.r.allchin@cefas.co.uk
Alain Aminot	IFREMER Centre de Brest B.P. 70 29280 Plouzané France	+33.298224361	+33.298224548	aaminot@ifremer.fr
Eugene Andrulowicz	Sea Fisheries Institute Department of Oceanography Marine Environment Quality Laboratory ul. Kollataja 1 PL 81-332 Gdynia Poland	+48.58201728	+48.58202831	eugene@mir.gdynia.pl
Gert Asmund	National Environmental Research Institute Department of the Arctic Environment Tagensvej 135 2200 Copenhagen N Denmark	+45.35821415	+45.35821420	gas@dmu.dk
Patrice Behan	Marine Institute Fisheries Research Centre Abbotstown Castleknock Dublin 15 Ireland	+353.1.8210111	+353.1.8205078	behan@frc.ie
Victoria Besada	Instituto Espanol de Oceanografia Centro Oceanografico de Vigo Apartado 1552 Cabo Estay-Canido E-36280 Vigo Spain	+34986 492111	+34986 492351	victoria.besada@vi.ieo.es
Martin Bloxham	Marine Institute Fisheries Research Centre Abbotstown Dublin 15 Ireland	+353.18210111	+353.18205078	mbloxham@frc.ie
José Biscaya	Instituto Hidrografico Rua das Trinas, 49 1296 Lisboa Codex Portugal	+351.13955119	+351.13960515	quimica@hidrografico.pt
Jacob de Boer	DLO- Netherlands Institute for Fisheries Research P.O. Box 68 Haringkade 1 1970 AB IJmuiden The Netherlands	+31.255564736	+31.255564644	j.deboer@rivo.dlo.nl

Name	Address	Telephone	Telefax	E-Mail
Stig Carlberg	SMHI Oceanographical laboratory Byggnad 31, Nya Varvet SE-42671 Västra Frölunda Sweden	+46.31751 8976	+46.31751 8980	stig.carlberg@smhi.se
Jean-François Chiffolleau	IFREMER Centre de Nantes B.P. 21105 Rue de l'Ile d'Yeu 44311 Nantes Cedex France	+33.240374177	+33.240374075	jfchiff@ifremer.fr
Marianne Cleemann	National Environmental Research Institute P.O. Box 358 Frederiksborgvej 399 DK-4000 Roskilde Denmark	+45.46301200	+45.46301114	mc@dmu.dk
Conor Duffy	Marine Institute Fisheries Research Centre Abbotstown Castleknock Dublin 15 Ireland	+353.1.8210111	+353.1.8205078	cduffy@frc.ie
Erik H.G. Evers	National Institute for Coastal and Marine Management/RIKZ Dept. of Analytical Chemistry P.O. Box 20907 NL-2500 EX The Hague The Netherlands	+31.703114312	+31.703114600	H.G.Evers@rikz.rws.minvenw. nl
Lars Føyn	Institute of Marine Research P.O. Box 1870 Nordnes 5024 Bergen Norway	+47.55238501	+47.55238584	lars@imr.no
Michael Haarich	Bundesforschungsanstalt für Fischerei Institut für Fischereiökologie Wüstland 2 D-22589 Hamburg Germany	+49.4031908650	+49.4031908603	bfa-fisch.ifo@bsh.d400.de Personnel email Haarich.ifo@bfa-fisch.de
Bo Jansson	Institute of Applied Environmental Research Stockholm University S-106 91 Stockholm Sweden	+46.86747220	+46.87581360	bo.jansson@itm.su.se
Jarle Klungsoyr	Institute of Marine Research P.O. Box 1870 Nordnes 5024 Bergen Norway	+47.55238500	+47.55238584	jarle.klungsoyr@imr.no
Mikael Krysell	SMHI Oceanographic Laboratory Byggnad 31, Nya Varvet SE-426 71 Västra Frölunda Sweden	+46.31751 8990	+46.31751 8980	mkrysell@smhi.se
Michel Lebeuf	Insitut Maurice-Lamontagne C.P. 1000 850 Route de la mer G5H 3Z4 Quebec Canada	+1.4187750690	+1.4187750542	lebeufm@dfo-mpo.gc.ca

Name	Address	Telephone	Telefax	E-Mail
Martine Leermakers	Vrije Universiteit Brussel Analytical Chemistry Pleinlaan 2 B-1050 Brussels Belgium	+32.2.6293266	+32.2.6293274	mleermak@vub.ac.be
Evin McGovern	Marine Institute Fisheries Research Centre Abbotstown Castleknock Dublin 15 Ireland	+353.1.8210111	+353.1.8205078	emcgovern@frc.ie
Brendan Mc Hugh	Marine Institute Fisheries Research Centre Abbotstown Castleknock Dublin 15 Ireland	+353.1.8210111	+353.1.8205078	bmchugh@frc.ie
Klaus Nagel	Baltic Sea Research Institute Seestrasse 15 D-18119 Warnemünde Germany	+49.3815197331	+49.3815197302	klaus.nagel@io- warnemuende.de
Teresa Nunes	Instituto Español de Oceanografía Centro Oceanografico de Vigo Apartado 1552 Cabo Estay-Canido E-36280 VIGO Spain	+34.986492111	+34.986492351	teresa.nunes@vi.ieo.es
Jon Ólafsson	Marine Research Institute P.O. Box 1390 Skulagata 4, IS-121 Reykjavik Iceland	+354.5520240	+354.5623790	jon@hafro.is
Ole Vagn Olsen	Danish Institute for Fisheries Research Kavalergarden 6 2920 Charlottenlund Denmark	+45.33963408	+45.33963434	vo@dfu.min.dk
Britta Pedersen (Chair)	National Environmental Research Institute P.O. Box 358 Frederiksborgvej 399 DK 4000 Roskilde Denmark	+45.46301209	+45.46301114	bpe@dmu.dk
Patrick Roose	Management Unit of the Mathematical Model of the North Sea 3° en 23° Linierégimentsplein 8400 Oostende Belgium	+3253700131	+3259704935	p.roose@mumm.ac.be
Ailve Rowe	Marine Institute Fisheries Research Centre Abbotstown Castleknock Dublin 15 Ireland	+353.1.8210111	+353.1.8205078	arowe@frc.ie
Jo Suijlen	National Institute for Coastal and Marine Management/RIKZ Dept. of Research Chemistry P.O. Box 20907 NL-2500 EX The Hague The Netherlands	+31703114307	+31703114321	j.m.suijlen@rikz.rws.minvenw. nl

Name	Address	Telephone	Telefax	E-Mail
Anne Talvari	Estonian Environmental Research Centre Marja 4D Tallinn Estonia	+6112919	+0039 372 6112 901	talvari@klab.envir.ee
Jacek Tronczynski	IFREMER DEL/PC B.P. 21105 44311 Nantes France	+33240374136	+33240374075	jtronczy@ifremer.fr
David Wells	Fisheries Research Services, Marine Laboratory P.O. Box 101 Victoria Road Aberdeen AB11 9DB UK	+44.1224 876544 +44. 1224295368 (direct)	+44.1224 295511	wellsd@marlab.ac.uk
Peter Woitke	Federal Environmental Agency FG II 2.5 P.O. Box 33 00 22 D-14191 Berlin Germany	+49.3089032566	+49.3089032285	peter.woitke@uba.de

ANNEX 2: AGENDA

Marine Chemistry Working Group 1999

Dublin, 8–12 March

1 OPENING OF THE MEETING

2 ADOPTION OF THE AGENDA

3 REPORT OF THE 86TH ICES STATUTORY MEETING

The following task will be covered under this agenda point:

The MCWG has been asked to contribute to the ICES strategic planning process through assisting the Marine Habitat Committee in the following tasks (ICES C.Res.1998/2:31u):

- i) formulating tactics to achieve the six objectives adopted by the Committee
- ii) suggesting and/or developing activities and products to fulfil the objectives
- iii) estimating the resources required for each activity according to categories that will be supplied

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPARCOM AND HELCOM

There are no official requests this year

4.2 Intergovernmental Oceanographic Commission (IOC)

At the MCWG meeting in 1998 it was decided that all members of the MCWG should try to seek information about IOC and report back at the next MCWG.

4.3 Laboratory Performance Study' 'QUASIMEME II'

Dr Wells has been requested to provide an update

4.4 Other Activities

Members who wish to make a presentation under this item should prepare a note for the MCWG

5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

All members who wish to make a presentation on this item should prepare a note for MCWG

6 REQUESTS FROM ACME AND REGULATORY AGENCIES

Requests from ACME which have arisen prior to this agenda being produced, have been included

7 PLENARY PRESENTATIONS

7.1 D. Wells, J.de Boer, M. Krysell, S. Carlberg and B. Pedersen

'QUASH, year 2'

7.2 J.M. Suijlen

'Organic compounds as tracers'

7.3 Gert Asmund

'The arctic dilemma' (a video)

7.4 B. McHugh, J. de Boer and J. Klungsøyr

Presentation of information on the MATT project under the EU-FAIR programme

8 SUB-GROUP ACTIVITIES AND DISCUSSIONS

8.1 Trace Metals Sub-Group

- 8.1.1 (ICES C.Res.1998/2:31 a) Review and endorse the updated list of contaminants which can be monitored on a routine basis.
- 8.1.2 (ICES C.Res.1998/2:31 b). Review a note on how to identify topics under 'New contaminants and their relevance to the marine environment' and plan how this can be implemented.
- 8.1.3 (ICES C.Res.1998/2:31 c). Review information on contaminant concentrations in biological media as environmental indicators and report the outcome.
- 8.1.4 (ICES C.Res.1998/2:31 d) Review information on QA systems used in laboratory involved in marine monitoring and report the outcome.
- 8.1.5 (ICES C.Res.1998/2:31 e) Review progress on supplementary work to the Icelandic cod liver study.
- 8.1.6 (ICES C. Res.1998 /2:31 f) Review and report on information on estuarine transport of trace metals.
- 8.1.7 (ICES C.Res.1998/2:31g) Review a note on tributyltin in the marine environment, with the view to submitting it to ACME.
- 8.1.8 (ICES C.Res.1998/2:31 v) Take note of the report from SGQAC.
- 8.1.9 Any other business raised by the subgroup (Among others, the metal subgroup needs to appoint a Chair to deal with matters which may arise intersessionally and who can chair the Sub-Group next year.

8.2 Organics Sub-Group

- 8.2.1 (ICES C.Res.1998/2:31 a) Review and endorse the updated list of contaminants which can be monitored on a routine basis.
- 8.2.2 (ICES C.Res.1998/2:31 b). Review a note on how to identify topics under 'New contaminants and their relevance to the marine environment' and plan how this can be implemented.
- 8.2.3 Review the updated list of contaminants that can be monitored on a routine basis and transmit the list to ACME.
- 8.2.4 (ICES C.Res.1998/2:31 d) Review information on QA systems used in laboratory involved in marine monitoring and report the outcome.
- 8.2.5 (ICES C.Res.1998/2:31g) Review a note on tributyltin in the marine environment, with a view to submitting it to ACME.
- 8.2.6 (ICES C.Res.1998/2:31 h) Review and report on the progress of the joint study on PCBs in fish-eating mammals.
- 8.2.7 (ICES C.Res.1998/2:31 i) Review and report on progress in the collaborative work on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe).
- 8.2.8 (ICES C.Res.1998/2:31 j) Review the note on synthetic musk compounds in the marine environment, with a view to submitting it to ACME.
- 8.2.9 (ICES C.Res.1998/2:31 k) Review and report on information on modelling PCB bioaccumulation in the Seine estuary.
- 8.2.10 (ICES C.Res.1998/2:31 l) Review an updated paper on polybrominated diethylethers (PBDEs) and polybrominated biphenyls (PBBs) with a view to submitting it to ACME.
- 8.2.11 (ICES C.Res.1998/2:31 m) Collate and critically review available data on the two main analytical techniques to measure PAH metabolites with the aim of establishing how robust each technique is with respect to its application to general monitoring and site specific monitoring and develop a strategy to calibrate results obtained by both techniques, including the conduct of intercalibration exercises.
(This is a request from WGBEC to resolve questions concerning the best technique for measuring PAH metabolites and the level of comparability among the laboratories in the application of these technique).
- 8.2.12 (ICES C.Res.1998/2:31 v) Take note of the report from SGQAC.
- 8.2.13 Any other business raised by the subgroup (Among others, the organic subgroup needs to appoint a chairperson to deal with matters which may arise intersessionally and who can chair the subgroup next year

8.3 Chemical Oceanography Sub-Group

- 8.3.1 (ICES C.Res.1998/2:31 a) Review and endorse the updated list of contaminants that can be monitored on a routine basis.
- 8.3.2 (ICES C.Res.1998/2:31 d) Review information on QA systems used in laboratory involved in marine monitoring and report the outcome.
- 8.3.3 (ICES C.Res.1998/2:31 n) Review progress on the application of high temperature techniques for the determination of total nitrogen in sea water.
- 8.3.4 (ICES C.Res.1998/2:31 o) Review and report on information on strategies for monitoring inputs of nutrients to the coastal zone.
- 8.3.5 (ICES C.Res.1998/2:31p) Review information on the experience of the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables.
- 8.3.6 (ICES C.Res.1998/2:31 q) Review the report on particulate organic carbon (POC) in oxidizing waters.
- 8.3.7 (ICES C.Res.1998/2:31 r) In consultation with the ICES Oceanographic Data Centre and WGMDM, develop guidelines for the use of appropriate units for reporting data on nutrients and oxygen in sea water.
- 8.3.8 (ICES C.Res.1998/2:31 s) Review preliminary guidelines concerning QA of nutrients, chlorophyll and oxygen data (also including CTD measurements).
- 8.3.9 (ICES C.Res.1998/2:31 t) Finalise the discussion on a standard chlorophyll *a* technique for the use within ICES programmes, and prepare a report for ACME, in collaboration with WGPE on the quality assurance of chlorophyll *a*.
- 8.3.10 (ICES C.Res.1998/2:31 v) Take note of the report from SGQAC.
- 8.3.11 Any other business raised by the subgroup (Among others, the chemical Oceanography subgroup needs to appoint a Chair to deal with matters which may arise intersessionally and who can chair the subgroup next year).

9 PLENARY DISCUSSION OF SUBGROUP WORK

10 ANY OTHER BUSINESS

Among others the group needs to suggest a new Chair for the next three years.

11 RECOMMENDATIONS AND ACTION LIST

12 DATE AND VENUE OF THE NEXT MEETING

13 CLOSURE OF THE MEETING

ANNEX 3: QUASIMEME TABLES

Table 1. Summary assessment of laboratory group performance in QUASIMEME CB-OCP exercises in biological tissues, June 1996–December 1998.

Determinand	Units	¹ Range of assigned values	² Range of \pm Target Bias (%)	³ Range of Between Lab CVs (%)	⁴ Range for % No. obs. with $ Z < 2$	⁵ Satisfactory group performances in total rounds
CB028	µg/kg	0.31–13.63	13–29	33.6–89.7	41.7–79.3	3/10
CB052	µg/kg	0.53–34.68	13–22	28.3–68.2	40.0–76.7	2/10
CB101	µg/kg	1.47–106.75	13–16	17.5–55.0	45.2–78.1	3/10
CB105	µg/kg	0.38–40.79	13–26	27.1–58.3	44.0–75.0	1/10
CB118	µg/kg	1.05–147.29	13–17	21.0–39.0	51.7–81.3	2/10
CB138	µg/kg	2.32–286.91	13–15	23.8–35.6	48.3–79.3	2/10
CB153	µg/kg	3.20–391.95	13–14	24.6–40.6	48.3–81.8	
CB156	µg/kg	0.15–16.60	13–45	27.0–82.4	53.3–84.0	6/10
CB180	µg/kg	0.43–90.03	13–24	22.8–45.2	51.9–87.5	7/10
HCB	µg/kg	0.07–19.53	13–82	30.4–67.8	48.1–80.6	5/10
<i>p,p'</i> -DDE	µg/kg	0.58–198.02	13–21	20.9–56.8	51.9–75.0	3/10
α -HCH	µg/kg	0.03–2.58	14–175	29.2–114.1	0.0–70.8	
β -HCH	µg/kg	0.07–2.52	14–81	0.0–93.4	26.7–47.4	3/6
γ -HCH	µg/kg	0.07–3.07	14–89	48.6–121.6	48.1–73.3	4/10
<i>p,p'</i> -DDD	µg/kg	0.25–53.59	13–32	22.2–82.2	45.8–75.0	4/10
<i>p,p'</i> -DDT	µg/kg	0.29–26.28	13–30	50.4–122.4	0.0–55.6	0/10
<i>o,p'</i> -DDT	µg/kg	0.09–17.71	13–68	98.7–160.7	37.5–52.9	0/9
Dieldrin	µg/kg	0.53–50.85	13–22	31.8–66.5	18.8–83.3	1/10
<i>Trans</i> -nonachlor	µg/kg	0.12–22.27	13–55	26.3–94.0	64.7–100.0	7/10
Lipid extr	%	0.94–56.15	13–18	5.6–35.5	69.2–100.0	7/8
Lipid total	%	1.11–58.34	10–26	4.5–40.2	0.0–100.0	7/8

¹Range of assigned values for all rounds of the QUASIMEME scheme examined. The determined assigned values are only indicative.

²Target bias or total allowable error. This is calculated as: total error % = fixed error (12.5) % + (constant error/concentration) %. Thus, the total error is dependent on the concentration of the determinand.

³Range of between-laboratory coefficients of variance (CVs) (%) over all rounds examined.

⁴Range of the number of laboratories achieving the set QUASIMEME standard of $|Z| < 2$ (expressed as %).

⁵Number of rounds in which an overall satisfactory performance has been achieved, expressed as a fraction of the total number of rounds for which total assigned values could be derived. Performance is considered satisfactory when the robust CV % – (total error \times 2) > 0.

Table 2. Summary assessment of laboratory group performance in QUASIMEME CB-OCP exercises in sediments, June 1996–December 1998.

Determinand	Units	¹ Range of assigned values	² Range of \pm Target Bias (%)	³ Range of Between Lab CVs (%)	⁴ Range for % No. obs. with $ Z < 2$	⁵ Satisfactory group performances in total rounds
CB028	µg/kg	0.15–34.08	17–46	20.0–52.3	39.1–94.4	7/10
CB052	µg/kg	0.19–28.36	17–47	28.4–72.7	52.9–88.2	6/10
CB101	µg/kg	0.50–33.59	23–48	17.3–47.3	60.0–85.7	5/10
CB105	µg/kg	0.14–5.76	14–36	25.4–111.7	42.9–100.0	6/10
CB118	µg/kg	0.36–25.54	20–47	22.6–58.3	52.9–78.3	7/10
CB138	µg/kg	1.03–37.93	24–47	25.1–42.7	41.2–83.3	4/10
CB153	µg/kg	0.94–45.34	25–48	18.1–44.4	52.0–82.6	3/10
CB156	µg/kg	0.10–3.67	16–33	27.9–71.7	43.8–81.3	7/10
CB180	µg/kg	0.59–26.68	24–48	19.5–59.8	41.7–75.0	2/10
HCB	µg/kg	0.12–13.92	16–41	23.7–57.8	40.0–88.9	5/10
<i>p,p'</i> -DDE	µg/kg	0.40–6.77	20–41	14.3–65.3	46.2–88.9	6/10
α -HCH	µg/kg	0.08–0.41	11–34	43.1–97.1	0.0–93.3	8/10
γ -HCH	µg/kg	0.14–0.58	11–32	39.6–118.9	46.7–83.3	6/10
<i>p,p'</i> -DDD	µg/kg	0.49–12.00	16–38	34.8–60.4	0.0–66.7	0/10
<i>p,p'</i> -DDT	µg/kg	0.25–4.40	11–33	44.5–124.3	0.0–73.3	0/10
<i>o,p'</i> -DDT	µg/kg	0.08–0.58	4–16	40.6–134.7	0.0–88.9	6/10
Dieldrin	µg/kg	0.17–1.69	9–24	37.5–86.2	50.0–90.0	3/10
<i>Trans</i> -nonachlor	µg/kg	0.05–0.42	6–12	60.5–114.7	50.0–50.0	8/10
TOC	%	2.42–4.20	6–7	9.1–26.1	58.8–100.0	4/4

Table 3. Summary assessment of laboratory group performance in QUASIMEME PAH exercises in sediments, June 1996–December 1998.

Determinand	Units	¹ Range of assigned values	² Range of \pm Target Bias (%)	³ Range of Between Lab CVs (%)	⁴ Range for % No. obs. with $ Z < 2$	⁵ Satisfactory group performances in total rounds
Acenaphthene	mg/kg	0.01–0.43	12–17	29.6–95.0	29.4–89.5	2/8
Anthracene	mg/kg	0.03–0.43	21–21	29.6–41.4	45.0–88.0	1/4
Benzo[<i>a</i>]anthracene	mg/kg	0.08–1.18	25–41	15.9–47.4	56.0–79.2	3/10
Benzo[<i>a</i>]pyrene	mg/kg	0.09–1.17	25–41	22.2–36.8	42.9–77.3	2/10
Benzo[<i>b</i>]fluoranthene	mg/kg	0.13–1.42	24–41	28.2–56.0	44.0–68.2	0/10
Benzo[<i>e</i>]pyrene	mg/kg	0.10–1.34	19–32	15.8–43.5	41.2–87.5	6/10
Benzo[<i>ghi</i>]perylene	mg/kg	0.10–1.22	25–37	12.8–54.2	52.4–87.5	3/10
Benzo[<i>k</i>]fluoranthene	mg/kg	0.07–0.57	20–20	32.9–52.1	20.0–68.2	0/4
Chrysene	mg/kg	0.10–1.48	25–41	18.9–46.7	36.4–75.0	2/10
Dibenz[<i>ah</i>]anthracene	mg/kg	0.02–0.13	19–20	49.0–70.4	33.3–81.8	1/4
Fluoranthene	mg/kg	0.18–2.46	24–41	16.8–34.2	60.0–81.8	6/10
Fluorene	mg/kg	0.03–0.35	17–17	39.5–61.9	52.4–85.7	1/4
Indeno[1,2,3- <i>cd</i>]pyrene	mg/kg	0.10–1.16	23–37	27.3–48.3	43.5–72.0	2/10
Naphthalene	mg/kg	0.06–0.87	18–19	51.8–84.4	50.0–100.0	0/4
Phenanthrene	mg/kg	0.14–1.44	24–41	20.1–35.4	56.0–80.0	5/10
Pyrene	mg/kg	0.14–2.16	25–41	14.2–30.1	68.0–83.3	5/10
TOC	%	2.73–3.71	4–5	11.0–13.8	66.7–100.0	4/4

Table 4. Summary assessment of laboratory group performance in QUASIMEME trace element exercises in biological tissues, June 1996–December 1998.

Determinand	Units	¹ Range of assigned values	² Range of \pm Target Bias (%)	³ Range of Between Lab CVs (%)	⁴ Range for % No. obs. with $ Z < 2$	⁵ Satisfactory group performances in total rounds
Arsenic	µg/kg	1300–6905	14–21	18.9–47.4	55.0–95.0	9/11
Cadmium	µg/kg	5.15–458	13–187	13.5–95.4	39.3–80.0	6/11
Chromium	mg/kg	0.10–2.31	13–49	49.6–112.0	42.1–95.7	1/11
Copper	mg/kg	0.26–6.27	13–31	12.1–34.1	26.3–91.4	9/11
Dry-weight	%	13.97–71.22	13–13	2.6–12.3	73.7–94.1	11/11
Lead	µg/kg	14.24–892	13–31	40.0–148.9	35.0–100.0	0/11
Mercury	µg/kg	27.87–122	17–45	15.1–40.6	71.0–90.9	11/11
Nickel	mg/kg	0.05–1.44	14–70	37.2–107.4	53.8–81.8	6/11
Selenium	µg/kg	396–1258	13–14	16.3–38.0	58.3–100.0	2/7
Zinc	mg/kg	4.47–25.95	13–28	9.7–20.4	74.3–100.0	11/11

Table 5. Summary assessment of laboratory group performance in QUASIMEME trace element exercises in sediments, June 1996–December 1998.

Determinand	Units	¹ Range of assigned values	² Range of \pm Target Bias (%)	³ Range of Between Lab CVs (%)	⁴ Range for % No. obs. with $ Z < 2$	⁵ Satisfactory group performances in total rounds
Aluminium §	%	1.24–6.41	26–62	22.9–54.6	42.4–96.4	1/10
Arsenic	mg/kg	2.21–23.89	26–63	12.2–42.9	48.1–96.2	9/10
Cadmium	µg/kg	23.14–10977	30–70	13.0–71.8	40.0–84.8	6/10
Chromium	mg/kg	28.62–323	24–66	11.9–40.1	63.6–100.0	9/10
Chromium-P*	mg/kg	45.77–136	11–23	20.0–32.3	54.5–84.6	1/4
Copper	mg/kg	1.54–189	37–79	7.3–64.9	45.9–100.0	9/10
Iron	%	2.78–4.71	32–63	6.6–12.1	78.0–93.8	6/6
Lead	mg/kg	7.82–233	37–79	8.6–44.7	44.4–95.3	9/10
Lithium	mg/kg	35.70–66.38	20–34	10.6–16.8	88.2–97.1	6/6
Manganese	mg/kg	747–1130	32–59	7.3–11.1	83.3–100.0	6/6
Mercury	µg/kg	6.09–2237	24–69	10.7–76.9	73.3–95.1	9/10
Nickel	mg/kg	3.07–60.58	34–76	9.6–54.8	29.4–100.0	9/10
Scandium	mg/kg	7.61–11.28	4–10	6.4–34.3	60.0–100.0	5/6
TOC	%	0.06–6.24	11–33	13.9–97.9	72.7–90.9	10/10
Zinc	mg/kg	10.11–1051	37–79	5.6–45.6	40.0–100.0	9/10

*P means partial dissolution without hydrofluoric acid.

§ Based on both total and partial methods. It is recommended that only values based on total digestion methods should be used in the table in the

Table 6. Summary assessment of laboratory group performance in QUASIMEME nutrient exercises, June 1996–December 1998.

Determinand	Units	¹ Range of assigned values	² Range of \pm Target Bias (%)	³ Range of Between Lab CVs (%)	⁴ Range for % No. obs. with $ Z < 2$	⁵ Satisfactory group performances in total rounds
Ammonia	$\mu\text{mol/l}$	0.90–22.10	7–34	12.8–64.4	33.9–92.2	8/10
Nitrite	$\mu\text{mol/l}$	0.42–1.77	7–12	3.8–15.9	80.0–92.2	10/10
Phosphate	$\mu\text{mol/l}$	0.05–1.65	8–61	5.3–76.3	66.7–94.1	9/10
Silicate	$\mu\text{mol/l}$	1.79–17.20	7–12	6.7–20.9	65.2–89.4	10/10
TOTAL-N	$\mu\text{mol/l}$	8.76–51.60	6–9	7.3–23.1	52.9–84.6	7/10
TOTAL-P	$\mu\text{mol/l}$	0.20–1.78	7–19	6.7–43.9	62.5–92.3	6/10
TOxN	$\mu\text{mol/l}$	1.19–22.41	7–27	3.1–16.2	83.3–94.5	10/10
Nutrients in Estuarine Water						
Ammonia	$\mu\text{mol/l}$	1.23–24.29	7–26	9.5–23.0	66.7–97.4	10/11
Nitrite	$\mu\text{mol/l}$	0.53–6.37	6–11	3.7–8.0	83.3–97.4	11/11
Phosphate	$\mu\text{mol/l}$	1.15–6.54	6–8	4.1–15.9	62.2–95.1	10/11
Silicate	$\mu\text{mol/l}$	3.26–21.86	6–9	6.7–10.1	78.4–91.1	11/11
TOTAL-N	$\mu\text{mol/l}$	5.73–65.05	6–10	7.5–21.9	57.1–88.2	9/11
TOTAL-P	$\mu\text{mol/l}$	1.28–6.62	6–8	5.6–21.2	47.6–91.7	8/11
TOxN	$\mu\text{mol/l}$	2.64–36.27	7–15	3.6–8.3	81.4–95.1	11/11

ANNEX 4: 'NEW' CONTAMINANTS AND THEIR RELEVANCE TO THE MARINE ENVIRONMENT

Bo Jansson
Stockholm University

The term 'new' contaminants are often used to describe contaminants that have not been studied extensively in the environment. The latter are then referred to as being 'classical' contaminants including families such as DDT and PCB. The discovery of 'new' contaminants are often done by environmental chemists in survey studies but can also be the result of new signals appearing in the monitoring of classical contaminants.

Another important way to find compounds that may be or become 'new' contaminants is to look at the properties of chemicals produced and used in society. The number of substances, or group of substances, that are in use today is not known but is estimated to be several tens of thousands. The list of compounds in use, as declared by the industry, 1981 in the European Union contain more than 100 000 entries, but it is not expected all of them are in use in significant amounts. To set priorities among this large number of chemicals is a big task and the basis for a ranking has to be a political decision. This paper will discuss some of the priorities already set or being presently discussed.

In the OSPAR Convention of 1992 (www.ospar.org) the contracting parties agreed to take persistency, toxicity and bioaccumulation into account in the prioritising process for chemicals. It was also said that these criteria indicate the inclusion of heavy metals, organohalogen compounds, organic compounds of phosphorus and silicon, biocides and oils. OSPAR have over the following years through expert judgements produced a list of substances of primary concern.

In the Esbjerg Declaration of 1995 (www.ospar.org) it was further underlined that the signing parties should 'continuously reducing discharges, emissions and losses of hazardous substances to the North Sea and thereby moving towards the target of their cessation within one generation with the ultimate aim of concentrations in the environment near background levels for naturally occurring substances and close to zero concentrations for man-made synthetic substances'. The definition of hazardous substances is not given but the same parameters as in the OSPAR convention were mentioned.

The task to identify the hazardous substances was given to OSPAR and an ad hoc group (DYNAMEC) was formed. This group has started its work and decided to make a list of compounds that are of possible concern for the marine environment. They will apply a ranking algorithm to the compounds on that list to produce a ranking of relative risk. The properties used for this ranking are persistency, bioaccumulation and toxicity and different cut-off values will be investigated. After this ranking a selection of compounds for priority action will be done. In parallel with the ranking procedure a 'safety net' will give possibilities to include compounds of special interest, for example compounds that occur in the marine environment or have endocrine disrupting effects.

Within the UN-ECE LRTAP (www.unece.org) convention were to new protocols signed 1998, one for metals and one for POPs (persistent organic pollutants). These protocols include lists of substances and what measures signing parties have to take to reduce the risk for trans-boundary transport via air of these compounds. The 16 substances or groups of substances in the POPs protocol were selected using persistency, bioaccumulation and toxicity, but also presence of a compound in remote areas was taken into account.

A global agreement is presently being negotiated within the UNEP POPs programme. (irptc.unep.ch). Initially there are 12 substances or group of substances on a list for actions, but there shall be a possibility to add more substances to the list if they fulfill specified criteria. A special 'Criteria group' is presently working on the setting of cut-off values for persistency, bioaccumulation and toxicity. Also in this procedure is the use of occurrence in remote areas foreseen.

A new directive has been proposed by the European commission in order to harmonise the legislation regarding water quality within the EU. The quality is planned to measure both biological and chemical parameters. There is presently work going on to decide on which parameters to use, and for the chemical a prioritisation process rather like the one in OSPAR will probably be the tool. Measured data is supposed to play an important role in the priority setting.

Lots of resources are today spent on risk assessments of chemicals and a complete evaluation of one substance is very expensive. This means that the prioritising of the compounds to be studied is very important. This has so far mainly been done by expert judgements and there are lists of compounds to be evaluated. The risk assessments in the EU follows a strict scheme set up in a technical guidance document. A modelling tool (EUSES) is used to estimate exposure if there are lack of measured data. It is a risk that these estimated exposures become very conservative and that resources to take measures against environmental and human risks are not spent in an optimal way.

As already mentioned, alarm signals in the environment has to play an important role in the setting of priorities between chemicals to be studied. Compounds found in remote areas indicate that they are persistent enough to survive a long transport, often through several environmental media. Another alarming signal is when a certain compound is found at increasing levels, as this indicate that it is emitted faster than it is degraded and sooner or later may reach effect levels. Adverse effects appearing in the environment that cannot be explained may also be due to chemicals and is of course also a serious warning that has to be investigated.

The MCWG will not be directly involved in the on-going work with prioritising of chemicals, but will probably be asked to comment on the results. Environmental chemists, however, have several important functions in this work with chemicals:

- Monitoring whether measures taken against emission of a chemical give the aimed effect in the environment
- Identify new contaminants that appear in the analyses
- Support the priority setting process
- Support risk assessors with exposure data
- By making all produced results easily available
- To initiate and participate in survey programs for chemicals to be assessed.

ANNEX 5: INFORMATION ON GERMAN SEABIRD EGG STUDIES (TRACE METALS)

Peter Woitke

Federal Environmental Agency of Germany
PO Box 33 00 22
14191 Berlin, Germany

A presentation on the use of seabird eggs in environmental marine monitoring was given by Anders Bignert at the MCWG meeting in Stockholm, 1998 [1]. Since seabird eggs seem to be an appropriate matrix, particularly for an assessment of temporal trends of mercury and organochlorine contaminants, it would be useful to have more detailed information on monitoring programmes and research studies using seabird eggs. This paper gives an overview on seabird egg studies which have been carried out in Germany with the objective to investigate temporal trends and spatial distributions of organic and inorganic pollutants in marine ecosystems.

Contamination levels in seabird eggs collected at several sampling sites along the German coast have been determined within several research projects of the German 'Institut für Vogelforschung', Wilhelmshaven or as part of the Environmental Specimen Bank of Germany [2]. Additionally, concentrations of various hazardous substances belong to the 'Common Parameter Package' of the recently released Trilateral Monitoring and Assessment Programme of the Wadden Sea (TMAP) [3] and are, therefore, determined regularly.

1 Research Projects on Seabird Egg Studies in Germany

Several research projects carried out in Germany since 1975 revealed the usefulness of seabird eggs for marine environmental monitoring studies. The 'Institut für Vogelforschung' collaborating with the 'Fachhochschule Wilhelmshaven' is one of the most experienced institutions in seabird monitoring investigations. Table 1 gives an overview on research projects of the institute with respect to seabird egg studies. Abstracts of these research projects can be found in Annex 1. As an example, essential results of a study on contaminant levels in seabird eggs along the German North Sea coast are listed in Table 2.

Table 1. Seabird egg studies and research projects of the 'Institut für Vogelforschung', Wilhelmshaven.

Title	Term	Project Leader	Financial Support
Loading of seabirds, sea mammals and land mammals with environmental poisons (pesticides and heavy metals)	01.05.1975 31.12.1981	Dr G. Vauk	Senator für Gesundheit und Umweltschutz, Bremen
Environmental contaminants in clutches of breeding birds from the North Sea coast of Germany	01.01.1981 31.12.1985	Dr P.H.Becker	Volkswagen-Stiftung
Pollutants in eggs of birds breeding at the German North Sea coast in 1986 compared to 1981	01.01.1986 01.01.1988	Dr P.H.Becker	Niedersächs. Minister für Ernährung, Landwirtschaft und Forsten, Volkswagen-Stiftung
Monitoring residues of mercury and organochlorines in seabird eggs	01.05.1987 30.09.1991	Dr P.H.Becker	Umweltbundesamt
Monitoring of environmental chemicals in seabirds: Trends in the 1990s	01.01.1995 31.12.1998	Dr P.H.Becker	Niedersächsische Wattenmeerstiftung

Table 2. Monitoring residues of organochlorines and mercury in seabird eggs [4].

Topic	Species	Contaminants [mg/kg fresh weight]	Results
Geographic variation (13 sampling sites along the German North Sea coast)	Oystercatcher	γ -HCH (0.002–0.016) Σ DDT (0.1–0.5) HCB (0.01–0.26) Σ PCB (4–16) Hg (0.2–0.8)	significant spatial variability higher contamination of samples from the river Elbe estuaries in comparison to the western and northern part of the North Sea coast
Temporal trends (1981 - 1987)	Oystercatcher Common Tern	γ -HCH (0.002 – 0.016) Σ DDT (0.1 – 0.5) HCB (0.01 – 0.26) Σ PCB (4 – 16) Hg (0.4 – 2.3)	significant temporal trends steep rise between 1986 and 1987 increase for most of the investigated contaminants between 1981 and 1987
Interspecific differences	Oystercatcher Common Tern Sandwich Tern Shelduck Ringed Plover	γ -HCH, Σ DDT, HCB, Σ PCB, Hg	significant differences between species highest levels of almost all contaminants in the fish- eating species (Common Tern and Sandwich Tern) highest γ -HCH concentrations in Shelduck and Ringed Plover

2 Environmental Specimen Bank of Germany (ESB)

As an important part of German ecological assessment programmes, the ESB collects, characterises and archives a variety of species from representative areas of Germany [2]. Among others, the main objectives of the ESB are:

- continuous control of contaminant concentrations in the samples before archiving,
- retrospective analysis of substances which have not yet been recognised as hazardous,
- evaluation of trends on local, regional or global development of pollution.

For an assessment of the pollution of German marine and coastal ecosystems and for retrospective investigations on its development, two representative areas have been selected, the German Wadden Sea National Park (North Sea) and the National Park of the Vorpommern Bodden Area (Baltic Sea). To achieve the above mentioned goals, a variety of species and matrices were chosen to characterize the environmental state of these areas, among them Herring Gull eggs.

According to the standard operating procedures of the ESB, 75 eggs per Herring Gull colony are sampled annually in May, and some biometric parameters have to be determined immediately (length, diameter, weight). In a clean room laboratory, the contents of all eggs from one colony are homogenised and subsamples of 10 g are prepared. These subsamples are stored frozen at -150°C for archiving purposes. A basic characterisation of the Herring Gull homogenate is carried out by determining a variety of organic and inorganic contaminants in some of the subsamples [5]:

- elements and inorganic species (Ba, Ca, Fe, K, Mg, Na, P, S, Sr, Zn, Cd, Co, Cr, Cu, Ni, Pb, Sb, Te, Bi, Sn, Se, As, Tl, Hg, Me-Hg);
- chlorinated hydrocarbons (aldrin, dieldrin, α -HCH, β -HCH, γ -HCH, HCB, p,p'-DDT, o,p'-DDT, p,p'-DDD, p,p'-DDE, OCS, PCB28, PCB52, PCB101, PCB138, PCB153, PCB180, PCP);
- PAHs (anthanthrene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[b]naphto[2,1-d]thiophene, benzo[c]phenanthrene, benzo[e]pyrene, benzo[ghi]fluoranthene, benzo[ghi]perylene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, coronene, dibenz[a,h]anthracene, fluoranthene, indeno[1,2,3-cd]pyrene, perylene, pyrene, triphenylene).

Collection, archiving and basic chemical characterisation of Herring Gull egg homogenates from two sampling sites on the North Sea coast (river Elbe estuary and river Weser estuary) have been carried out since 1988. Herring Gull egg homogenates representative for a Baltic Sea marine ecosystem (one sampling site) have been stored in the ESB since 1991. Table 3 contains examples of temporal trends of selected heavy metals determined in Herring Gull eggs [6].

Table 3. Temporal trend monitoring of marine ecosystems carried out by the Environmental Specimen Bank. Examples of contaminant concentrations in Herring Gull egg homogenates from two sampling sites at the North Sea coast between 1988 and 1997.

Parameter	Sampling Site	Concentration [µg/g dry weight]	Trend
As	Elbe estuary Weser estuary	0.35 – 0.65 0.2 – 0.5	decreasing at both sampling sites
Hg	Elbe estuary Weser estuary	1.5 – 4.5 0.5 – 1.2	decreasing at both sampling sites
Cu	Elbe estuary Weser estuary	2.0 – 2.5 2.5 – 2.8	relatively constant, slightly increasing at both sites
Se	Elbe estuary Weser estuary	2.2 – 3.0 1.8 – 3.2	varying concentrations at both sites, no significant trend

3 Trilateral Monitoring and Assessment Programme (TMAP) of the Wadden Sea

The objective of the TMAP is an integrated monitoring and assessment of the Wadden Sea ecosystem as a whole [2]. A variety of parameters is investigated within the framework of the TMAP on the basis of five issues (climate change, input of nutrients and contaminants, fisheries, recreational activities, agricultural practice) with the aim to document the implementation of common ecological targets (targets on habitat and species, water and sediment, landscape and culture). Pollution is one of the issues of concern in the TMAP. Hence, contaminants in seabird eggs belong to the 'Common Package of Parameters' determined in this monitoring programme.

Based on several TMAP Expert Workshops in 1995 and 1996, a TMAP Manual was released in 1997 [7]. This manual contains an overview on the structure and contents of the TMAP as well as guidelines for the determination of the monitoring parameters together with a description of the TMAP data management system. Annex 2 is the present version of the TMAP guideline 'Contaminants in bird eggs'.

A two-year trilateral pilot project 'Contaminants in bird eggs' was carried out in 1996/97 to develop a harmonised trilateral programme and to test sampling sites and methods. An abstract of this pilot project can be found in Annex 3.

References

- [1] MCWG (1998) Report of the Marine Chemistry Working Group. Stockholm, ICES CM 1998/E:2
- [2] Paulus M, Klein R, Wagner G, Muller P (1996) Biomonitoring and Environmental Specimen Banking. *Environ Sci Pollut Res* 3 169-177
- [3] The Trilateral Monitoring and Assessment Programme (1996) Expert Workshop 1995/1996. Wadden Sea Ecosystem No. 6
- [4] Becker PH (1989) Seabirds as monitor organisms of contaminants along the German North Sea coast. *Helgoländer Meeresunters* 43 395-403
- [5] Environmental Specimen Bank of Germany (1996) Standard Operating Procedures for Sampling, Transport, Storage and Chemical Characterization of Environmental and Human Samples. Erich Schmidt Verlag, Berlin
- [6] Environmental Specimen Bank of Germany (1998) Results 1996 and 1997, Draft Report. Federal Environmental Agency of Germany, Berlin (*internet*: <http://www.umweltbundesamt.de/uba-info-daten/daten/umweltprobenbank-des-bundes.htm>)
- [7] TMAP 1997 TMAP Manual. Common Wadden Sea Secretariat (CWSS), Wilhelmshaven.

Further References of the 'Insitut für Vogelforschung'

- Becker, P.H., B. Conrad, & H. Sperveslage (1980): Vergleich der Gehalte an chlorierten Kohlenwasserstoffen und PCB's in Silbermöwen (*Larus argentatus*)-Eiern von Mellum 1975 und 1979. *Vogelwarte* 30: 294-296
- Becker, P.H., A. Bütthe, & W. Heidmann (1985): Schadstoffe in Gelegen von Brutvögeln der deutschen Nordseeküste. I. Chlororganische Verbindungen. *J. Orn.* 126: 29-51
- Becker, P.H., W. Ternes, & H.A. Rüssel (1985): Schadstoffe in Gelegen von Brutvögeln der deutschen Nordseeküste. II. Quecksilber. *J. Orn.* 126: 253-262
- Becker, P.H., A. Bütthe, & W. Heidmann (1988): Rückgänge von Schadstoffgehalten in Küstenvögeln? *J. Orn.* 129: 104-106
- Becker, P.H. (1989): Seabirds as monitor organisms of contaminants along the German North Sea coast. *Helgoländer Meeresunters.* 43: 395-403
- Becker, P.H., B. Conrad, & H. Sperveslage (1989): Chlororganische Verbindungen und Schwermetalle in weiblichen Silbermöwen (*Larus argentatus*) und ihren Eiern mit bekannter Legefolge. *Vogelwarte* 35: 1-10
- Becker, P.H., & H. Sperveslage (1989): Organochlorines and Heavy Metals in Herring Gull, *Larus argentatus*, Eggs and Chicks from the same clutch. *Bull. Environ. Contam. Toxicol.* 42: 721-727
- Becker, P.H. (1991): Population and contamination studies in coastal birds with special reference to the Common Tern (*Sterna hirundo*). In: C.M. Perrins, J.D. Lebreton, & G.J.M. Hirons (eds.): *Bird population studies: Relevance to conservation and management*. Oxford University Press, Oxford: 433-460
- Becker, P.H., C. Koepff, W.A. Heidmann, & A. Bütthe (1991): Schadstoffmonitoring mit Seevögeln. *TEXTE* 2/92: 1-260. Umweltbundesamt, Berlin
- Becker, P.H., C. Koepff, & W. Bruns (1991): Test device for measuring the strength of eggshells in environmental research. *Reports Appl. Measurement* 7: 1-4
- Becker, P.H. (1992): Seabirds as monitors of environmental chemicals in the Wadden Sea. *Proc. Seabird Group Conf. Glasgow 1992*, 5
- Becker, P.H. (1992): Egg mercury levels decline with the laying sequence in Charadriiformes. *Bull. Environ. Contam. Toxicol.* 48: 162-167
- Becker, P.H. (1992): Seevogelmonitoring: Brutbestände, Reproduktion, Schadstoffe. *Vogelwelt* 113: 262-272
- Becker, P.H., W.A. Heidmann, A. Bütthe, D. Frank, & C. Koepff (1992): Umweltchemikalien in Eiern von Brutvögeln der deutschen Nordseeküste: Trends 1981-1990. *J. Orn.* 133: 109-124
- Becker, P.H. (1993): Seevögel als Anzeiger für die Belastung der Umwelt mit Quecksilber. *Jber. Institut für Vogelforschung* 1: 27
- Becker, P.H. (1993): Seevögel als Bioindikatoren. *Wilhelmshavener Tage* 4. Brune Druck, Wilhelmshaven, 79-93
- Becker, P.H., R.W. Furness, & D. Henning (1993): Mercury dynamics in young Common Tern (*Sterna hirundo*) chicks from a polluted environment. *Ecotoxicology* 2: 33-40
- Becker, P.H., S. Schuhmann, & C. Koepff (1993): Hatching failure in Common Terns (*Sterna hirundo*) in relation to environmental chemicals. *Environ. Pollut.* 79: 207-213
- Thompson, D.R., P.H. Becker, & R.W. Furness (1993): Long-term changes in mercury concentrations in herring gulls *Larus argentatus* and common terns *Sterna hirundo* from the German North Sea coast. *J. Appl. Ecol.* 30: 316-320

- Becker, P.H., R.W. Furness, & D. Henning (1993): The value of chick feathers to assess spatial and interspecific variation in the mercury contamination of seabirds. *Environ. Monitoring Assessment* 28: 255-262
- Lewis, S.A., P.H. Becker, & R.W. Furness (1993): Mercury levels in eggs, internal tissues and feathers of herring gulls *Larus argentatus* from the German Wadden Sea. *Environ. Pollut.* 80: 293-299
- Beyerbach, M., P.H. Becker, A. Bütte, E. Denker, W.A. Heidmann, & G. Staates de Yanes (1993): Variation von PCB-Gemischen in Eiern von Vögeln des Wattenmeeres. *J. Orn.* 134: 325-334
- Becker, P.H. (1994): Gefährdung von Küstenvögeln durch Umweltchemikalien. In: Lozan, J.L., E. Rachor, K. Reise, H. v. Westernhagen, & W. Lenz (Hrsg.): Warnsignale aus dem Wattenmeer: 270-278, Blackwell Wissenschaftsverlag, Berlin
- Becker, P.H., D. Henning, & R.W. Furness (1994): Differences in Mercury Contamination and Elimination during Feather Development in Gull and Tern Broods. *Arch. Environ. Contam. Toxicol.* 27: 162-167
- Becker, P.H., D. Henning, & H. Wendeln (1994): Schadstoffanreicherung im Nahrungsnetz des Wattenmeeres. *Ber. Ökosystemforsch. Wattenmeer* 4 (1994), Bd. 2: 72-75
- Denker, E., P.H. Becker, M. Beyerbach, A. Bütte, W.A. Heidmann, & G. Staates de Yanes (1994): Concentrations and metabolism of PCBs in eggs of waterbirds on the German North Sea coast. *Bull. Environ. Contam. Toxicol.* 52: 220-225
- Furness, R.W., D.R. Thompson, P.H. Becker, L. Monteiro, & J.P. Granadeiro (1994): The use of feathers for monitoring mercury pollution. *J. Orn.* 135: 525
- Mattig, F.R., & P.H. Becker (1994): Variabilität der Schadstoffe im Nahrungsnetz. In: Lozan, J.L., E. Rachor, K. Reise, H. v. Westernhagen, & W. Lenz (Hrsg.): Warnsignale aus dem Wattenmeer: 103-106, Blackwell Wissenschaftsverlag, Berlin
- Furness, R.W., D.R. Thompson & P.H. Becker (1995): Spatial and temporal variation in mercury contamination of seabirds in the North Sea. *Helgoländer Meeresunters.* 49: 605-615
- Mattig, F.R. & P.H. Becker (1995): Schadstoffanreicherung im Nahrungsnetz des Wattenmeeres. *Jber. Inst. f. Vogelforschung* 2: 22
- Garthe, S., J. Ludwig & P.H. Becker (1996): Gefährdung der Vogelwelt an Flüssen. In: Lozan, J.L. & H. Kausch (eds): Warnsignale aus den Flüssen und Ästuaren. Blackwell, Berlin: 234-240
- Mattig, F.R., F. Bairlein & P.H. Becker (1996): Physiologische Bewertung der PCB-Belastung des Alpenstrandläufers (*Calidris alpina*). *Verh. Dtsch. Zool. Ges.* 89.1: 165
- Mattig, F.R., P.H. Becker, H. Bietz & K. Gieáing (1996): Schadstoffanreicherung im Nahrungsnetz des Wattenmeeres. Forschungsbericht 10802085/21, TP A4.5.1: 1-349, Umweltbundesamt, Berlin
- Becker, P.H. (1997): Schadstoffmonitoring mit Seevögeln. *Jber. Institut für Vogelforschung* 3: 32
- Bietz, H., F.R. Mattig, P.H. Becker & U. Ballin (1997): Spatial and temporal variation in heavy metal contamination of *Nereis* and *Cerastoderma* in the Wadden Sea. *Arch. Fish. Mar. Res.* 45 (3): 243-254
- Mattig, F.R., U. Ballin, H. Bietz, K. Gieáing, R. Kruse & P.H. Becker (1997): Organochlorines and heavy metals in benthic invertebrates and fish from the back barrier of Spiekeroog. *Arch. Fish. Mar. Res.* 45 (2): 113-133
- Sommer, U., K.R. Schmieder & P.H. Becker (1997): Untersuchung von Seevogeleiern auf chlorierte Pestizide, PCBs und Quecksilber. *BIOforum* 20 (3/97): 68-72
- Becker, P.H. & U. Sommer (1998): Die derzeitige Belastung der Flussseseschwalbe *Sterna hirundo* mit Umweltchemikalien in Mitteleuropa. *Vogelwelt* 119: 243-249

- Becker, P.H., S. Thyen, S. Mickstein, U. Sommer & K.R. Schmieder (1998): Monitoring Pollutants in coastal bird eggs in the Wadden Sea. Final Report of the Pilot Study 1996-1997. Wadden Sea Ecosystem 8. Common Wadden Sea Secretariat Wilhelmshaven: 59-101
- Exo, K.-M., P.H. Becker & U. Sommer (1998): Umweltchemikalien in Eiern von Binnenland- und Wattenmeerbrütern des Austernfischers (*Haematopus ostralegus*). J. Ornithol. 139: 401-405
- Muñoz Cifuentes, J. & P.H. Becker (1998): Eier der Flußseeschwalbe (*Sterna hirundo*) als Indikator für die aktuelle Belastung von Rhein, Weser und Elbe mit Umweltchemikalien. Z. Umweltchem. Ökotox. 8: 15-21
- Becker, P.H. (1998): Spatial and temporal distribution of contaminants in seabird eggs. Quality Status Report of the North Sea. Subregion 10: The Wadden Sea: In press
- Muñoz Cifuentes, J. & P.H. Becker: The Kelp Gull as bioindicator of environmental chemicals in the Magellan Region - a comparison with other coastal sites in Chile. Scientia Marina: In press

Annex 1: Abstracts of research projects on seabird egg studies carried out at the Institut für Vogelforschung

- A1.1 Loading of seabirds, sea mammals and land mammals with environmental pollutants (pesticides and heavy metals) Time: 01.05.1975–31.12.1981

Abstract

The aim of this project was the determination of the contamination level of different species of seabirds and sea mammals and a comparison of different species to evaluate the individual variation in the concentration of several environmental pollutants. The project should lead to an assessment of the usefulness of several species as indicators for spatial and temporal variations of contaminant levels in the marine environment. A correlation should be established between biology (feeding ecology) and pollution of the investigated species.

- A1.2 Environmental contaminants in clutches of breeding birds from the North Sea coast of Germany Time: 01.01.1981–31.12.1985

Abstract

Eggs of seven seabird and coastal bird species were collected in seven regions of the North Sea coast in 1981 to investigate their contamination with organochlorines and heavy metals. The selected species belong to several families differing in feeding habit and migration behaviour: Shelduck (*Tadorna tadorna*), Oystercatcher (*Haematopus ostralegus*), Ringed Plover (*Charadrius hiaticula*), Herring Gull (*Larus argentatus*), Black-headed Gull (*Larus ridibundus*), Common tern (*Sterna hirundo*), Sandwich Tern (*Sterna sandvicensis*). The aim of this study was to investigate differences in the contamination level within species depending on the sampling area and between different species.

- A1.3 Pollutants in eggs of birds breeding at the German North Sea Coast 1986 compared to 1981 Time: 01.01.1986–01.01.1988

Abstract

Clutches of three species of breeding coastal birds, Oystercatcher (*Haematopus ostralegus*), Herring Gull (*Larus argentatus*) and Common Tern (*Sterna hirundo*) differing in feeding habit, migration behaviour and level of contamination were analysed for organochlorines and heavy metals. In 1986, the investigated eggs were collected at the same coastal region as in 1981. Therefore, a comparison of the contamination levels between the two years was possible, particularly with regard to changes in concentrations of substances which were at high levels in 1981.

- A1.4 Monitoring Residues of Organochlorines and Mercury in Seabird Eggs, West Germany Time: 01.05.1987–30.09.1991

Abstract

From 1987 to 1990 Common Tern (*Sterna hirundo*) and Oystercatcher (*Haematopus ostralegus*) eggs were used for monitoring environmental chemicals on the German North Sea coast (9 -14 sampling sites). Eggs of fish-eating terns showed the highest level of environmental contaminants among 11 coastal bird species. The microgeographic contamination patterns indicate the input of various chemicals by the rivers Elbe, Weser and Ems into the North Sea. Highest residues were found in eggs from the Elbe estuary and the inner German Bight. The mercury concentrations in Common Tern eggs from the Elbe are among the highest which have ever been found in bird eggs. In a Common Tern colony with a high burden of PCBs and Σ DDT at the Elbe estuary the egg residue levels were linked with reduced hatching success. An investigation of temporal trends from 1981 to 1990 revealed that concentrations of several contaminants increased in the eggs (mercury, PCBs, lindane), and that levels of HCB and α -HCH decreased. The advantages of birds' eggs as samples in monitoring studies are confirmed by studies of the residues' variation within the clutch, the sample site and the breeding season.

Abstract

Seabirds can be regarded as suitable indicators for a contamination of the marine environment. Based on investigations carried out at the Institut fuer Vogelforschung in the Eighties, seabird eggs are part of the Trilateral Monitoring and Assessment Programme of the Wadden Sea (TMAP) and should be regularly sampled. A regular sampling of seabird eggs has been carried out in selected areas of the Wadden Sea coast supported by the National Park Services of Schleswig-Holstein and Niedersachsen since 1986. Within this research project seabird eggs of the years 1991 - 1998 were analysed. The results can be used to evaluate trends in the concentration of organohalogenes and heavy metals in seabirds as well as to demonstrate changes in the spatial distribution.

Annex 2: TMAP Guideline ‘Contaminants in bird eggs’

A two-year trilateral pilot project ‘Contaminants in bird eggs’ was carried out in 1996/97 to develop a harmonized trilateral programme and to test sampling sites and methods. Based on its results and previous projects in the Wadden Sea area (Becker 1989 & 1991, Becker et al. 1991 & 1992), guidelines were elaborated in the framework of the JAMP in 1996 (OSPAR 1997) which will also be applied for the TMAP.

Objective

The monitoring of the contamination of bird eggs with different pollutants in the Wadden Sea is carried out in order

- to detect and assess the response of natural processes in the ecosystem to changes in pollution levels. The processes concerned here are food chain fluxes and reproduction (including recruitment). There are links with primary production and decomposition;
- to detect and assess the response of species to changes in pollution levels which may affect the abundance and physiological functioning of species leading to structural changes in the ecosystem.

Furthermore, the monitoring has the aim to assess

- the effectiveness of measure take for reduction of contamination (temporal trend monitoring),
- the existing level of marine contamination (spatial distribution monitoring).

Assessment

Changes in the abundance of birds may reflect natural fluctuations (including climate, weather, predation). Also, changes may be caused by contaminant levels or by other anthropogenic factors. The assessment therefore requires the monitoring information on these impacts.

The ecological targets regarding birds, as agreed at the Trilateral Governmental Conference in Leeuwarden (1994), will be used for the assessment in the Wadden Sea:

- favourable conditions for migratory and breeding birds,
- favourable food availability,
- natural breeding success,
- sufficiently large undisturbed roosting and moulting areas,
- natural flight distances.

Monitoring areas

Sampling sites should reflect important breeding areas and species. To collect the necessary number of eggs over the period of the monitoring programme sampling sites should be chosen, where sufficient pairs of birds can be expected to breed for the required number of years and where disturbances can be reduced to a minimum. Both coastal areas adjacent to the open sea and known ‘hot spots’ such as estuaries should be included (OSPAR 1997).

Monitoring areas in the Wadden Sea shall be selected on the national level.

Parameters

For the selection of monitoring parameters, the JAMP guidelines (OSPAR 1997) have been taken into account. The following heavy metals are analysed in bird eggs (according to JAMP):

- ‘JAMP metals’: cadmium (Cd), mercury (Hg), lead (Pb), zinc (Zn), copper (Cu)
- additionally: methyl mercury (Met-Hg), arsenic (As), selenium (Se), tin (Sn)

The following organic contaminants are analysed in bird eggs (according to JAMP):

- PCBs (28, 52, 101, 105, 118, 138, 153, 156, 180),
- organochlorine pesticides, e.g., HCHs (α -, γ -HCH), HCB, p,p'-DDT, p,p'-DDD, p,p'-DDE, dieldrin, transnonachlor, (cis)-chlordane, (trans)-chlordane.

It should be examined regularly, whether additional compounds, like toxaphene or other pesticides, or 'new' environmental contaminants should be included into the programme.

Sampling

- Species: Common Tern (*Sterna hirunda*), Oystercatcher (*Haematopus ostralegus*)

For each species, site and year 10 eggs should be sampled with one egg taken randomly from each of 10 clutches from the first laying cycle within the year (after 1–5 days incubation)

- Matrix: whole egg content
- Sampling frequency: annual sampling
- Sampling period: generally May/June (during the peak of the first laying cycle within the year which is species-, year-, and site-specific).

Analytical procedures

Sample preparation, extraction and analysis of contaminants from samples follows the procedures as described for the JAMP (OSPAR 1997).

Quality assurance

Participation in intercalibration exercises is envisaged to ensure that the methods in use comply with international standards. The requirement of JAMP guidelines on quality assurance have to be taken into account (OSPAR 1997).

Literature

Becker, P. H., 1989: Seabirds as monitor organisms of contaminants along the German North Sea Coast. Helgoländer Meeresunters. 43: 395-403.

Becker, P.H., 1991: Population and contamination studies in coastal birds: The Common Tern *Sterna hirunda*. In: Perrins, C.M., Lebreton, J.D. and Hirons, G.J.M. (Editors): Bird population studies: relevance to conservation and management. Oxford Univ. Press. Oxford. 433-460.

Becker, P.H., Koepff, C., Heidmann, W.A. & Bütke, A., 1991: Schadstoffmonitoring mit Seevögeln. Forschungsbericht UBA-FB 91-081. TEXTE 2/92, Umweltbundesamt, Berlin: 260 pp.

Becker, P.H., Heidmann, W.A., Bütke, A., Frank, D. & Koepff, C., 1992: Umweltchemikalien in Eiern von Brutvögeln an der deutschen Nordseeküste: Trends 1981-1990. J. Orn. 133: 109-124.

OSPAR, 1997: JAMP Guidelines for Monitoring Contaminants in Biota (9/6/97), 40 pp.

Annex 3: Monitoring Pollutants in Coastal Bird Eggs in the Wadden Sea. Final Report of the Pilot Study 1996–1997

Peter H. Becker, Stefan Thyen, Susanne Mickstein, Ute Sommer and Klaus R. Schneider Wadden Sea Ecosystem No. 8 (1998). Common Wadden Sea Secretariat, Trilateral Monitoring and Assessment Group and Joint Monitoring Group of Breeding Birds in the Wadden Sea, Wilhelmshaven, page 59–101.

Abstract

To get practical experience with the parameter ‘Monitoring of Pollutants in Coastal Bird Eggs’ of the Trilateral Monitoring and Assessment Programme (TMAP), investigations concerning pollutant residues in bird eggs were carried out during a two-year pilot study on the Wadden Sea coast. In 1996 and 1997, residues of PCBs, DDT and metabolites, HCB, and HCHs and of mercury were analysed in Common Tern (*Sterna hirundo*) and Oystercatcher (*Haematopus ostralegus*) eggs according to methods tested during previous years. To cover as extensive a part of the Wadden Sea as possible, the eggs were collected along the entire Dutch and German North Sea coast.

Depending on species, breeding site, and year, the results indicate varying concentrations of pollutants in eggs. Altogether, Common Tern eggs were mostly more contaminated by the investigated chemicals than Oystercatcher eggs which is explained by different feeding, breeding, and migration behaviour. In general, eggs from breeding sites in the inner German Bight (Elbe estuary and Trischen in Lower Saxony and Schleswig-Holstein, respectively) were contaminated on much higher levels than those collected at western and northern breeding sites of the Wadden Sea area indicating the high importance of the Elbe as input source of the studied industrial chemicals and pesticides. Considerable contamination especially by PCBs and γ -HCH (Lindane) was also ascertained on Griend, the Netherlands, suggesting that the Wadden Sea ecosystem is also influenced by pollutant loads from the river Rhine. Elevated PCB concentrations found in 1997 in Oystercatcher eggs from the German part of the Dollard (on average 1055 ng/g fresh weight of egg content) indicate recent discharges of PCBs within the catchment area of the river Ems.

Because monitoring of pollutants in coastal bird eggs has been carried out in Germany since 1981 and continued each year since 1986 by the Institut für Vogelforschung, Wilhelmshaven and co-operating laboratories, long-term trends could be calculated. At most study sites, the results reveal decreasing levels of mercury and most organochlorines. However, constant or increasing Lindane concentrations were found at the Oystercatcher breeding sites. These results and their probable causes are assessed considering the ‘Ecological Targets’ of the Trilateral Co-operation on the Protection of the Wadden Sea Ecosystem. Most results are favourable in view of Wadden Sea pollution. However, there are some circumstances which prevented a full achievement of the ecotargets so far (for example recent discharges of pesticides and even prohibited industrial chemicals, persistence of the pollutants). These problems are discussed and need further investigations and protection efforts, as well as the implementation of the TMAP in general and the monitoring of pollutants in coastal bird eggs in particular. Furthermore, the results of the pilot project qualify chemical monitoring of coastal birds representing high trophic levels as a very meaningful and important tool for the assessment of the situation of the Wadden Sea ecosystem and, therefore, for the Wadden Sea conservation. Gaps in the TMAP are addressed leading to the explicit recommendation of the additional implementation of the parameter ‘breeding success of coastal birds’ as soon as possible to enable the assessment of effects of chemicals on the bird populations. Furthermore, the extension of the area of investigation to the Danish part of the Wadden Sea and to the Rhine delta in the Netherlands is proposed.

ANNEX 6: MARINE INSTITUTE MED/BIOTA ICES REPORTING DATABASE AND QC DATABASE

M.J. Bloxham

Marine Institute Fisheries Research Centre, Dublin, Ireland

In recent years considerable emphasis has been placed on the production of high quality analytical data. This has been achieved by developing appropriate quality assurance (QA) systems incorporating the analysis of certified reference materials (CRMs) and involvement in intercomparison exercises such as QUASIMEME. However, a limiting factor in this process has been the storage of QA data and the relationship of such information with the analytical results of real samples.

This is apparent when reporting data to the ICES databank, which currently requires limited QA data. For example, for a given year and analytical method, it is only possible to report the mean result and standard deviation for one CRM. This is also the case for QUASIMEME intercomparison data.

In order to facilitate the transfer of Irish marine contaminant data to ICES, a generic Microsoft Access database has been adapted by the Marine Institute FRC and the Marine Institute Data Centre using an existing Access database (MED/Biota) developed by National Institute for Water Research (NIVA), Norway. All data stored in this database has to conform to ICES reporting formats which enables relatively trouble free data transfer. The Marine Institute FRC database is capable of exporting the relevant data into the correct ASCII formats for reporting environmental data to ICES. This removes the need for manipulation of data files into the right format that has historically been time consuming and problematical.

In order to overcome the limitations of the ICES reporting format the MED/Biota database has been adapted to allow for the input of QC data relating to individual batches of samples. Each sample in the Med/Biota database is linked to an Access QA database through the use of unique identifying codes. A brief description of the relevant sections of the two databases is given below.

Figure 1 shows the contaminant data in the MED/Biota database for a shellfish sample collected in 1996 (year 96, Sample sequence number 368). The homogenised sample (H) was analysed for Cd, Cr, Cu, Hg, Pb and Zn and reported on a dry weight basis (D). The column on the far right gives the QC reference number, a unique identifier made up of year (97) and batch number (0035).

The QC reference number in the Med/Biota contaminant database can be cross-referenced with the QC sequence number in the QC database (Figure 2). The QC master form also includes information such as date of analysis, the analytical method and reference material details.

Figure 3 shows the QC trace metals form. Again the QC sequence number is used which enables easy traceability. The data for each contaminant in the CRM is also recorded.

Currently the two databases are not linked electronically, although this is expected to occur in the near future. However, the current system allows the data to be easily queried and exported to a spreadsheet such as Microsoft Excel for further analysis such as incorporation into quality control charts.

Figure 1. Contaminant data form in the MED/Biota database.

AMAP - CONTAMINANT

Marine Environmental Data/Biota Contaminant - Current Year

Reporting institute: FRD Monitoring year: 96 Sample sequence number: 368
 Sub-sample number: 1 Individual or bulk: N Tissue: SB

name	Validity flag	Qualifier flag	Value	valsn	unit	Basis	Rep	am	An	unit1	QC reference
Cadmium	A		1.09	109 E-05	M	D	01	1	FR	M	97035
Chromium	A		0.60	60 E-07	M	D	01	1	FR	M	97035
Copper	A		6.0	60 E-06	M	D	01	1	FR	M	97035
Mercury	A		0.09	9 E-08	M	D	01	1	FR	M	97009
Lead	A		0.50	50 E-07	M	D	01	1	FR	M	97035
Zinc	A		122	122 E-04	M	D	01	1	FR	M	97035

Record: 14 of 557 of 645

Buttons: Analyt. Method, ERDQ Method, Parameter

Record: 14 of 557 of 645

QFLAG NUM

Figure 2. Master form in the QC database.

QCREFT

Marine Institute Fisheries Research Centre Chemistry Section Quality Control Database

Year of analysis: 97 QC sequence number: 97035
 Analyst: Conor Duff Date analyzed: 25/07/97
 Reference material identifier: CPN278 Reference material tissue: SB Reference material type: MUSSEL TISSUE
 Analytical method: TOC

Record: 14 of 364 of 368

Form View NUM

Figure 3. Trace metals form in the QC database.

QCREF1

Marine Institute Fisheries Research Centre
Chemistry Section Quality Control Database

Trace metals

Year of analysis: 57

QC sequence number: 97035

CdCONC: 0.30 µg g⁻¹ dry weight

CrCONC: 0.83 µg g⁻¹ dry weight

CuCONC: 9.4 µg g⁻¹ dry weight

NiCONC: µg g⁻¹ dry weight

PbCONC: 1.97 µg g⁻¹ dry weight

ZnCONC: 74 µg g⁻¹ dry weight

Records: 14 of 368

Form View

ANNEX 7: THE ENVIRONMENTAL DISTRIBUTION AND EFFECTS OF TRIBUTYL TIN— AN UPDATE TO 1999

Robin J. Law

Centre for Environment, Fisheries and Aquaculture Science
CEFAS Burnham Laboratory
Burnham on Crouch
Essex CM0 8HA, UK

Erik H. G. Evers

National Institute for Coastal and Marine Management/RIKZ
PO Box 20907
2500 EX The Hague
The Netherlands

The focus of this update to earlier reviews of the environmental fate and effects of tributyltin (TBT) derived from antifouling preparations is timely, as it comes 10–15 years after controls were instituted on the use of TBT on small vessels (< 25 m in length). During this period numerous studies have documented the environmental improvements in estuaries and enclosed waters which followed the return to copper-based antifouling preparations, although now often incorporating “booster biocides” such as Irgarol 1051 (Law, 1997; Thomas, 1998). Attention has also focused increasingly on the impact of the continued use of TBT paints on larger sea-going vessels, and it is in the light of this continued interest that the present review note has been prepared for MCWG 1999. Our intention was to summarise the current knowledge of the fate and distribution (and, where possible, effects) of TBT in open sea areas, shipping lanes, and close to ports and harbours.

The Distribution of Butyltins in Seawater

Studies of the distribution of butyltins along a heavy tanker route in the Strait of Malacca in 1996 indicated recent inputs, with a TBT/DBT ratio > 2 (Hashimoto *et al.*, 1998). In open ocean areas away from the shipping route butyltins were generally undetectable. The distribution pattern was consistent with that of oil slicks resulting from oil tanker traffic along that route, suggesting that such large vessels represented the major source. Studies undertaken in 1996 by Swennen *et al.* (1997) of several species of sublittoral gastropods also found that imposex abundance was related to the proximity to shipping lanes in the Malacca Strait and the Gulf of Thailand. Hashimoto *et al.* (1998) also reported studies conducted in Tokyo Bay in 1993, 1994 and 1996. Higher concentrations of TBT, were observed in this inshore area (up to ca. 11 ng l⁻¹), although MBT and DBT concentrations were substantially higher, probably as a result of wastewater discharges.

The decrease in concentrations of butyltin compounds in French waters observed following the 1982 ban has now ceased, and the current concentrations are still above the toxicity threshold of 1 ng l⁻¹ (Michel and Averty, 1999). The overall concentration range observed for TBT was 1.7 to 280 ng l⁻¹, with high concentrations being recorded in some ports and marinas. For marinas, the highest concentrations were observed in the eastern Channel and eastern Mediterranean coasts, up to 88 and 199 ng l⁻¹ respectively. Lower concentrations were observed in marinas located along the Atlantic, western Channel and western Mediterranean coasts, rarely exceeding 20 ng l⁻¹.

Mussels collected at a control site in the Canadian St. Lawrence Estuary (at the Bic Provincial park) contained low, but ubiquitous, amounts of organotins. This suggests a low contamination of the seawater mass circulating along the south shore of the St. Lawrence Estuary by TBT during the summer (Saint-Louis *et al.*, (1997).

Port areas continue to be major sources of contamination, with continuing harmful effects on both natural (Huet *et al.*, 1996) and cultivated mollusc populations.

Imposex in Dogwhelk Populations

The incidence of imposex in dogwhelk *Nucella lapillus* populations is widely used as a biomonitor of TBT levels in seawater. This phenomenon is fully developed at ambient TBT concentrations of 1–2 ng l⁻¹, and females are fully sterilised at concentrations above 5 ng l⁻¹ (Gibbs and Bryan, 1996; Matthiessen and Gibbs, 1998). In a recent study of imposex along the coasts of south and south-west Wales, samples were collected in October 1996 and August 1997 between Milford Haven and Barry in the Severn estuary. This indicated that the highest levels of TBT are confined to shipping areas (Morgan *et al.*, 1998). Whilst none of these populations were sterile, many of the samples close to ports exhibited levels of imposex indicating TBT levels well above the UK EQS of 2 ng l⁻¹. In addition, the authors noted

that ports in the Shetlands, Norway, the Tyne estuary and Cork harbour, which are used by large commercial vessels are known hot-spots of TBT pollution as indicated by the incidence of imposex in dogwhelks (Minchin *et al.*, 1996; Moore *et al.*, 1996; Morgan *et al.*, 1998). Sullom Voe in the Shetlands is a large oil terminal that is served by a number of offshore pipelines, and is also visited by a large number of oil tankers (700-900 per annum) using TBT-based antifoulings (Atkins, 1998). The Voe is a narrow seaway with a restricted water flow and water exchange. There are no dockyard facilities for other vessels, and there is no significant pleasure boat or fish farming activity in the area. Any TBT present in the water of the Voe is therefore derived from the visiting tankers. In 1987 female dogwhelks in the Voe suffered from severe imposex with up to 90% of females around the loading jetties having blocked reproductive tracts (Davies and Bailey, 1991). The reproductive capacity of the populations in the Voe decreased between 1987 and 1990, in 1987 47% of females sampled were sterile, whilst in 1990 this had risen to 65%. All females sampled at the terminal site were sterile, and it seems that dogwhelk populations within the Voe are now maintained by recruitment from adjacent areas (Atkins, 1998).

In 1992 studies were conducted at 45 locations in Icelandic waters, and imposex was found to occur in dogwhelks at 38 of these sites. The level of imposex was highest in the vicinity of the larger harbours (such as Reykjavik and Hafnarfjörður), and the effects could be observed almost 18 km away from these harbours (Svavarsson and Skarphedinsdóttir, 1995). Similar effects have been observed in 41 populations of dogwhelks *Nucella lapillus* along the Norwegian coast (Følsvik *et al.*, 1998). Dogwhelks near large port facilities (such as Stavanger, Florø and Måløy) were more heavily affected than others. The concentration of TBT in the Dogwhelks could be correlated with the degree of imposex.

The incidence of imposex in populations of the dogwhelk *Lepsiella scobina* was compared before and after restrictions were introduced on the use of TBT-based antifouling paints in New Zealand, and two areas surveyed in 1988/89 were studied again in 1994/95. In an area subject only to inputs from pleasure craft (Porirua Inlet) there was a significant decline in the incidence of imposex, but this was not mirrored in Wellington Harbour, which handles both commercial and pleasure traffic (Smith, 1996). Minchin and Minchin (1997) assessed imposex in dogwhelks *Nucella lapillus* from 66 locations in Bantry Bay, SW Ireland in 1996. The highest imposex levels were found in the harbour of the fishing port Castletownbere, which is the second largest fishing port in SW Ireland. Stations within 600m of the centre of the harbour were devoid of dogwhelks, although they were common at some of these sites in the 1960s. Dogwhelks beyond this zone showed a high incidence of imposex, which declined with distance from the source. The major input in this case was from fishing vessels of 25 to 50m in length, which may still be legally painted with TBT-based antifoulings. Prouse and Ellis (1997) studied the incidence of imposex in dogwhelks *Nucella lapillus* from harbours in eastern Canada, and found Halifax harbour, Nova Scotia, to be the most severely affected. Six of the eleven sites surveyed yielded dogwhelks with imposex frequencies between 65 and 100%, and dogwhelks were absent from the other 5 sites although they appeared to provide a good habitat. These 5 sites were located within the inner harbour close to marinas, shipyards, and docking facilities for large vessels, and this grouping was considered consistent with them forming a central block too contaminated with TBT and possibly other chemicals for *Nucella* to survive. The lack of imposex and TBT in dogwhelks at Argentia, a decommissioned United States naval base in Newfoundland, suggested that the current source of TBT in Halifax harbour and the other ports studied was the continuing release from large vessels on which TBT is not currently controlled.

As a result of these studies, it is evident that where large numbers of commercial vessels use a restricted waterway, it is very likely that local dogwhelk populations will exhibit significant levels of imposex. This indicates that close to many of the ports and harbours in Europe TBT inputs from large shipping will be a significant input irrespective of other sources of TBT (Atkins, 1998). Dogwhelks in the vicinity of these installations are therefore likely to be affected by TBT for the foreseeable future unless additional controls on its use on commercial vessels are implemented.

Imposex in Whelk Populations

A recent study in the southern North Sea has demonstrated imposex in whelks (*Buccinum undatum*) resulting from TBT contamination from shipping (Ten Hallers-Tjabbes *et al.*, 1994), with a peak of 100% incidence close to the entrance channel to Rotterdam harbour. It is also considered likely that the use of TBT in antifouling paints resulted in the local extinction of whelks within the Dutch Wadden Sea following their depletion by fishing (Cadée *et al.*, 1995; Mensink *et al.*, submitted). These authors suggested that a failure to control the continued use of TBT and the absence of fishery-free zones in the North Sea would cause the extinction of whelks there also, although their interpretation has been criticised by others on the grounds that the observed effects cannot be linked unequivocally to TBT (ORTEP, 1996). The decline of North Sea whelks between the late 1960s to early 1970s and the early 1990s has been documented by Ten Hallers-Tjabbes *et al.* (1996).

In the Eastern Scheldt, nearly all female common whelks (> 91%) showed imposex, more than half of them the advanced stages, although reproduction did take place in 1994 and 1995 (Mensink *et al.*, 1997b). Despite the ban on the

use of TBT in antifouling paints for vessels < 25m in 1990, the incidence of imposex has not reduced in this area in subsequent years. Some continued use of TBT in marinas has been indicated by monitoring of concentrations in water (Ritsema, 1994), and this area is subject to agricultural inputs of triphenyltin as well as TBT release from large vessels. However, whole body levels of triphenyltin in whelks from the Eastern Scheldt did not show a significant difference between females with advanced stages of imposex and visually unaffected females (Mensink *et al.*, 1997a).

It should be noted that whereas dogwhelks live intertidally and mainly on hard substrates, and so are affected predominantly by coastal inputs of TBT, the whelk lives subtidally to 200m depth (Ten Hallers-Tjabbes and Boon, 1995). In the open sea therefore these animals will be affected primarily by inputs from passing shipping traffic.

TBT in Marine Mammals

Recent findings of TBT in tissues (primarily liver) of marine mammals and other organisms in nearshore areas and the open ocean is cause for concern (Tanabe *et al.*, 1998; Kannan and Falandysz, 1997, 1999; Kannan *et al.*, 1998; Law *et al.*, 1998). That TBT accumulates in the tissues of marine mammals has been shown previously for animals from the Indian and Pacific Oceans, and particularly for finless porpoise *Neophocoena phocaenoides* from the Seto-inland Sea in Japan (Iwata *et al.*, 1995).

Recently, butyltins were found in sperm whales (*Physeter macrocephalus*) stranded at the Dutch and Danish coast (Ariese *et al.*, 1998). These animals live and feed exclusively in the deep ocean. Recent studies of animals stranded in the UK have shown detectable concentrations of butyltins in both coastal and pelagic marine mammals, the latter animals feeding over the continental shelf edge and slope, and in the deep oceanic waters of the Atlantic Ocean (Law *et al.*, 1998; Law *et al.*, submitted). The highest concentration of total butyltin (Σ BT; MBT + DBT + TBT) found in harbour porpoise liver was $640 \mu\text{g kg}^{-1}$ wet weight, whilst in grey seals Σ BT concentrations were much lower indicating either that the seals have a lower dietary intake of butyltins or a higher catabolic capacity for these compounds than porpoises. A similar order of concentration (up to $312 \mu\text{g kg}^{-1}$ wet weight) was observed for 16 pelagic marine mammals analysed, of two mysticete and ten odontocete species. In both studies about 20% of the total butyltin burden in liver was TBT, with DBT the major component.

Southern sea otters (*Enhydra lutris nereis*) found dead along the coast of California contained total butyltins in the range of 40 - $9200 \mu\text{g kg}^{-1}$ wet weight, which varied depending on location and gender (Kannan *et al.*, 1998). At locations close to harbours handling large vessels legally painted with organotin antifoulings, TBT predominated its degradation products which suggests recent exposure. Otters collected within enclosed marinas contained concentrations at least ten times higher than those from open locations. Mean concentrations of Σ BT in female sea otter livers ($1420 \mu\text{g kg}^{-1}$ wet weight) were almost twofold greater than those in males ($750 \mu\text{g kg}^{-1}$ wet weight), possible due to their higher feeding rates and less dilution effect as a result of their smaller body size. Otters affected by infectious diseases, contained higher concentrations of BTs (mean: $1570 \mu\text{g kg}^{-1}$ wet weight) than those which died of trauma or unknown causes ($220 \mu\text{g kg}^{-1}$ wet weight).

These data indicate the widespread distribution of butyltin residues into deep offshore waters and oceanic food-chains, but further studies are needed in order to elucidate the potential impact of butyltin body burdens on individual marine mammals and populations if TBT inputs continue as at present.

Disposal of TBT-contaminated Dredgings

The accumulation of TBT and its degradation products (MBT and DBT) in sediments can result from two processes. Firstly, TBT can be adsorbed to sediment particles from the dissolved phase. These organotin species can then be subject to degradation and desorption processes. These processes are strongly influenced by the physicochemical characteristics of the sediment such as grain size and organic matter content. Secondly, close to harbours, dry docks and associated activities, paint flakes containing TBT can be deposited directly to sediments following release during the removal of antifouling paints from vessels prior to repainting. This is often conducted using sandblasting or high-pressure water hoses, and the recovery of wastes generated in this way should be mandatory (Michel and Averty, 1999).

Stronkhorst (1996) studied the effects of TBT use on ships and in dockyards around Rotterdam and the resulting concentrations of TBT in coastal waters. He emphasised the importance of sediments as both a sink and a source for TBT, as a major source of coastal contamination resulted from the dumping of dredged harbour sediment. Stronkhorst *et al.* (1995) determined an ecological criterion of $500 \mu\text{g kg}^{-1}$ dry weight for TBT in sediment, above which environmental harm would result. This value was exceeded in some samples from both Amsterdam and Rotterdam harbours in 1994/95, the concentration ranges observed being 30 to 2,000 and 10 to 2,100 $\mu\text{g kg}^{-1}$ dry weight respectively (Stronkhorst, 1996). Stewart and Thompson (1997) determined butyltin concentrations in a series of 5

sediment cores from harbours and marinas in Canada. The marina core showed a maximum in TBT concentration at 8cm depth, indicating a reduction in TBT flux to the surface sediments following a ban on the use of TBT paints on vessels < 25m in length. However, no such trend was visible in harbour cores, with the highest concentrations of TBT in superficial sediments. The presence of TBT throughout the sediments cores implies that it must be considered a persistent contaminant, and the profiles observed in harbour cores do not suggest any amelioration of TBT burdens at these sites following the partial ban in TBT usage. In Halifax harbour also, TBT concentrations in sediments from the inner harbour have increased between 1988 and 1994 (Prouse and Ellis, 1997).

Concentrations of TBT and its degradation products DBT and MBT are often very high in sediments, particularly those in areas frequented by shipping or where inputs from pleasure boats were high as degradation is slow.

In SW Spain, TBT is the predominant species in water, with the highest concentrations being observed near wharves, docks and shipyards. In sediments, DBT and MBT predominate as a result of degradation processes, and the progression TBT → DBT → MBT becomes more apparent with increasing distance from these foci (Gomez-Ariza *et al.*, 1995).

Coastal sediments from the German part of the North Sea and Baltic sea contained up to 7100 µg kg⁻¹ and 84000 µg kg⁻¹ net weight TBT, respectively (Kalbfus *et al.* 1996).

Total butyltin concentration in surface sediments of the Polish Gdynia seaport was high in comparison to other coastal areas, ranging from 1800 to 2900 µg kg⁻¹ dry weight (Kannan and Falandysz, 1997).

North Sea sediments at a new disposal site for dredged harbour sediments off the Dutch coast contained 18 µg TBT kg⁻¹ dw on average (fraction < 63 µm; n = 16; Ariese *et al.*, 1997). Average levels of DBT and MBT in these sediments were 11 and 25, respectively.

For a proper comparison of organotin residues in estuarine and marine sediments, we strongly recommend authors to express organotin concentrations as tin (Sn) on individual basis, preferentially in the fine fraction (e.g. < 63 µm) and based on dry weight, unless clearly stated otherwise.

As far as the persistence of tributyltin in marine environments is concerned, the results of many studies indicate that biological degradation is the most important factor limiting its persistence. TBT half-lives in aerobic surficial sediments in laboratory experiments ranged from 360 to 775 days, but in anaerobic sediments no degradation was observed and the half-life seems to be of the order of tens of years (Dowson *et al.*, 1996). In Chinhae Bay estuarine sediment cores DBT was found to be more persistent than TBT with half-lives of 11.6 and 6.9 years, respectively (Hwang *et al.*, 1999).

The disposal of TBT-contaminated sediments following dredging operations in harbours and navigation channels therefore poses particular difficulties for coastal waters, both as butyltin compounds may be re-released to the water column during settling, and because of the high sediment concentrations which may result at disposal sites and potential for more widespread effects on fauna.

Conclusions

Whilst reduced TBT concentrations have been observed in coastal areas frequented by small craft, this has not been the case for sites affected by inputs from large vessels (CEFIC, 1994). Similarly, although some affected dogwhelk populations have recovered since the partial bans on TBT were enacted, effects can still be observed in populations close to harbours receiving large vessels. No recovery studies have been mounted for whelks, as in only one area in the North Sea has the effect of TBT been investigated for these animals. Recent studies along major shipping routes however indicate that water concentrations of TBT in the vicinity of large vessel traffic are still elevated relative to those in the open sea. The cessation in the decline of TBT concentrations in water in many areas, its continued impact on distant, non-target, organisms, and the persistence of butyltins in sediments and associated problems for dredgings disposal all provide support for an extension to the partial ban on TBT to include its use in antifouling paints for vessels > 25m in length.

Acknowledgements

The authors would like to thank all those members of the Marine Chemistry Working Group and their colleagues who supplied information from their national programmes for incorporation into this review note.

References

- Ariese, F., Burgers, I., Hattum, B. van, Horst, B. van der, Swart, K. and G. Ubbels (1997). Chemical monitoring Loswal northwest dumping location. Start situation 1996. Report R-97/05, Institute for Environmental Studies, Free University, Amsterdam, The Netherlands.
- Ariese, F., Hattum, B. van, Hopman, G., Boon, J. P. and Ten Hallers-Tjabbes, C.C. (1998). Butyltin and phenyltin compounds in liver and blubber samples of sperm whales (*Physeter macrocephalus*) stranded in the Netherlands and Denmark. Report W98/04, Institute for Environmental Studies, Free University, Amsterdam, The Netherlands, 14 p.
- Atkins, W.S., International Ltd (1998). Assessment of the risks to health and to the environment of tin organic compounds in antifouling paint and of the effects of further restrictions on their marketing and use. Draft Final Report to European Commission Directorate General III, February 1998, Volume A.
- Cadée, G.C., Boon, J.P., Fischer, C.V., Mensink, B.P. and Ten Hallers-Tjabbes, C.C. (1995). Why the whelk (*Buccinum undatum*) has become extinct in the Dutch Wadden Sea. *Netherlands Journal of Sea Research* **34**, 337-339.
- CEFIC (1994). Use of organotin compounds in anti-fouling paints. Results of TBT monitoring studies. Document MEPC 35/17 for the 35th meeting of the Marine Environment Protection Committee of the International Maritime Organisation, 1994.
- Davies, I.M. and Bailey, S.K. (1991). The impact of tributyltin from large vessels on dogwhelk (*Nucella lapillus*) populations around Scottish oil ports. *Marine Environmental Research*, **32**, 201-211.
- Dowson, P.H., Bubb, J.M. and Lester, J.N. (1996). Persistence and degradation pathways of tributyltin in freshwater and estuarine sediments. *Estuarine and Coastal Shelf Science*, **42**, 551-562.
- Følsvik, N., Berge, J.A., Brevik, E.M. and Walday, M. (1998). Quantification of organotin compounds and determination of imposex in populations of dogwhelks (*Nucella lapillus*) from Norway. *Chemosphere*, **38**, 681-691.
- Gibbs, P.E. and Bryan, G.W. (1996). Reproductive failure in the gastropod *Nucella lapillus* associated with imposex caused by tributyltin pollution: a review. In *Organotin, Environmental Fate and Effects* (M.A. Champ and P.F. Seligman, editors). Chapman and Hall, London. pp. 259-280.
- Gomez-Ariza, J.L., Morales, E., Beltrán, R., Giraldez, I. And Ruiz-Benitez, M. (1994). Sampling and storage of sediment samples for organotin speciation. *Química Analítica*, **13**, S76-S79.
- Gomez-Ariza, J.L., Beltrán, R., Morales, E., Giraldez, I. And Ruiz-Benitez, M. (1995). Acid extraction treatment of sediment samples for organotin speciation; occurrence of butyltin and phenyltin compounds on the Cadiz coast, south-west Spain. *Applied Organometallic Chemistry*, **9**, 51-64.
- Hashimoto, S., Watanabe, M., Noda, Y., Hayashi, T., Kurita, Y., Takasu, Y. and Otsuki, A. (1998). Concentration and distribution of butyltin compounds in a heavy tanker route in the Strait of Malacca and in Tokyo Bay. *Marine Environmental Research*, **45**, 169-177.
- Huet, M., Paulet, Y.M. and Le Pennec, M. (1996). Survival of *Nucella lapillus* in a tributyltin-polluted area in west Brittany: a further example of a male genital defect (Dumpton syndrome) favouring survival. *Marine Biology*, **125**, 543-549.
- Hwang, H.M., Oh, J.R., Kahng, S.-H. and Lee, K.W. (1999). Tributyltin compounds in mussels, Oysters, and sediments of Chinhae Bay, Korea. *Marine Environmental Research*, **47**, 61-70.
- Isensee, J., Waterman, B. and Berger, H.-D (1995). Emissions of antifouling-biocides into the North Sea - an estimation. *Dt. Hydrogr. Z.* **46**, 355-367.
- Iwata, H., Tanabe, S., Mizuno, T. and Tatsukawa, R. (1995). High accumulation of toxic butyltins in marine mammals from Japanese coastal waters. *Environmental Science and Technology* **29**, 2959-2962.

- Jak, R.G., Ceulemans, M., Scholten, M.C.Th. and van Straalen, N.M. (1998). Effects of tributyltin on a coastal north Sea plankton community in enclosures. *Environmental Toxicology and Chemistry*, **17**, 1840-1847.
- Kalbfus, W., Zellner, A., Frey, S. and Knorr, Th. (1996). Analysis of butyltin species in water, sediment and environmental matrices. *Report no. UBA-FB*. November 1996, 50 pp.
- Kannan, K. and Falandysz, J. (1997). Butyltin residues in sediment, fish, fish-eating birds, harbour porpoise and human tissues from the Polish coast of the Baltic Sea. *Marine Pollution Bulletin*, **34**, 203-207.
- Kannan, K., Guruge, K.S., Thomas, N.J., Tanabe, S. and Giesy, J.P. (1998). Butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. *Environmental Science and Technology*, **32**, 1169-1175.
- Kannan, K. and Falandysz, J. (1999). Response to the comment on: Butyltin residues in sediment, fish, fish-eating birds, harbour porpoise and human tissues from the Polish coast of the Baltic Sea. *Marine Pollution Bulletin*, **38**, 61-63.
- Law, R.J. (1997). Review note on Irgarol 1051 in the marine environment. Report of the ICES Advisory Committee on the Marine Environment, 1997. *ICES Cooperative Research Report* 222, pp. 137-140.
- Law, R.J., Blake, S.J., Jones, B.R. and Rogan, E. (1998). Organotin compounds in liver tissue of harbour porpoises (*Phocoena phocoena*) and grey seals (*Halichoerus grypus*) from the coastal waters of England and Wales. *Marine Pollution Bulletin*, **36**, 241-247.
- Law, R.J., Blake, S.J. and Spurrier, C.J.H. (1999). Butyltin compounds in liver tissue of pelagic marine mammals stranded on the coasts of England and Wales. *Marine Pollution Bulletin*, *in press*.
- Matthiessen, P. and Gibbs, P.E. (1998). Critical appraisal of the evidence for tributyltin-mediated endocrine disruption in molluscs. *Environmental Toxicology and Chemistry*, **17**, 37-43.
- Mensink, B.P., Boon, J.P., Ten Hallers-Tjabbes, C.C., van Hattum, B. and Koeman, J.H. (1997a). Bioaccumulation of organotin compounds and imposex occurrence in a marine food chain (Eastern Scheldt, The Netherlands). *Environmental Technology*, **18**, 1235-1244.
- Mensink, B.P., Fischer, C.V., Cadée, G.C., Fonds, M., Ten Hallers-Tjabbes, C.C. and Boon, J.P. (submitted). Shell damage and mortality in the common whelk, *Buccinum undatum*, caused by beam trawl fishery. *Journal of Sea Research*.
- Mensink, B.P., van Hattum, B., Ten Hallers-Tjabbes, C.C., Everaarts, J.M., Kralt, H., Vethaak, A.D. and Boon, J.P. (1997b). Tributyltin causes imposex in the common whelk, *Buccinum undatum*: mechanism and occurrence. NIOZ-Rapport 1997-6. ISSN 0923-3210. 56 pp.
- Michel, P. and Averty, B. (1999). Contamination of French coastal waters by organotin compounds: 1997. *Marine Pollution Bulletin*, **38**, 268-275.
- Minchin, A. and Minchin, D. (1997). Dispersal of TBT from a fishing port determined using the dogwhelk *Nucella lapillus* as an indicator. *Environmental Technology*, **18**, 1225-1234.
- Minchin, D., Stroben, E., Oehlmann, J., Bauer, C., Duggan, C.B. and Keatinge, M. (1996). Biological indicators used to map organotin contamination in Cork Harbour, Ireland. *Marine Pollution Bulletin*, **32**, 188-195.
- Moore, J.J., Little, A.E., Harding, M.J.C., Rodger, G.K. and Davies, I.M. (1996). Surveys of dogwhelks *Nucella lapillus* in the vicinity of Sullom Voe, Shetland, August 1995. Oil Pollution Research Unit, Neyland, Pembrokeshire. Report no. OPRU/3/96.
- Morgan, E., Murphy, J. and Lyons, R. (1998). Imposex in *Nucella lapillus* from TBT contamination in south and south-west Wales: a continuing problem around ports. *Marine Pollution Bulletin*, **36**, 840-843.

- ORTEP Association (1996). The present status of TBT-copolymer antifouling paints. Proceedings of an International One Day Symposium on Antifouling Paints for Ocean Going Vessels. 21st February 1996, The Hague, The Netherlands.
- Poloczanska, E.S. and Ansell, A.D. (1999). Imposex in the whelks *Buccinum undatum* and *Neptunea antiqua* from the west coast of Scotland. *Marine Environmental Research*, 47, 203-212.
- Prouse, N.J. and Ellis, D.V. (1997). A baseline survey of dogwhelk (*Nucella lapillus*) imposex in Eastern Canada (1995) and interpretation in terms of tributyltin (TBT) contamination. *Environmental Technology*, 18, 1255-1264.
- Ritsema, R. (1994). Dissolved butyltins in marine waters of the Netherlands three years after the ban. *Applied Organometallic Chemistry*, 8, 5-10.
- Saint-Louis, R., Gobeil, C. and Pelletier, E. (1997). Tributyltin and its degradation products in the St. Lawrence Estuary (Canada). *Environmental Technology*, 18, 1209-1218.
- Smith, P.J. (1996). Selective decline in imposex levels in the dogwhelk *Lepsiella scobina* following a ban on the use of TBT antifoulants in New Zealand. *Marine Pollution Bulletin*, 32, 362-365.
- Stewart, C. and Thompson, J.A.J. (1997). Vertical distribution of butyltin residues in sediments of British Columbia harbours. *Environmental Technology*, 18, 1195-1202.
- Svavarsson, J. and Skarphedinsdottir, H. (1995). Imposex in the dogwhelk *Nucella lapillus* (L.) in Icelandic waters. *Sarsia*, 80, 35-40.
- Stronkhorst, J. (1996). TBT contamination and toxicity of sediments. The present status of TBT-copolymer antifouling paints. Proceedings of an International One Day Symposium on Antifouling Paints for Ocean Going Vessels. 21st February 1996, The Hague, The Netherlands. p. 47-60.
- Stronkhorst, J., Bowmer, C.T. and Otten, H. (1995). TBT contamination and toxicity of harbour sediments in the Netherlands. Paper presented at the Conference on Costs and Benefits of TBT-based and Alternative Antifoulants, 4-6 December 1995, Malta.
- Swennen, C., Ruttanadukul, N., Ardseungnern, S., Singh, H.R., Mensink, B.P. and Ten Hallers-Tjabbes, C.C. (1997). Imposex in sublittoral and littoral gastropods from the Gulf of Thailand and Strait of Malacca in relation to shipping. *Environmental Technology*, 18, 1245-1254.
- Tanabe, S., Prudente, M., Mizuno, T., Hasegawa, J., Iwata, H. and Miyazaki, N. (1998). Butyltin contamination in Marine mammals from North Pacific and Asian Waters. *Environmental Science and Technology*, 32, 192-198.
- Ten Hallers-Tjabbes, C.C., Kemp, J.F. and Boon, J.P. (1994). Imposex in whelks (*Buccinum undatum*) from the open North Sea: relation to shipping traffic intensities. *Marine Pollution Bulletin* 28, 311-313.
- Ten Hallers-Tjabbes, C.C. and Boon, J.P. (1995). Whelks (*Buccinum undatum* L.) and dogwhelks (*Nucella lapillus* L.) and TBT – a cause for confusion. *Marine Pollution Bulletin*, 30, 675-676.
- Ten Hallers-Tjabbes, C.C., Everaarts, J.M., Mensink, B.P. and Boon, J.P. (1996). The decline of the North Sea whelk (*Buccinum undatum* L.) between 1970 and 1990: a natural or a human-induced event? *Mar. Ecol. PSZN I*, 17, 333-343.
- Thomas, K.V. (1998). Determination of selected antifouling booster biocides by high performance liquid chromatography atmospheric pressure chemical ionisation mass spectrometry. *Journal of Chromatography A*, 825, 29-35.

ANNEX 8: MONO- AND NON-ORTHO CHLORINATED BIPHENYLS IN MARINE MAMMALS OF THE NORTHERN ATLANTIC OCEAN AND THE BALTIC SEA: A LITERATURE SEARCH IN AQUATIC SCIENCES AND FISHERIES ABSTRACT (ASFA) FOR THE PERIOD SINCE 1990

Michael Haarich

Federal Fisheries Research Centre
Hamburg, Germany

Background

At the MCWG meeting 1998 in Stockholm, the Organic Subgroup was requested to review and assess data on CBs, especially non- and mono-ortho CBs, in marine mammals, as a contribution to the OSPAR Quality Status Report. One intersessional action was to perform a literature search on relevant publications in Aquatic Sciences and Fisheries Abstract (ASFA).

In the meantime, a report on this subject has been prepared by ICES (with WGBEC, WGMMA and WGEAMS) and is published as Annex 10 to the ACME Report 1998. And forwarded to the OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME 99/4/5).

ASFA search

The ASFA literature search was performed for the period since 1990 using CD-ROM for publications entered into the data base until March 1998 and supplemented online until October 1998, using following search items: NE-Atlantic, Arctic, Baltic Sea; seal*, whale*, dolphin*, porpoise*, mammal*, marine; CB*, PCB*, organochlorine*, chlorine*, coplanar, mono-ortho, non-ortho.

Results

A number of 36 entries were identified, of which 11 are cited in the reference list of the above mentioned ICES paper. For 25 of the 36 references, the full paper was available to the author or could be studied in the local university libraries for details. In this 25 papers, data on concentrations for single mono- and non-ortho congeners were published as follows:

	mono-ortho CBs	mono- and non-ortho CBs
as value	3 publications	7 publications
as graph only	2 publications	1 publication

A weakness of some publications was that in spite of being reviewed units and/ or basis (lipid or wet weight) were missed in the diagrams at the axis and/or the legends and sometimes even in the relevant parts of the text, and in some cases no information about the sampling period or date of finding was reported.

ASFA does not supply a complete list of the relevant literature, as some journals are not included in the data base, e.g., Marine Pollution Bulletin, Biologie, Analyst.

A list of the references found by ASFA supplemented by relevant information in Annex 1 below, and is available as dBase-file on request.

Annex 1

	TITLE	AUTHORS	SOURCE	ISSUE	PAGES	YEAR
1	Levels of selected individual polychlorinated biphenyls in different tissues of harbor seals (<i>Phoca vitulina</i>) from the southern coast of Norway	Bernhoft A; Skaare JU	Environ. Pollution	86 (1)	99-107	1994
2	The kinetics of individual polychlorinated biphenyl congeners in female harbor seals (<i>Phoca vitulina</i>) with evidence for structure-related metabolism	Boon JP; Reijnders PJH; Dols J; Wensvoort P; Hillebrand MTJ	Aquat. Toxicol.	10 (5-6)	307-324	1987
3	CB pattern in the harbour porpoise: Bioaccumulation, metabolism and evidence for cytochrome P450 IIB activity	Bruhn R; Kannan N; Petrick G; Schulz-Bull DE; Duinker JC	CHEMOSPHERE	31 (7)	3721-3732	1995
4	Mono-ortho and non-ortho substituted PCBs in Arctic ringed seal (<i>Phoca hispida</i>) from the Svalbard area: Analysis and determination of their toxic threat	Daelemans FF; Mehlum F; Lydersen C; Schepens PJC	CHEMOSPHERE: Proceed. of the 12th international symposium on chlorinated-dioxins and related compounds (DIOXIN 92)	27 (1-3)	429-437	1993
5	Congener-specific data on polychlorinated biphenyls in tissues of common porpoise from the Puck Bay, Baltic Sea	Falandysz; Yamashita N; Tanabe S; Tatsukawa R; Rucinska L; Skora K	Arch. Environ. Contam. Toxicol.	26 (3)	267-272	1994
6	Critical evaluation of polychlorinated biphenyl toxicity in terrestrial and marine mammals: Increasing impact of non-ortho and mono-ortho polychlorinated biphenyls from land to ocean	Kannan N; Tanabe S; Ono M; Tatsukawa R	Arch. Environ. Contam. Toxicol.	18(6)	850-857	1989
7	Organochlorine pesticides and PCBs in the east ice harp seal (<i>Phoca groenlandica</i>) population	Kleivane L; Espeland O; Fagerheim KA; Hylland K; Polder A; Skaare JU	Marine Environ. Res.	43 (1-2)	117-130	1997
8	Residues of planar polychloroaromatic compounds in Baltic fish and seal	Koistinen J	CHEMOSPHERE (DIOXIN 89)	20 (7-9)	1043-1048	1990
9	An isotope dilution high resolution gas chromatographic - high resolution mass spectrometric method for the determination of coplanar polychlorinated biphenyls: Application to fish and marine mammals	Kuehl DW; Butterworth BC; Libal J; Marquis P	CHEMOSPHERE	22 (9-11)	849-858	1991
10	Coplanar PCB and metal residues in dolphins from the U.S. Atlantic coast including Atlantic bottlenose obtained during the 1987/88 mass mortality	Kuehl DW; Haebler R; Potter C	CHEMOSPHERE	28 (6)	1245-1253	1994
11	Contaminant levels in harbor seals from the northeastern United States	Lake CA; Lake JL; Haebler R, McKinney R, Boothman WS, Sadove SS	Arch. Environ. Contam. Toxicol.	29 (1)	128-134	1995
12	Marine mammals as global pollution indicators for organochlorines	Moessner S; Ballschmiter K	CHEMOSPHERE	34 (5-7)	1285 - 1296	1997
13	Can seal eating explain elevated levels of PCBs and organochlorine pesticides in walrus blubber from eastern Hudson Bay (Canada) ?	Muir DCG; Segstro MD; Hobson KA; Ford CA; Stewart REA; Olpinski S	Environ. Pollution	90 (3)	335-348	1995
14	Chlorinated hydrocarbon contaminants in Arctic marine mammals	Norstrom RJ; Muir DCG	Sci. Total Environ.	154 (2-3)	107-128	1994
15	Indications of P450 monooxygenase activities in beluga (<i>Delphinapterus leucas</i>) and narwhal (<i>Monodon monoceros</i>) from patterns of PCB, PCDD and PCDF accumulation	Norstrom RJ; Muir DCG; Ford CA, Simon M; Macdonald CR; Beland P	Marine Environ. Res./Responses of marine organisms to pollutants. Part 1	34 (1-4)	267-272	1992
16	Determination of levels of polychlorinated dibenzo- <i>p</i> -dioxins, dibenzofurans, biphenyls and pesticides in harp seals from the Greenland Sea	Oehme M; Schlabach M; Hummert K; Luckas B; Nordoy ES	Sci. Total Environ.	162 (2-3)	75-91	1995
17	Effects of persistent organic pollutants on biota in the Baltic Sea	Olsson M	Arch. Toxicol.	16 suppl	43-52	1994
18	Diseases and environmental contaminants in seals from the Baltic and Swedish west coast	Olsson M; Karlsson B; Ahnland E	Sci. Total Environ.	154 (2-3)	217-227	1994
19	Organochlorines in Baltic seals in the 1980s	Stenman O; Tissari A	ICES CM	1990N:12	8 pp	1990
20	Coplanar polychlorinated biphenyl congener levels and patterns and the identification of separate populations of harbor seal (<i>Phoca vitulina</i>) in Denmark	Storr-Hansen E; Spliid H	Arch. Environ. Contam. Toxicol.	24 (1)	44-58	1993

21	Distribution patterns of polychlorinated biphenyl congeners in harbor seal (<i>Phoca vitulina</i>) tissues: Statistical analysis	Storr-Hansen E; Spliid H	Arch. Environ. Contam. Toxicol.	25 (3)	328-345	1993
22	Toxic threat to marine mammals: Increasing toxic potential of non-ortho and mono-ortho PCBs from land to ocean	Tanabe S; Kannan N; Ono M; Tatsukawa R	CHEMOSPHERE	18 (1-6)	485-490	1989
23	Chemical contaminants in harbor porpoise (<i>Phoca phocoena</i>) from the North Atlantic coast: Tissue concentrations and intra- and- inter-organ distribution	Tibury KL; Stein JE; Meador JP; Krone CA; Chan SL	CHEMOSPHERE	34 (9-10)	2159 - 2181	1997
24	Geographical variation of persistent organochlorine concentrations in blubber of ringed seal (<i>Phoca hispida</i>) from the Canadian Arctic: Univariate and multivariate approach	Weis IM; Muir CG	Environ. Pollut.	96 (3)	321 - 333	1997
25	Determination of individual chlorobiphenyls (CBs) including non-ortho and mono-ortho chloro substituted CBs in marine mammals from Schottish waters	Wells DE, Echarri I	Int. J. Environ. Anal. Chem.	47 (2)	75-97	1992
26	Concentrations and accumulation patterns of organochlorine contaminants in the blubber of harbor porpoise, <i>Phoca phocoena</i> , from the coast of Newfoundland, the Gulf of St. Lawrence and the Bay of Fundy-Gulf in Maine	Westgate AJ; Muir, D CG; Gaskin DE; Kingsley M CS	Environ. Pollution	95 (1)	105 - 119	1997
27	Congener specific PCB and polychlorinated camphene (toxaphene) levels in Svalbard ringed seals (<i>Phoca hispida</i>) in relation to sex, age, condition and cytochrome P450 activity	Wolkers A.; Burkow IC; Lydersen C; Dahle S; Monshower M; Witkamp RF	Sci. Total Environ.	216, 1-2	1 - 11	1998
28	Fate of PCBs from the Irving Whale: A preliminary interpretation	Alexander DR; Bastien-Daigle S	Conference on the Green Plan Toxic Chemicals Programs, Ottawa, Ontario, Jan. 28-31, 1997, CAN. TECH. REP. FISH. AQUAT. SCI			1997
29	Persistent organochlorine compounds in the blubber of ringed seals (<i>Phoca hispida</i>) from the Belcher Islands, North West Territories, Canada	Cameron ME, Metcalfe TL, Metcalfe CD, Macdonald CR	Marine Environ. Res.	43 (1-2)	99-116	1997
30	A review of environmental contaminant levels in traditional food in northern Canada	Chan HM	CAN. TECH. REP. FISH. AQUAT. SCI	MIC-97-02577	35-39	1997
31	A database for environmental contaminants in traditional food in northern and Arctic Canada: Development and applications	Chan HM	Food Addit. and Contam.	15 (2)	127 - 134	1998
32	Method to Represent the Qualitative and Quantitative Characteristics of PCB Mixtures - Marine Mammal Tissues and Commercial Mixtures as Examples	Duinker JC; Knap AH; Binkley KC; van Dam GH; Darrel-Rew A; Hillebrand MTJ	Mar. Pollut. Bull.	19, 2	74-79	1988
33	Organochlorines in mother and pup pairs in two Arctic seal species: Harp seal (<i>Phoca groenlandica</i>), hooded seal (<i>Cystophora cristata</i>)	Espeland O; Kleivane L; Haugen S; Skaare JU	Marine Environ. Res.	44 (3)	315 - 330	1997
34	Chlorinated organic contaminants in blubber biopsies Northwestern Atlantic balaenopterid whales summering in the Gulf of St. Lawrence	Gauthier JM; Metcalfe CD, Sears R	Marine Environ. Res.	44 (2)	201 - 223	1997
35	Overview of the chemical contamination in the Estuary and Gulf of Saint Lawrence	Gobeil C	Conference on the Green Plan Toxic Chemicals Programs, Ottawa, Ontario, Jan. 28-31, CAN. TECH. REP. FISH. AQUAT. SCI 1997			
36	Contributions of coplanar and non-planar polychlorinated biphenyls to the toxic equivalence of grey seal (<i>Halichoerus grypus</i>) milk	Green NJL; Jones KC; Harwood J	CHEMOSPHERE	33 (7)	1273-1281	1996

	SPECIES	CONTAM	AREA	PERIOD	KEYWORDS	DATA_REC
1	Harbor seal (<i>Phoca vitulina</i>)	CBs, non-ortho CBs	Southern Norway	Summer 1988	different tissues, coplanar	median values of single CBs includ. mono- and non-ortho
2	Harbor seal (<i>Phoca vitulina</i>)	CBs, non-ortho CBs	North Sea, Dutch Wadden Sea		experiment in captivity, food of different origin, metabolism study	experimental data
3	Harbor porpoise (<i>Phoca phocoena</i>)	CBs, non-ortho		no information		Single CBs includ. mono-ortho, bar graphs
4	Arctic ringed seal (<i>Phoca hispida</i>)	CBs, PCDD, PCDF	Svalbard, Spitsbergen, Northern Norway		toxicity, TEQ, different tissues	Means of single CBs includ. mono- and non-ortho CBs on lipid basis
5	Harbor porpoise (<i>Phoca phocoena</i>)	CBs, non-ortho CBs	Baltic Sea, Puck Bay, Poland			Single CBs includ. mono- and non-ortho
6	finless porpoise (<i>Neophocena phocaenoides</i>), Dall's porpoise (<i>Phocoenoides dalli</i>) Bairds beaked whale (<i>Berardius bairdii</i>), killer whale (<i>Orcinus orca</i>)	CBs, non-ortho CBs				
7	harp seal (<i>Phoca groenlandica</i>)	CBs, HCB, HCHs, DDT, SCHL	White Sea	Apr-May 1993		sum PCB; single CB concentration recalculation from ratios to CB 153 possible (bar graph)
8	ringed seal (<i>Phoca hispida</i>), grey seal (<i>Halichoerus grypus</i>)	non-ortho CBs, PCDD, PCDF	Baltic Sea			
9	Bottlenose dolphin (<i>Tursiops truncatus</i> , Fish (50 spp))	non-ortho CBs		1987	analytical method	Single CBs includ. mono- and non-ortho on lipid basis
10	Bottlenose dolphin (<i>Tursiops truncatus</i>), common dolphin (<i>Delphinus delphis</i>), white-sided dolphin (<i>Lagenorhynchus acutus</i>)	CBs, non-ortho CBs, Hg, Pb, Cd, Mn, Cr	ANW ASW	June 87/June 88		TCDD-TE-concentration %
11	Harbor Seal (<i>Phoca vitulina</i>)	CBs, OCPs, PAHs, PCDF, PCDD, Hg	Long Island, Massachusetts	1990-1992, 1980	different tissues	Mean values CBs including mono- and non-ortho CBs, DDEPP, HCB, CHLA, TNONC, Mirex
12	harbor seal (<i>Phoca vitulina</i>), northern fur seal (<i>Callorhinus ursinus</i>), belukha whale (<i>Delphinapterus leucas</i>), common dolphin (<i>Delphinus dephis</i>) bowhead whale (<i>Balaena mysticetus</i>)	CBs, HCHs, DDTs	Western North Atlantic, North Pacific, Bering Sea, Arctic Ocean	no information		individual single CBs includ. mono-ortho CBs, HCHs and DDTs
13	Walrus (<i>Odobenus rosmarus</i>)	CBs, non-ortho-CBs, DDT, toxaphenes chlordanes, dieldrin, PCDD, PCDF	Polar Arctic West, East Hudson Bay, Foxe Basin, Loks Land, East Baffin Island, Canada	1990-1992		single CBs incl. non- and mono-ortho CBs, ,ratios to sum PCB of CBs 81, 126, 153 and 169; single PCDDs and PCDFs, HCHA, Oxychlordane, DDEPP, Toxaphene, Mirex, DIELD, sums of HCB, CBZ, HCHs, CHLA, DDTs,

14	fur seal (<i>Callorhinus ursinus</i>), ringed seal (<i>Phoca hispida</i>), hooded seal (<i>Cystophora cristata</i>), bearded seal (<i>Erignathus barbatus</i>), walrus (<i>Odobenus rosmarus</i>), beluga (<i>Delph. leucas</i>) porpoise (<i>Phocoena phocoena</i>) polar bear (<i>Urus maritimus</i>), narwhal	CBs, sum, DDTs,	Arctic		references to other contaminants	Total PCB, Patterns
15	Beluga (<i>Delphinapterus leucas</i>) , Narwhal (<i>Monodon monoceros</i>)	CBs, PCDDs, PCDFs	Lake Ontario, Great Lakes, St. Lawrence River, Baffin Islands		Cytochrome P450 CYP1A, principal component analysis	only ratios CB52/CB153 and CB126/Cb153
16	harp seal (<i>Phoca groenlandica</i>)	PCBs, PCDD, PCDF, DDTs	Greenland Sea	1991		individual single CB values including mono- and non-ortho CBs, TCDDs, TCDFs, OCDDs, OCDFs, HCHs, HCB, DDTs
17	Baltic ringed seal (<i>Phoca hispida</i>), grey seal (<i>Halichoerus grypus</i>)	PCBs, coplanar, DDT, toxaphenes, chlordanes, PBDE, TCPMe	Baltic Sea		EUROTOX Congress; study	
18	Baltic ringed seal (<i>Phoca hispida</i>), grey seal (<i>Halichoerus grypus</i>)	DDT, PCBs, methylsulfones, toxaphenes, chlordanes, PBDE, PCDD, PCDF, metals	Baltic Sea, North Sea Swedish west coast			Summed values PCB on lipid basis as graph
19	Ringed seal (<i>Phoca hispida</i>), grey seal (<i>Halichoerus grypus</i>)	DDTs, CBs, chlordanes, t-nonachlor, PCDD, PCDF, HCHs, HCB	Baltic Sea		different tissues	
20	harbor seal (<i>Phoca vitulina</i>)	coplanar CBs	Kattegat, Wadden Sea, Limfjord	1988		Single CBs includ. mono-ortho
21	harbor seal (<i>Phoca vitulina</i>)	coplanar CBs, CBs,	ANE, Baltic Sea		statistics	
22		non-ortho CBs				
23	Harbor porpoise (<i>Phoca phocoena</i>)	CBs, chlorinated hydrocarbons	North Atlantic coast	1991	tissue distribution	Single CBs includ. mono-ortho as graph on lipid basis, sums of PCBs, lipid% and Dry weight %
24	Ringed seal (<i>Phoca hispida</i>)	OCs, CBs, DDTs, CBz, chlordanes, toxaphene, HCHs	Canadian Arctic (13 locations)	1983-1989		Single CBs includ. mono-ortho, toxaphenes, sums of HCHs, CHL, DDT, PCB
25	whale, porpoise, dophin. seal	CBs, coplanar CBs	ANE, North Sea, Scotland	1990, partly no information	TEC	Single CBs includ. mono- and non-ortho on wet weight basis, sum of PCBs on lipid and ww-basis
26	Harbor porpoise (<i>Phoca phocoena</i>)	CBs, toxaphenes CHB, DDT, chlordanes CHL	Newfoundland, Gulf of St. Lawrence, Bay of Fundy-Gulf, Maine	1989-1991		Mean concentrations of sum of CHBs, CBZs, HCHs, CHL, DDTs, PCBs, bar graphs male/female
27	Ringed seal (<i>Phoca hispida</i>)	CBs specific congeners, toxaphenes	Svalbard, Norway		cytochrome P450	
28	Whale	PCBs				
29	Ringed seal (<i>Phoca hispida</i>)	CBs, DDTs, chlordanes, HCHs	Belcher Islands, North West Territories, Canada; Holman Island (Pacific coast)	May-June 1991		Single CBs includ. mono-ortho; mean values on lipid basis

30	mammals (59 species)	chlordan, Hg, PCB, toxaphene	northern Canada			dietary exposure, mathematical models, risk assessment
31	marine mammals	CBs, chlordan, toxaphene	northern Canada, Arctic			
32	Harbour Porpoise (<i>Phocoena phocoena</i>), Goosebeaked Whale (<i>Ziphius cavirostris</i>)	PCBs	North Sea, Dutch coast, Bermuda Island			
33	Harp seal (<i>Phoca groenlandica</i>), hooded seal (<i>Cystophora cristata</i>)	sums, CBs (22), DDTs, chlordan, HCHs, HCB	Greenland Sea, Jan Mayen	March 1990		Single CBs includ. mono-ortho measured but not published; recalc. possible from sum and ratios (bar graphs)
34	mink (<i>Balaenoptera acurostrata</i>), fin (<i>B. physalus</i>), blue (<i>B. musculus</i>) and humpback (<i>Megaptera novaeangliae</i>) whales	CBs, OCs, non-ortho CBs, sums, DDTs, HCHs, dieldrin, HCB, cis-nonachlor, t-nonachlor	NW Atlantic coast, Gulf of St. Lawrence	1991, 1992	coplanar CBs	Single CBs includ. mono-ortho; CB105 nearly all values nd
35						
36	Grey seal (<i>Halichoerus grypus</i>)	CBs, non-ortho CBs	Scotland	1990-1993	toxicity, TEQ, milk	ranges of non-ortho-CBs on lipid basis

ANNEX 9: POLYCYCLIC MUSK FRAGRANCES IN THE AQUATIC ENVIRONMENT

Dr Gerhard G. Rimkus

Official Food and Veterinary Institute (LVUA) Schleswig-Holstein
Department of Residue and Contamination Analysis
P. O. Box 2743, D-24517 Neumünster / Germany

Abstract

The polycyclic musk fragrances, mainly 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta[g]-2-benzopyrane (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyltetrahydro-naphthalene (AHTN) are synthetic musk fragrances which are used in almost all scented consumer products, such as perfumes, cosmetics and laundry detergents. Concerning their chemical structures the polycyclic musks are indane and tetraline derivatives highly substituted mainly by methyl groups. Their production has been increased continuously during the last years with a world-wide production volume today of about 6,000 t/a. After their application in private households they are dumped via the sewage treatment plants into the aquatic environment. In this review the analysis of polycyclic musk compounds in environmental samples is shortly presented and all published data of polycyclic musk compounds in water, sediment, suspended particulate matter (SPM), sewage sludge, and biota are summarized and discussed. The highest HHCB and AHTN concentrations were analysed in water (maximum concentrations: 6 µg HHCB/L, 4.4 µg AHTN/L) and sludge (maximum concentrations: 63 mg HHCB/kg dry matter, 34 mg AHTN/kg dry matter) from sewage plants, and in fish (maximum concentrations: 159 mg HHCB/kg lipid, 58 mg AHTN/kg lipid) from sewage ponds. In all other samples from different aquatic ecosystems these chemicals were unequivocally detected in varying concentrations dependent on the distance to sewage treatment plants. Even in marine water samples from the German Bight HHCB and AHTN could be quantified at the lower ng/L level. Very often HHCB and AHTN formed the major organic contaminants, in all samples their concentrations exceeded those of musk xylene and musk ketone. Also several by-products and impurities of the commercial polycyclic musks were analysed in river and waste water samples in not negligible amounts. The apparently ubiquitous distribution of polycyclic musks in the aquatic environment demonstrates the persistence and lipophilicity of these pollutants. The high log K_{ow} values of HHCB and AHTN (5.70–5.90) do not directly correlate with their relatively low bioconcentration factors derived from fish experiments, this discrepancy may be explained by a particular metabolism in fish. There are indications of a possible species dependent metabolism. For a general risk assessment of this new group of environmental pollutants besides the missing toxicological data, further studies on the distribution of the polycyclic musk fragrances including their by-products in the aquatic environment, on possible degradation processes in sediment/sludge as well as on the metabolism in fish are urgently needed.

Introduction

Musk is one of the most important and often used fragrances in perfumery. Due to the high cost and uncertainty of supply of the original natural musk, this has been replaced since many decades by synthetic musks with fragrance and other properties similar to those of the natural substances. The phenomenal growth demand for musk has created a world-wide synthetic musk industry. Today almost all of the musks used in cosmetics and fragrance products are of synthetic origin.

Already in the first years of this century substituted trinitro and dinitro benzenes, the group of the so-called nitro musks, were used as the first synthetic musk fragrances. In the 1950's, another important group of synthetic musk compounds, the polycyclic musk fragrances, was introduced. Tab. 1 summarizes the chemical names, trade names, CAS names and numbers, the chemical structures, and the molecular formulae of seven polycyclic musk compounds. The polycyclic musks are indane and tetraline derivatives highly substituted mainly by methyl groups. These artificial musks do not occur in the nature, and there is no chemical or structural relationship with the natural macrocyclic musk compounds. Their industrial synthesis is relatively complex and, therefore, in comparison to the nitro musks, they are more expensive. Nevertheless, polycyclic musks are considered to be essential ingredients in fragrances for numerous consumer products because of their typical musky scent and their substantive property to bind fragrances to fabrics. HHCB and AHTN are the two most important compounds in this group, they probably share over 95 % of the market for polycyclic musks [1]. The production of AHTN was discontinued in 1980 because of the evidence of strong adverse neurotoxic effects [2], thus its compilation in Tab. 1 is only of historical importance. Polycyclic musks are used in almost all consumer products, such as perfumes, cosmetics, soaps, shampoos, laundry detergents, fabric softeners, household cleaners, air fresheners, and other household products. According to the data of a study on the world-wide synthetic musk market [3], polycyclic musk production has increased annually, with a world-wide production of about 4,300 tons/year in 1987. According to this study, polycyclic musks accounted for about 61% of the total world market of synthetic musk fragrances in 1987, with an upward tendency. In 1996 [4], the world-wide production volume of polycyclic musks, mainly HHCB and AHTN, were numbered with about 5,600 tons/year and a share of about 70% of the total world market of synthetic musks, again indicating the upward trend. According to a survey by the Research

Institute of Fragrance Materials (RIFM) [1], the use volumes of HHCB and AHTN in Europe in 1992 and 1995 were 3,285 and 2,067 tons/year, respectively. According to RIFM it cannot be concluded whether this apparent decrease in use represents a real downward trend or is caused by market fluctuations. Nevertheless, the polycyclic musks HHCB and AHTN are high volume chemicals in Europe with an average use per capita in 1995 of about 15.5 mg/day [1]. The increase in polycyclic musk production and the corresponding decline in nitro musk production is based primarily on the restrictions on the use of musk ambrette [3] which were issued because of some toxicologically adverse effects. Furthermore, it can be assumed that the critical discussions about some environmental and toxicological properties of the nitro musks and a partial phase-out of musk xylene in some West European countries promoted their replacement by polycyclic musks [4-6].

Recently Eschke et al. [7,8] identified for the first time the polycyclic musk compounds in water and fish samples from the German river Ruhr and some municipal sewage treatment plants. During a non-target screening of water samples taken during 1992-1994 from the river Elbe and its tributaries more than 250 individual organic compounds were identified among them also HHCB and AHTN [9]. These first results already indicate the significantly lipophilic and persistent nature of the polycyclic musks with their tendency to bioaccumulate in fish and other aquatic organisms. In the meantime a number of further studies reported about these compounds in the aquatic environment, which in summary give a general idea of their environmental behaviour. In this review all published data of polycyclic musk compounds in water, sediment, suspended particulate matter, sewage sludge and biota are summarized and discussed, and in particular, the bioconcentration of these lipophilic compounds in biota of the aquatic environment is assessed.

Analysis of Polycyclic Musk Fragrances in Environmental Samples

The combination of capillary gas chromatography and mass spectrometry (GC/MS) has been proved as a versatile and mostly used analysis technique for the detection of polycyclic musk fragrances in environmental samples. The EI mass spectra show several characteristic mass fragments [7,8,10,11] which can be used for identification and routine analysis. In addition, they are well suited as indicative mass ions in the Selected Ion Monitoring (SIM) mode. Thus, GC/EI/MS in the SIM mode permits the screening of polycyclic musk compounds at a high level of specificity and sensitivity. This sensitivity cannot be increased by chemical ionisation techniques [10]. For the trace analysis of polycyclic musks various MS systems are used, such as quadrupole mass spectrometers [10-12], ion trap systems [7,8,13-15], high resolution (HR) mass spectrometer [16,17], and a hybrid system [18]. The ion trap GC/MS/MS technique [19] reduced considerably the background noise and, as a consequence, the analytical sensitivity and selectivity were increased remarkably. Due to their chemical structure the polycyclic musk compounds can not be detected with sufficient sensitivity by specific GC detectors (e.g. ECD, NPD), in contrast to the nitro musks [20]. Recently, an HPLC method for the determination of traces of HHCB in aqueous samples was reported [21]. The fluorescence and UV detection limits of the described method were determined to be 5 µg/L and 1.5 mg/L, respectively. It should be mentioned that, in comparison to GC/MS, the HPLC method possesses only a low separation efficiency and the typical HPLC detectors perform only moderate sensitivity and specificity. Nevertheless, some authors used HPLC methods for bioaccumulation studies [22,23].

For the simultaneous determination of polycyclic and nitro musks suitable analysis techniques with MS detection were developed for the matrices water [7,11], sediment [24], and biota [25,26]. A disadvantage of these methods may be the insensitive detection of nitro musks by EI-MS. In an investigation of Norwegian air samples [27] nitro and polycyclic musks were analysed for the first time by GC/MS methods. GC/NCI/MS and GC/EI/MS were compared. Nitro musks easily form negative ions resulting in high sensitivity of the GC/NCI/MS/SIM technique [28]. The analysis of polycyclic musks by NCI/MS is not as sensitive as by EI/MS [10,15], but nevertheless in most of the environmental samples the concentration levels of polycyclic musks are distinctly higher than those of nitro musks compensating this loss of sensitivity. Finally, polycyclic and nitro musks were also determined simultaneously in human adipose tissue [16] and human milk [17] by GC/HRMS with limits of determination in the range of 0.1 - 1 ng/g lipid [16] and 0.5 - 2 ng/g lipid [17], respectively.

Due to its chemical structure HHCB occurs in two diastereomeric forms [29] which could not be separated on capillary columns commonly used in pesticide and PCB residue analysis. Only in 2 studies HHCB was separated into these diastereomers: in extracts of human adipose tissue [16] and in fish extracts [30] using a methylpolysiloxane phase with 12 - 15 % phenyl groups and a polyethylene glycol phase, respectively. The ratio of the isomers seems to change in the extract of human samples in comparison to the standard substance [16]. Recently it was possible to separate the diastereomers of HHCB into the two pairs of enantiomers and also the 2 enantiomers of AHTN and ATII on chiral GC columns followed by GC/MS detection [31]. In extracts of biota samples various changes of the enantiomeric ratios could be observed [31]. These chiral analysis seem to be helpful to support the environmental investigations on bioaccumulation and metabolism of polycyclic musks.

The clean-up procedures for the trace analysis of polycyclic musks in environmental samples are very similar to those of the conventional pesticide and PCB residue analysis, because of the comparable lipophilicity and polarity of all these substances. Thus, clean-up often includes liquid-liquid extraction by various organic solvents, soxhlet extraction, solid-phase extraction (SPE) and adsorption chromatography on various adsorbents, such as silica gel, florisil, or aluminium oxide. Recently also an accelerated solvent extraction (ASE) system was used to determine polycyclic musks in freshwater fish samples collected from several Italian rivers and lakes [30], this new method provided a rapid and selective extraction procedure. For fatty tissues, the gel permeation chromatography (GPC) has proved as a very efficient and useful tool [7,8,10,15,16,19,25,26]. An automated GPC-HPLC combination [32] has been successfully applied for the routine analysis of fat and biota samples [10,15], providing very clean extracts for the GC/MS analysis. For the screening of water samples other recently developed techniques, such as solid-phase microextraction (SPME) [11] and Empore (disk extraction [33], have been reported as rapid and reliable methods. In addition, semipermeable membrane devices (SPMDs) were used for monitoring musk compounds in river water [34] and municipal waste water [34,35]. In a non-target screening also by-products and impurities of the commercial polycyclic musks which are structurally related to the original compounds were identified in river and waste water samples by SPMDs [34]. SPMDs proved to be also valuable tools to study in depth the bioaccumulation and metabolism of musk compounds in freshwater fish and mussels [34].

Unacceptably high losses were observed [15] using concentrated sulphuric acid for the clean-up of raw extracts which is often practised in PCB analysis [36]. Also the adsorption column chromatography on florisil [37] or silica gel [38] resulted in variably high losses of some polycyclic musk fragrances [15] due to apparently increased adsorption. Thus, in order to obtain satisfactory results using these chromatographic clean-up techniques the elution conditions have to be modified according to the individual analytes.

In this context, the possibility of intralaboratory contamination of samples especially by HHCB during the clean-up process has been critically discussed [10] and, therefore, should be emphasized. Due to the physico-chemical properties of these compounds and their wide-spread occurrence as fragrances the risk of contamination of samples during the clean-up procedures in the laboratory environment must be carefully observed, and appropriate steps for its avoidance are strongly recommended. Particular caution is demanded in case of handling low contaminated materials and fatty samples.

Polycyclic Musk Fragrances in Water

In the last years numerous water samples from e.g. rivers, canals, the North Sea and sewage treatment plants were analysed for polycyclic musk fragrances. The analysis data of totally 264 samples are summarized in Tab. 2. For the purpose of comparison also the corresponding concentrations of musk xylene and musk ketone as far as available are listed in Tab. 2. In general almost all water samples including suspended particulate matter were directly extracted, only in one study [14] the water samples were analysed before and after centrifugation.

The highest HHCB and AHTN concentrations were found in the influents and effluents of sewage treatment plants. Data were available from Germany, Sweden and the Netherlands [7,12,33]. The mean and maximum concentrations of HHCB and AHTN ranged at the µg/L level (maximum values: 6 µg HHCB/L, 4.4 µg AHTN/L), only the Dutch values were an order of magnitude lower, which could perhaps be explained by the applied semi-quantitative analysis method. In this context it should be mentioned that these studies were primarily indicative and cannot be considered as representative, because representative sampling should be e. g. time- and volume-proportional, covering dry weather and rainy periods as well. However, even if the reported concentrations are not directly comparable they give an impression about the main source of contamination by polycyclic musks in the aquatic environment. Thus polycyclic musks, especially HHCB and AHTN, may be used as organic bioindicators of sewage water in aquatic ecosystems. The corresponding concentrations of ADBI, musk xylene and musk ketone were significantly lower in sewage water samples. Recently amino metabolites of musk xylene and musk ketone were found in effluent samples [43], their concentrations were 4 to 40 times higher than the parent compounds. These results indicate for the nitro musks that besides adsorption by the sludge this transformation pathway of reduction plays an important role. This study explains the relatively low concentrations of musk xylene and musk ketone in sewage water compared to the high levels of HHCB and AHTN. For a mass balance Eschke et al. [7] analysed the HHCB and AHTN in influents and effluents of several sewage treatment plants. The relatively high concentrations in effluent samples seem to indicate only poor retention of polycyclic musk fragrances by adsorption and/or degradation in sewage treatment plants. In many sewage water samples the AHTN concentrations were higher or equal to the HHCB, a result which is in contrast to the higher use volumes of HHCB [1]. This discrepancy may be explained by differences in the environmental behaviour of both chemicals. In summary, more detailed studies are urgently needed to understand the various environmental processes of polycyclic and nitro musks in sewage treatment plants.

Surface water from several river systems, such as the rivers Elbe and Ruhr including some tributaries in Germany, the rivers Rhine and Meuse in the Netherlands, the river Tamagawa in Japan, and the small river Glatt in Switzerland were analysed in the last years for polycyclic musk fragrances. The water concentrations depend on the distance of the sampling site to tributaries of sewage treatment plants and the dilution factor of the respective water system which may change during the seasons. Longitudinal profiles from the river Ruhr [8] and the river Tamagawa [42] showed maximum peaks directly at effluents of sewage treatment plants with adjacent downstream dilution. The mean HHCB concentrations ranged at the 100-400 ng/L level, the corresponding mean AHTN values varied in the range of 50-240 ng/L. The few ADBI and musk ketone data were at a significantly lower level, very often musk xylene could not be detected, or the values were near the limit of detection. In almost all water samples the HHCB concentrations exceeded those of AHTN. Winkler et al. [14] analysed the polycyclic and nitro musk fragrances besides several organochlorine pesticides, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in water samples of the river Elbe which were taken weekly or biweekly. During the whole sampling period the HHCB and AHTN concentrations in all water samples were significantly higher than those of the other organic contaminants. These results indicated that the polycyclic musk fragrances HHCB and AHTN are the predominant and significant contaminants in water from the river Elbe. In the same study [14] water samples were analysed without and after centrifugation. The water concentrations of HHCB, AHTN and ADBI after centrifugation were not as much reduced as assumed for non-polar and lipophilic substances. Thus these fragrances seem to be preferably dissolved in the water phase and adsorbed only to a minor extent on particulate matter.

In an extended study representative surface water samples were collected from various rivers, lakes and canals in the city of Berlin, Germany, and analysed for nitro and polycyclic musks [11]. HHCB, AHTN and ADBI were present in all water samples, the highest concentrations were found in samples collected directly at the sewers of municipal sewage treatment plants or downstream from them. The highest concentrations ever reported in surface or sewage water samples were analysed in a small brook almost consisting totally of sewage effluents (12.5 µg HHCB/L, 6.8 µg AHTN/L). Also surface water in the Netherlands and Belgium was monitored [33]. In the river Scheldt (Antwerp) and the river Eem (Baarn) the HHCB and AHTN concentrations were at the level observed for sewage water.

HHCB and AHTN could also be unambiguously analysed and quantified at the lower ng/L level in marine water samples from the German Bight of the North Sea [18]. These concentrations were in the same order of magnitude as those measured for α - and β -HCH, nitrobenzene, some thiophosphates and methylthiobenzothiazole (MTB) and higher than those of musk xylene, musk ketone, and PCBs [18]. Thus also in these marine water samples HHCB and AHTN belong to the major organic contaminants.

Hitherto there is only little knowledge about temporal trends because the analysis in environmental samples started only some years ago. Marine water samples from the German Bight of the years 1990 and 1995 were analysed [18]. HHCB showed a trend towards higher concentrations in 1995 at some sampling stations, while for AHTN there was no statistically significant trend. Also for the river Meuse an increasing tendency for the water concentrations of HHCB and AHTN seemed to be observed [41] reflecting the growth in production and the increased use of polycyclic musks. In contrast Eschke et al. [7,40] analysed water samples from the River Ruhr in 1994 and in 1995/1996 and found a strong decrease for musk xylene and musk ketone, but also lower medians of HHCB and AHTN. Further detailed studies and monitoring programmes are necessary to obtain statistically significant data about temporal trends of polycyclic musk fragrances in the aquatic environment.

Gatermann [34] identified several by-products and impurities of the commercial polycyclic musks in river and waste water samples by GC/MS after enrichment in SPMDs. These side products are structurally related to the original compounds. So it is known that the commercial HHCB contains about 15 % of the ethyl-tetramethylindan-isomer [29]. Because of their relatively high amount in technical musk products and the similar persistence and bioaccumulation of these lipophilic by-products they could be analysed in not negligible concentrations in environmental samples. They were also found in human adipose tissue samples [16]. Therefore these by-products have to be included into risk assessment studies.

In an environmental risk assessment for the polycyclic musks HHCB and AHTN [1] exposure concentrations of 0.5 µg HHCB/L and 0.2 µg AHTN/L in surface water were used which were derived from measured data. A comparison of these values with the compiled concentrations in Tab. 2 resulted in higher levels in several aquatic ecosystems. A risk assessment model should consider the worst case and therefore exposure concentrations of HHCB and AHTN for model calculations should be raised.

Schlett [44] determined the odour threshold concentrations for several fragrance substances in water and found relatively low concentrations for the polycyclic musks HHCB (80 ng/L) and AHTN (40 ng/L). A comparison with the concentrations in surface water samples (Tab. 2) shows that these odour thresholds are often exceeded. Another study [45] determined higher geometric mean odour and taste threshold concentrations for HHCB (5 and 50 µg/L,

respectively). It seems that these values are too high caused by variations of the odour testing method in panels. Polycyclic musk fragrances were also analysed in potable water which was partially produced by surface waters [44], and these organoleptic properties may cause consumer complaints. In this context it should be mentioned that on a chiral GC column it was possible to separate the 4 stereoisomers of HHCB and sniffing at the corresponding 4 peaks indicated, that only two isomers with the absolute configuration (4S) have a powerful musky odour, whereas the other isomers have only a very weak and not characteristic odour [29]. Taste and odour complaints from consumers are nowadays a major problem for suppliers of drinking water [45]. The general assessment of polycyclic musk fragrances in the aquatic environment should also consider this severe hygienic problem of odoriferous potable water which is a crucial and sensitive aspect of consumer protection.

In summary, in all kinds of water samples - from the sewage treatment plant up to the open sea - the polycyclic musk fragrances HHCB and AHTN were unequivocally determined in relatively high concentrations. In many cases their concentration levels exceeded those of other organic contaminants, and often HHCB and AHTN represent the predominant and significant contaminants. The highest values in river systems were analysed near the tributaries of sewage treatment plants and in rivers with low dilution rates. In water samples also structurally related by-products were analysed in relevant concentrations. HHCB and AHTN may be used as organic bioindicators of sewage water in aquatic ecosystems. There are only few data about temporal trends of this contamination but some reports indicate a probable increase. The production of potable water from surface water may be negatively influenced due to hygienic problems caused by the low odour threshold concentrations of HHCB and AHTN.

Polycyclic Musk Fragrances in Sediment, Suspended Particulate Matter (SPM), and Sewage Sludge

Hitherto there are only few data about the contamination of sediment, suspended particulate matter (SPM), and sewage sludge by polycyclic musk fragrances and, therefore the understanding about their adsorption at particles in the aquatic environment is incomplete and needs more extensive investigations. All available published data are summarized in Tab. 3.

There are only few German data about the contamination of river sediments. In a monitoring programme sediment samples from the German rivers Elbe and Weser and from some smaller rivers in the Federal State of Lower Saxony were analysed 1996 for polycyclic and nitro musk fragrances [24]. The lowest HHCB and AHTN concentrations were found in the river Ems, the highest in the river Elbe (sampling site: Schnackenburg) and the river Leine. In these last 2 samples also ATII was detected (1.3 and 1.8 µg/kg dry matter, respectively). In all samples the concentrations of AHMI and DPMI were below the limit of determination (0.5 µg/kg dry matter). The high HHCB and AHTN concentration in the sediment of the relatively small river Leine could be explained with the influence of the municipal sewage treatment plant of the city of Hannover in the neighbourhood of the sampling site. In all samples the highest concentrations were measured for HHCB, but they contained also musk xylene and musk ketone, but at a lower level. In this context the data of the river Ems are interesting: none of the polycyclic musks was detectable, but the nitro musks could be unequivocally detected. The authors of this study stated a slightly upward trend for musk xylene and musk ketone in the sediment samples from 1995 to 1996 and supposed that there was a still increasing accumulation of nitro musks in the sediments. Eschke [cited in 1] reported indicative concentrations for sediment samples from the river Ruhr (HHCB: 150-300 µg/kg dry matter, AHTN: 150-300 µg/kg dry matter). These values are much higher than those of the monitoring programme mentioned above [24] indicating the extensive pollution of the river Ruhr system by these chemicals.

In 3 extended studies SPM samples from the river Elbe [14], from several surface waters in the Federal State of Hesse [46] and from the rivers Rhine and Meuse in the Netherlands [41] were analysed for the polycyclic and nitro musks (Tab. 3). In all SPM samples from the river Elbe [14] the mean HHCB and AHTN concentrations were higher than those of the organochlorine pesticides and PCBs and in the same order of magnitude as the PAHs. Thus also in SPM from the river Elbe HHCB and AHTN were the major contaminants. In most samples also ADBI and musk ketone were analysed at a lower level. In contrast to the other organic contaminants there was no seasonal variability in the levels of musk fragrances during the one-year sampling period. In this study [14] also the partition coefficients k of the polycyclic musks were calculated from the analysis data ($k = c_{\text{SPM}}/c_{\text{W}}$ [L/kg], c_{SPM} = concentration of substance in SPM, c_{W} = concentration of substance in water after centrifugation). The mean partition coefficients of HHCB, AHTN and ADBI were calculated as 4,490, 9,550, and 6,630, respectively. For comparison the mean k values of musk ketone and the very non-polar HCB are 1,700 and 112,000, respectively. The mean portion of water dissolved HHCB, AHTN and musk ketone was 92 %, 83 %, and 95 %, respectively. The n-octanol/water partition coefficient (K_{OW}) is a useful tool to estimate the sorption of hydrophobic organic chemicals to natural organic matter. There is an approximate difference in the K_{OW} values of musk ketone and the polycyclic musks of about 2 orders of magnitude [14,20,49], however, their k values are all nearly in the same order of magnitude. Thus the non-polar polycyclic musk fragrances are more dissolved in water as supposed by their relatively high K_{OW} values. This remarkable discrepancy was discussed in detail [14]. In addition these data indicate that AHTN is probably stronger bound to SPM than HHCB. This characteristic of AHTN

would explain that, in contrast to the higher use volumes of HHCB, in many SPM samples the HHCB and AHTN mean concentrations were of similar magnitude (Tab. 3). However, this would not explain the relatively high AHTN concentrations in waste water as mentioned above. Higher HHCB and AHTN concentrations than in the river Elbe were analysed in several SPM samples from Hessian waters [46]. The maximum levels were found in the little rivers Schwarzbach and Rodau with high portions of sewage water (13.7 mg HHCB/kg dry matter, 12.7 mg AHTN/kg dry matter). Additionally, in this study [46] it was mentioned that the concentration of musk xylene in SPM samples from the Federal State of Baden-Württemberg were decreasing from 1994 to 1995. In a Dutch study of SPM samples from the Rivers Rhine and Meuse [41] it is remarkable that the mean concentrations of AHTN were by a factor 3 higher than those of HHCB approximately.

Only 2 studies reported about the concentrations of HHCB and AHTN in sewage sludge (Tab. 3). As expected the highest values are found in the sewage treatment plants which collect the waste water from the private households. The HHCB and AHTN concentrations were all at the mg/kg level. The mean HHCB concentrations were always higher than those of AHTN. In a Dutch study [47,48] the HHCB and AHTN concentrations in primary, activated and digested (by various techniques) sludge were analysed; the influence of various techniques obviously were of minor importance. The removal of HHCB and AHTN in the sewage treatment plant was estimated (HHCB: 45%, AHTN: 40%) [47,48], however, degradation and evaporation was neglected. Eschke [cited in 1] reported concentrations of 45 mg HHCB/kg dry matter and 42 mg AHTN/kg dry matter in sewage sludge. In sludge of industrial sewage treatment plants the HHCB and AHTN concentrations were 2-3 orders of magnitude lower [46]. Musk xylene and musk ketone could only be analysed in non-digested sewage sludge [46], after the digestion process all their concentrations were below the limit of detection. This observation indicates that reduction of nitro musks occurs in the sewage sludge during the digestion process [43], and that similar degradation reactions in this medium also cannot be excluded for the polycyclic musk fragrances.

Polycyclic Musk Fragrances in Biota

In two German studies the polycyclic musk fragrances were analysed in the extracted muscle lipid (mussels: extracted lipid from the whole soft body) of a large variety of biota samples, such as fish, mussels, and shrimps. These data give an overview of the general contamination situation, they are compiled in Tab. 4, together with the concentrations of musk xylene and musk ketone as far as available. Because of the low sample numbers no mean or median values are calculated.

Fish samples from the German rivers Ruhr, Elbe, and Stör, a tributary of the river Elbe, and blue mussels and shrimps from the North Sea were analysed, in addition, several kinds of fish from the ponds of 2 German municipal sewage treatment plants were investigated. According to the higher concentrations of polycyclic musks in the water of the river Ruhr, also the levels in corresponding fish were higher than those from the river Elbe. The low HHCB and AHTN levels in the fat fish eel from the river Elbe were remarkable, but also the concentrations of the organochlorine compounds in these eel samples were atypically low for fish from this polluted river indicating that the eels have not lived all time in the river system Elbe. HHCB and AHTN concentrations in fish from the small river Stör including the levels of musk xylene and musk ketone resembled very much those values in fish from sewage ponds, the sampling site of these samples was located only 3 km downstream from a municipal sewage treatment plant. In trouts from aquaculture the HHCB and AHTN concentrations exceeded those of musk xylene and musk ketone which were reported in former studies [5,28]. At low levels the polycyclic musks were also detected in mussels and shrimps. Additionally also in some herring samples from coastal waters and shrimps from Asian aquaculture polycyclic musks could be found [5,15,50]. In 2 pike samples from southern Sweden no HHCB, AHTN or ADBI were detected [8]. The highest concentrations could be analysed in fish samples from sewage ponds with maximum values of 159 mg HHCB/kg lipid and 58 mg AHTN/kg lipid. Also on a fresh weight basis the HHCB and AHTN levels of these fish samples were partially above 1 mg/kg fresh weight. In fish from sewage ponds and polluted waters also ADBI, AHDI and ATII were quantified. In general the concentrations in fish from a sewage pond in Northern Germany were higher than those from a sewage pond in the Federal State of North-Rhine Westfalia. An exception were 2 eel samples from a pond in the Federal State of Schleswig-Holstein with significant low HHCB and AHTN values. There were also remarkable differences of the pollution levels among the different species of fish from the same pond which need further investigations for explanation. In this context also the metabolism of the polycyclic musk fragrances in fish, which may vary in rate and form among the fish species has to be discussed and considered. Some results of fish tests [22,23] gave first indications of metabolism (cf. next chapter).

In general the HHCB and AHTN concentrations significantly exceed those of musk xylene and musk ketone. Mostly the HHCB levels were higher than those of AHTN, among the nitro musks musk ketone performs the major component. Thus in many fish samples the following order of concentration could be observed: HHCB > AHTN > musk ketone > musk xylene. Eschke et al. [8] also analysed the polycyclic musks in livers and adipose tissue of fish. As expected the concentrations in adipose tissue were comparable with those in muscle lipid. However, in the liver with its higher lipid

content the HHCB and AHTN concentrations based on fresh weight were higher. Similar results were also found in 2 fish livers by Rimkus et al. [15].

Recently, in a Czech monitoring programme fish from 4 sampling sites of the river Elbe and from other Czech waters were analysed for polycyclic and nitro musks as well [25]. In all fish samples the presence of musk fragrances was proved. The HHCB and AHTN levels were generally distinctly higher than those of nitro musks, the highest concentrations (3.194 mg HHCB/kg lipid, 1.289 mg AHTN/kg lipid) were found downstream of a detergent production plant. Fish collected downstream from an urban area also showed higher HHCB and AHTN concentrations.

The analysis of 28 fish samples from 8 Italian rivers and lakes were reported lately [30]. Also in these samples HHCB and AHTN were the most frequently detected compounds, at levels from < 0.004 to 0.047 mg/kg fresh weight and 0.004 to 0.105 mg/kg fresh weight, respectively. AHMI was detected only in 3 trout samples at a very low level, ADBI and ATII could not be found in these samples. Elevated lipid contents correspond to higher concentrations of the polycyclic musks HHCB and AHTN, confirming the bioaccumulation of these lipophilic compounds.

For the first time these chemicals were recently determined in various biota samples from a variety of Canadian aquatic ecosystems [26]. In contrast to the European data, in these samples musk ketone was the dominant fragrance component, and the levels of HHCB, AHTN, and musk xylene were about one to two orders of magnitude lower. These results reveal the different application modes in these two parts of the world. While in Canada still the nitro musks are dominant, in Western Europe the polycyclic musks are the prevailing musk components in fragrances due to the partial phase-out of musk xylene.

Calculated exposure concentrations of 0.125 mg HHCB/kg fresh weight and 0.146 mg AHTN/kg fresh weight were used in an environmental risk assessment [1]. These concentrations may be exceeded in biota samples from water systems near the outlet of sewage treatment plants.

Bioaccumulation of Polycyclic Musk Fragrances in Fish

The documented high concentrations of HHCB and AHTN in biota samples may lead to the conclusion of strong bioaccumulation of polycyclic musks in the lipid phase of fish. The n-octanol/water partition coefficient (K_{OW}) is an useful and important parameter to estimate the lipophilicity of a chemical and to predict its bioconcentration in aquatic organisms. The log K_{OW} values of some polycyclic musks were measured and calculated, the published data are compiled in Tab. 5. The log K_{OW} values of HHCB and AHTN determined in 2 studies are congruent, the values calculated with various programmes were all on higher levels. With the exception of DPMI the measured values of the polycyclic musks ranged from 5.4 to 5.9. In comparison, the values of organochlorine pesticides and PCBs are of the same order of magnitude (e.g. p,p'-DDT: 5.8 - 6.9 [54], dieldrin: 5.2 - 5.4 [54], HCB: 5.77 [55], PCB No. 101: 6.65 [55]), those of musk xylene (4.9 [20,56]) and musk ketone (4.2 - 4.3 [20,56]) are significantly lower. Already this rough comparison of the log K_{OW} values of HHCB and AHTN with those of well known environmental pollutants indicate their high lipophilicity.

The bioconcentration which is defined as the direct uptake of a chemical by an organism only from water, is quantified by the bioconcentration factor (BCF). The log K_{OW} value is especially useful to predict BCFs of chemicals in aquatic organisms. Usually linear Quantitative Structure-Activity Relationship (QSAR) correlations between log BCF_w (bioconcentration factor on a wet weight basis) and log K_{OW} are observed [57,58]. By the use of such a QSAR regression equation [57,59] high BCF_w values of HHCB and AHTN in the range of 30,000 - 38,000 were estimated. Another study [1] resulted in calculated BCF_w values of 20,654 and 13,964 for HHCB and AHTN, respectively, which were at the same level.

A semi-quantitative assessment of the bioconcentration under natural conditions in the River Ruhr was carried out [1]. Ratios were calculated for the median and maximum concentrations of HHCB and AHTN in fish muscle and water. Although there were some limitations of this rough assessment the resulting ratios were one to two orders of magnitude lower than expected by the above mentioned BCF_w calculation. An analogous calculation with the published data from the River Elbe results in similarly low BCF_w values.

Hitherto in 2 fish test studies [22,23,60] the BCF_w values of HHCB and AHTN were derived by experiment. Van Dijk [22,23] investigated the bioconcentration of ¹⁴C-HHCB and ¹⁴C-AHTN at two concentrations (approximately 1 and 10 µg/L) with bluegill sunfish (*Lepomis macrochirus*) in a flow-through system. Based on actual concentrations of the parent compounds in exposure water and at the plateau level in fish, the BCF_w values of HHCB and AHTN for the whole fish were 1,584 and 597, respectively. In this bioconcentration study also unidentified water-soluble metabolites were reported in fish tissue. It was concluded that both, HHCB and AHTN were metabolized to one or more polar

metabolites in fish in a relatively short time and then excreted to the water phase. The polar fraction of metabolites in tissue proved to be identical with that in water, analysed by TLC and HPLC. Up to now there is no knowledge about the chemical structure of these metabolites and neither of their environmental behaviour and possible toxic impact. This metabolism in fish may explain the relatively low measured BCF_w values of HHCB and AHTN, which are based on the actual concentrations of the parent compounds. Also in a recent study [60] with zebrafish (*Brachydanio rerio*) in a flow-through system these results were confirmed (HHCB: $BCF_w = 620$, AHTN: $BCF_w = 600$, determined by the kinetic of accumulation and clearance). In both studies rapid uptake and depuration was observed indicating that the uptake was highly reversible. These measured bioconcentration factors were significantly lower than the BCF_w values of musk xylene and comparable to those of musk ketone [20].

Thus, the measured BCF_w values of HHCB and AHTN were lower than expected, probably due to a strong metabolism in fish. Gatermann [34] studied the bioaccumulation factors (BAF_{LS}) of HHCB and AHTN in various fish species from a sewage pond in Schleswig-Holstein (Tab. 4). He found similar and well-comparable factors within a fish species, but significant differences between the species. The lowest values were estimated for eels (HHCB: 1,700; AHTN: 2,400) and rudds (2,600; 5,100), the highest for mussels (44,400; 40,100) and tenches (56,000; 31,600) resulting in a factor of about 20 between the minimal and maximal values. Therefore a species dependent metabolism was assumed. Similar differences were also reported [25] in some fish species from the Czech part of River Elbe. In general, bioconcentration studies in the laboratory are normally performed with small fish which is characterized by a higher activity and faster metabolism resulting in smaller BCFs. Therefore environmental bioconcentration may be underestimated by these laboratory studies, in addition, the aspect of fish species dependence has been neglected so far. The high concentrations of HHCB and AHTN in biota samples primarily may be explained by the corresponding large concentrations in water and not by high bioconcentration factors. In summary the high $\log K_{OW}$ values of HHCB and AHTN do not correlate with their relatively low bioconcentration, additionally, their solubilities in water is higher as calculated by QSARs [1] and, correspondingly, the adsorption to organic matter (SPM) is lower than supposed by the $\log K_{OW}$ [14]. Further studies are urgently needed to investigate the mentioned metabolism of HHCB and AHTN in various fish species, to identify the chemical structures of these compounds and to understand their biological and environmental behaviour and distribution.

Aquatic Toxicity and Risk Assessment

Hitherto there is only little knowledge about the aquatic toxicity of the polycyclic musks. For HHCB and AHTN toxicity was tested with algae, *Daphnia magna*, and fish (blue gill sunfish and fat head minnow)[1]. These only experiments were carried out from private laboratories thus the reports are not open and available, however, the final results are summarized in [1]. The lowest reported NOEC values were 0.068 mg/L (fish) for HHCB and 0.035 mg/L (fish) for AHTN [1]. These data were used for an environmental risk assessment [1] according to the EU Technical Guidance Document for Environmental Risk Assessment for New and Existing Substances [61]. In this risk assessment predicted environmental concentration (PEC) and/or measured concentrations are compared to the predicted no effect concentration (PNEC). An assessment factor of 10 was applied to the lowest NOEC values to derive PNEC. Then risk is expressed as the PEC/PNEC ratio. For aquatic organisms the ratios for both HHCB and AHTN were calculated less than 0.1, this is considered as a relatively low risk [1]. However, this risk assessment has only a very preliminary character because of the limited and insufficient data basis and approach. For a final risk assessment for example the potential degradation and/or metabolism products have to be included. This assessment has to consider critically also the long-lived and persistent character of these high volume chemicals with their ubiquitous distribution. In this context also their sorption by the human skin and occurrence in human milk and adipose tissue [5,10,16,17,19,62] may be mentioned. On the basis of the precautionary principle strong endeavours should be made to move in the long term towards cessation of production and discharges into the environment of these synthetic musk compounds because of their poor degradability.

Conclusions

The polycyclic musk fragrances, especially HHCB and AHTN, are high volume chemicals with an upward trend in production and usage. After their application in private households they are dumped via the sewage treatment plants into the aquatic environment. Thus the highest HHCB and AHTN concentrations were analysed in water and sludge from sewage plants, and in fish from sewage ponds. In all other samples from different aquatic ecosystems these chemicals were found in varying concentrations dependent on the distance to sewage treatment plants and on the influence of dilution. The apparently ubiquitous distribution of HHCB and AHTN in the aquatic environment demonstrates their persistence. Very often HHCB and AHTN form the major organic pollutants, they may be used as organic bioindicators of sewage water. In all samples from Europe their concentrations exceeded those of musk xylene and musk ketone indicating the shift in use from nitro musks to polycyclic musk fragrances. The adsorption to sediment, SPM, and sewage sludge seems to be lower than expected. The high K_{OW} values of HHCB and AHTN do not correlate with their relatively low bioconcentration factors, explained by a possible metabolism in fish. There are

indications that this metabolism is species dependent. Thus further studies are urgently needed to deepen the understanding of the distribution of polycyclic musks including their by-products between the various phases of the aquatic environment, the possible degradation processes in sediment or sludge, the metabolism in fish, and their aquatic toxicity. Therefore a final risk assessment will have to consider all these results. Due to their properties the polycyclic and nitro musks should be included in the group of persistent organic pollutants (POPs).

References

- [1] van de Plassche, E.J., Balk, F., 1997. Environmental risk assessment of the polycyclic musks AHTN and HHCB according to the EU-TGD. RIVM Report No. 601503008, RIVM, Bilthoven, The Netherlands.
- [2] Ohloff, G., 1990. Riechstoffe und Geruchssinn. Die molekulare Welt der Düfte. Springer-Verlag, Berlin, Heidelberg, pp. 195-220.
- [3] Barbetta, L., Trowbridge, T., Eldib, I. A., 1988. Musk aroma chemical industry. Perfumer & Flavorist 13, 60-61.
- [4] Gebauer, H., Bouter, T., 1997. Moschus. Euro Cosmetics 1, 30-35.
- [5] Rimkus, G., Brunn, H., 1996. Synthetische Moschusduftstoffe - Anwendung, Anreicherung in der Umwelt und Toxikologie, Teil 1: Herstellung, Vorkommen in Lebensmitteln, Aufnahme durch den Menschen. Ernährungs-Umschau 43, 442-449.
- [6] Brunn, H., Rimkus, G., 1997. Synthetische Moschusduftstoffe - Anwendung, Anreicherung in der Umwelt und Toxikologie, Teil 2: Toxikologie der synthetischen Moschusduftstoffe und Schlußfolgerungen. Ernährungs-Umschau 44, 4-9.
- [7] Eschke, H.-D., Traud, J., Dibowski, H.-J., 1994. Untersuchungen zum Vorkommen polycyclischer Moschus-Duftstoffe in verschiedenen Umweltkompartimenten - Nachweis und Analytik mit GC/MS in Oberflächen-, Abwässer und Fischen (1. Mitteilung). UWSF - Z. Umweltchem. Ökotox. 6, 183-189.
- [8] Eschke, H.-D., Dibowski, H.-J., Traud, J., 1995. Untersuchungen zum Vorkommen polycyclischer Moschus-Duftstoffe in verschiedenen Umweltkompartimenten, 2. Mitteilung: Befunde in Oberflächen-, Abwässern und Fischen sowie in Waschmitteln und Kosmetika. UWSF - Z. Umweltchem. Ökotox. 7, 131-138.
- [9] Franke, S., Hildebrandt, S., Schwarzbauer, J., Link, M., Francke, W., 1995. Organic compounds as contaminants of the River Elbe and its tributaries, Part II: GC/MS screening for contaminants of the Elbe water. Fresenius J. Anal. Chem. 353, 39-49.
- [10] Rimkus, G.G., Wolf, M., 1996. Polycyclic musk fragrances in human adipose tissue and human milk. Chemosphere 33, 2033-2043.
- [11] Heberer, Th., Gramer, S., Stan, H.-J., 1998. Occurrence and distribution of organic contaminants in the aquatic system in Berlin. Acta Hydrochim. Hydrobiol., in press.
- [12] Paxeus, N., 1996. Organic pollutants in the effluents of large wastewater treatment plants in Sweden. Wat. Res. 30, 1115-1122.
- [13] Lagois, U., 1996. Vorkommen von synthetischen Nitromoschusverbindungen in Gewässern. gwf- Wasser Abwasser 137, 154-155.
- [14] Winkler, M., Kopf, G., Hauptvogel, C., Neu, T., 1998. Fate of artificial musk fragrances associated with suspended particulate matter (SPM) from the River Elbe (Germany) in comparison to other organic contaminants. Chemosphere 37, 1139-1156.
- [15] Rimkus, G.G., Wolf, M., 1999. Polycyclic musk fragrances in biota from aquatic ecosystems. Chemosphere, in preparation.
- [16] Müller, S., Schmid, P., Schlatter, Ch., 1996. Occurrence of nitro and non-nitro benzenoid musk compounds in human adipose tissue. Chemosphere 33, 17-28.

- [17] Mayer, R., 1998. Simultane Bestimmung von Nitro- und polycyclischen Moschusduftstoffen in Frauenmilch mittels GC/HRMS. Poster F3, Deutscher Lebensmittelchemikertag 1998, September 14-16, Munich, Germany.
- [18] Bester, K., Hühnerfuss, H., Lange, W., Rimkus, G.G., Theobald, N., 1998. Results of non target screening of lipophilic organic pollutants in the German Bight II: Polycyclic musk fragrances. *Wat. Res.* 32, 1857-1863.
- [19] Eschke, H.-D., Dibowski, H.-J., Traud, J., 1995. Nachweis und Quantifizierung von polycyclischen Moschus-Duftstoffen mittels Ion-trap GC/MS/MS in Humanfett und Muttermilch. *Dtsch. Lebensm.-Rundsch.* 91, 375-379.
- [20] Rimkus, G.G., Butte, W., Geyer, H.J., 1997. Critical considerations on the analysis and bioaccumulation of musk xylene and other synthetic nitro musks in fish. *Chemosphere* 35, 1497-1507.
- [21] Schüssler, W., Nitschke, L., 1998. Determination of trace amounts of Galaxolide[®] (HHCB) by HPLC. *Fresenius J. Anal. Chem.* 361, 220-221.
- [22] van Dijk, A., 1996. Accumulation and elimination of ¹⁴C-AHTN by Bluegill Sunfish in a dynamic flow-through system. Report to RIFM, RCC Umweltchemie AG, Project 364825, cited in [1].
- [23] van Dijk, A., 1996. Accumulation and elimination of ¹⁴C-HHCB by Bluegill Sunfish in a dynamic flow-through system. Report to RIFM, RCC Umweltchemie AG, Project 381418, cited in [1].
- [24] Lach, G., Steffen, D., 1997. Orientierende Untersuchungen von Gewässersedimenten auf Nitro- / Polymoschusverbindungen und die Flammschutzmittel TCEP und TCPP. *Oberirdische Gewässer* 3/97, Niedersächsisches Landesamt für Ökologie, Hildesheim, Germany.
- [25] Hajslova, J., Gregor, P., Chladkova, V., Alterova, K., 1998. Musk compounds in fish from Elbe River. *Organohalogen Compounds* 39, 253-256.
- [26] Gatermann, R., Hellou, J., Hühnerfuss, H., Rimkus, G., Zitko, V., 1999. Polycyclic and nitro musks in the environment: a comparison between Canadian and European aquatic biota samples. *Chemosphere*, in press.
- [27] Kallenborn, R., Gatermann, R., Planting, S., Rimkus, G.G., Lund, M., Schlabach, M., Burkow, I.C., 1999. Determination of synthetic musk compounds in Norwegian ambient air samples. *J. Chromatogr. A*, submitted.
- [28] Rimkus, G.G., Wolf, M., 1995. Nitro musk fragrances in biota from freshwater and marine environment. *Chemosphere* 30, 641-651.
- [29] Frater, G., Müller, U., Bajgrowicz, A., Petrzilka, M., 1995. Musky and odorless diastereomers of Galaxolide. In: Baser, K.H.C. (Ed.), *Flavours, Fragrances and Essential Oils. Proceedings of the 13th International Congress of Flavours, Fragrances and Essential Oils*, Istanbul, Turkey, October 15-19, 1995.
- [30] Draisci, R., Marchiafava, C., Ferretti, E., Palleschi, L., Catellani, G., Anastasio, A., 1998. Evaluation of musk contamination of freshwater fish in Italy by accelerated solvent extraction and gas chromatography with mass spectrometric detection. *J. Chromatogr. A* 814, 187-197.
- [31] Gatermann, R., Franke, S., 1999. Personal communication, University of Hamburg, Hamburg, Germany.
- [32] Rimkus, G. G., Rummler, M., Nausch, I., 1996. Gel permeation chromatography - high-performance liquid chromatography combination as an automated clean-up technique for the multiresidue analysis of fats. *J. Chromatogr. A* 737, 9-14.
- [33] Verbruggen, E., 1997. Levels of AHTN and HHCB in Dutch surface water and effluents by biomimetric extractions. Letter of RITOX, Utrecht, The Netherlands, cited in [1].
- [34] Gatermann, R., 1998. Verteilung, Anreicherung und Transformation nitroaromatischer und polycyclischer Moschusduftstoffe sowie weiterer N- und P-haltiger Problemstoffe in der Umwelt. Ph.D. Thesis, University of Hamburg, Hamburg, Germany.

- [35] Leonards, P.E.G., van Stee, L.L.P., Vreuls, R.J.J., Brinkman, U.A.Th., 1997. Extraction methods for organic pollutants from municipal waste water. In: Abstract Book of the 8th Symposium on Handling of Environmental and Biological Samples in Chromatography, Almerimar - El Ejido, Almeria, Spain, October 26-29, 1997.
- [36] Murphy, P.G., 1972. Sulfuric acid for the cleanup of animal tissues for analysis of acid stable chlorinated hydrocarbon residues. J. Assoc. Off. Anal. Chem. 55, 1360-1362.
- [37] Stijve, T., Cardinale, E., 1972. On the residues associated with the use of technical grade BHC with special reference to the occurrence and determination of three pentachlorocyclohex-1-ene isomers. Mitt. Geb. Lebensmittelunters. Hyg. 63, 142-152.
- [38] Steinwandter, H., Schlüter, H., 1977. Eine einfache Multimatrixmethode zur Bestimmung von Chlorkohlenwasserstoff-Pesticiden und polychlorierten Biphenylen. Fresenius Z. Anal. Chem. 286, 90-94.
- [39] Wassergütestelle Hamburg, ARGE Elbe, 1997, unpublished data, cited in [46].
- [40] Eschke, H.-D., 1996. Organische Spurenstoffe in der Ruhr. In: Ruhrwassergüte 1996, Ruhrverband, Essen, Germany, pp. 86-90.
- [41] Breukel, R.M.A., Balk, F., 1996. Musken in Rijn en Maas. RIZA Werkdocument 96.197x, RIZA, The Netherlands, cited in [1].
- [42] Yun, S.-J., Teraguchi, T., Zhu, X.-M., Iwashima, K., 1994. Identification and analysis of dissolved organic compounds in Tamagawa River. J. Environm. Chem. 4, 325-333.
- [43] Gatermann, R., Hühnerfuss, H., Rimkus, G., Attar, A., Kettrup, A., 1998. Occurrence of musk xylene and musk ketone metabolites in the aquatic environment. Chemosphere 36, 2535-2547.
- [44] Schlett, C., 1995. Analytik und Vorkommen von Geruchsstoffen in der Ruhr. In: Ruhrwassergüte 1995, Ruhrverband, Essen, Germany, pp. 111-115.
- [45] Young, W.F., Horth, H., Crane, R., Ogden, T., Arnott, M., 1996. Taste and odour threshold concentrations of potential potable water contaminants. Wat. Res. 30, 331-340.
- [46] Fooker, C., Gühr, R., Häckl, M., Seel, P., 1997. Orientierende Messungen gefährlicher Stoffe - Landesweite Untersuchungen auf organische Spurenverunreinigungen in hessischen Fließgewässern, Abwässern und Klärschlämmen, 1991 - 1996. Umweltplanung, Arbeits- und Umweltschutz, Heft 233, Hessische Landesanstalt für Umwelt, Wiesbaden, Germany.
- [47] Blok, H., 1997. Measurement of musk fragrances in sludges of sewage treatment plants in The Netherlands. BKH Consulting Engineers, The Netherlands, cited in [1].
- [48] Omegam, 1997. Analytical results of musks in sludges. Reported to BKH, Omegam Projects 57880, 57448, 57140, cited in [1].
- [49] Eschke, H.-D., 1994. Organische Xenobiotika und Schwermetalle in Fischen aus dem Einzugsgebiet der Ruhr. In: Ruhrwassergüte 1994, Ruhrverband, Essen, Germany, pp. 62-68.
- [50] Rimkus, G., Wolf, M., 1997. Nachweis von polycyclischen Moschusduftstoffen in Fisch- und Humanproben. Lebensmittelchemie 51, 94-95.
- [51] Eschke, H.-D., 1999. UWSF - Z. Umweltchem. Ökotox., in preparation.
- [52] Rudio, J., 1993. Partition coefficient n-octanol/water of GALAXOLIDE according to OECD guideline No. 117. Givaudan-Roure Corporate Safety & Environmental affairs, Test report No. 93 - E67, cited in [1].
- [53] Rudio, J., 1993. Partition coefficient n-octanol/water of FIXOLIDE according to OECD guideline No. 117. Givaudan-Roure Corporate Safety & Environmental affairs, Test report No. 93 - E64, cited in [1].

- [54] de Bruijn, J., Busser, F., Seinen, W., Hermens, J., 1989. Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the "slow-stirring" method. *Environ. Toxicol. Chem.* 8, 499-512.
- [55] Chessells, M., Hawker, D.W., Connell, D.W., 1991. Critical evaluation of the measurement of the 1-octanol/water partition coefficient of hydrophobic compounds. *Chemosphere* 22, 1175-1190.
- [56] Tas, J.W., Balk, F., Ford, R.A., van de Plassche, E.J., 1997. Environmental risk assessment of musk ketone and musk xylene in The Netherlands in accordance with the EU-TGD. *Chemosphere* 35, 2973-3002.
- [57] Geyer, H.J., Rimkus, G.G., Scheunert, I., Hansen, L.G. McKay, D., Kettrup, A., Kaune, A., Zeeman, M., Muir, D.C.G., 1999. Bioaccumulation and Occurrence of endocrine-disrupting chemicals (EDCs), persistent organic pollutants (POPs) and other organic compounds in fish and other organisms including human. In: Hutzinger, O. and Beek, B. (Eds.), *Bioaccumulation, Handbook of Environmental Chemistry, Vol. 2 Part J*. Springer-Verlag, Berlin, Heidelberg, Germany, in press.
- [58] Nagel, R., Loskill, R., (Eds.), 1991. *Bioaccumulation in aquatic systems, contributions to the assessment*. VCH, Weinheim.
- [59] Geyer, H.J., Rimkus, G., Wolf, M., Attar, A., Steinberg, C., Kettrup, A., 1994. Synthetische Moschus-Duftstoffe und Bromocyclen - Neue Umweltchemikalien in Fischen und Muscheln bzw. Muttermilch und Humanfett. *UWSF-Z. Umweltchem. Ökotox.* 6, 9-17.
- [60] Ewald, F., 1998. Kinetik der Akkumulation und Clearance der polycyclischen Moschusduftstoffe Galaxolide und Tonalide in Zebrabärblingen. Diploma Thesis, University of Oldenburg, Oldenburg, Germany.
- [61] EU Technical Guidance Documents in support of Directive 96/67/EEC on risk assessment of new notified substances and Regulation (EC) No. 1488/94 on risk assessment of existing substances (Parts I, II, III and IV). EC catalogue numbers CR-48-96-001, 002, 003, 004-EN-C. Office for Official Publications of the European Community, Luxembourg.
- [62] Rimkus, G.G., 1998. Synthetic musk fragrances in human fat and their potential uptake by dermal resorption. In: Frosch, P.J., Johansen, J.D., White, I.R. (Eds.), *Fragrances: beneficial and adverse effects*. Springer-Verlag, Berlin, Heidelberg, Germany, pp. 136-149.

ANNEX 10: DRAFT GUIDELINES FOR QUALITY CONTROL AND METADATA SUPPORT OF DISCRETE HYDROGRAPHICAL DATA IN MARINE ENVIRONMENTAL MONITORING PROGRAMMES

Introduction

These guidelines describe the minimum requirements for quality control and metadata support of discrete hydrographical data (mainly salinity, temperature, oxygen, hydrogen sulphide, nutrients, pH, alkalinity and chlorophyll-a) assembled in marine monitoring programmes. All hydrographical data reported to national or international data banks (including the commissions) should be quality controlled and supported at least according to the routines outlined in these guidelines, unless otherwise is specified by the commissions.

Sound and practical quality assurance of environmental data can be divided into the following steps:

- 1) Sampling strategy and sampling procedures, including storage
- 2) Analytical quality control (internal and external)
- 3) Documentation of supporting information
- 4) Automatic screening of data
- 5) Manual validation of the automatic screening
- 6) Procedures for data storage and recovery

These guidelines intend to describe the procedures in steps 3-5, i.e., the chain of actions to be taken from when the analyst reports data through to the stage when the data is ready for storage in a data bank. The main aims of these three steps are to give the data an identity (supporting information), identify data that do not conform to the expected quality, and to provide these data with the appropriate quality flag, depending on why the data has been identified. As a general guideline, data should never be deleted from an existing data set. Questionable or apparently wrong data should merely be quality flagged, thus preventing them from being extracted from the data bank using the normal extraction procedures. A list of applied quality flags, with explanations, is given in Annex 1. Depending on which data is wanted, different levels of extraction efficiency could be applied, allowing data with certain quality flags to be, or not to be, extracted.

For guidelines on the internal and external quality control of the analytical steps, refer to e.g. the HELCOM Guidelines (www.helcom.fi), JAMP Guidelines of OSPARCOM (web address).

Documentation of supporting information (metadata)

Aim

The documentation of supporting information has three main aims. The first is to provide the user of the data with enough information to identify the origin of the data (where and when the sample was taken and analysed) and the circumstances around the sampling and analysis (weather conditions, ship, equipment etc). The second aim is to provide enough information for the data to be transformed into other units if necessary (e.g. from per volume to per mass). The third aim is to describe the quality of the data, and will contain information from, or references to, the external and the internal quality control procedures carried out to support the analytical steps.

Procedure

The following information has to be known for each and every hydrographical data:

Metadata for every station/cast:

- Station code (or name)
- Year
- Ship code
- Series/cast no.
- Position (latitude, longitude)

- Date
- Time (UTC)
- Bottom depth
- Wind direction and speed
- Air temperature and pressure
- Weather codes (as described in Annex 2)

Supporting data for every data point:

- Depth or pressure
- Unit
- Water temperature (Reversing thermometer or CTD¹)
- Salinity (discrete samples from every bottle preferable, CTD¹ possible)

Additional supporting data to enable unit conversion

- For oxygen: Sample temperature at the addition of reagents, if significantly different from the in-situ water temperature.
- For nutrients: Temperature at which the calibration solution was fabricated (if made volumetrically)

Footnote 1: In certain CTD systems the temperature and salinity will have to be averaged over e.g. 0.5 metres.

Supporting data for every parameter/laboratory:

- Analytical method
- Information regarding accreditation/certification (EN 45001 etc.)
- Information on measurement uncertainty, and how it was calculated
- Results from the use of Certified Reference Materials (CRMs)
- Participation and results from intercomparison exercises

Other supporting information, like type of sampling equipment, identity of responsible sampler, all calibrations and other analytical information, has to be documented at the data delivering institutes, according to their own quality system.

Outcome

Records (in electronic or printed form) of all supporting information needed

Automated screening of data

Aim

The automated screening of data should be used to identify data and supporting information that do not fulfil the given quality requirements, and that has to be taken through further steps of screening. Remember that automated screening alone will not be enough, it always has to be followed by a manual validation process. The automated screening can (but does not have to) be divided into two steps: The first step is applied after each hydrographic station or series of analyses and identifies data that appear not to match the expected pattern (e.g. by falling outside the expected concentration range in that particular sea area). This check can usually be carried out as soon as the data is reported from the analysts and are entered into a computer. The second step is applied for a whole cruise or series of cruises, and identifies data and supporting information that do not fit into the total picture, where all supporting and oceanographic information is taken into account.

For practical reasons the two steps may well be merged into one, applied for a whole cruise or series of data. For the same reason, it is highly recommendable to carry out these checks in some kind of automated or otherwise computerised fashion, as this will save considerable time and effort in comparison to a manual procedure.

Step 1. For each station/cast, carry out the following automated checks:

- All data fall within the expected concentration range (identified for each sea area and/or season)
- All data have the expected number of decimals
- All depths are less than the reported bottom depth
- Secchi depth is less than the bottom depth
- Increasing density (or salinity) with increasing depth
- $[\text{Total-P}] \geq [\text{PO}_4]$
- $[\text{Total-N}] \geq [\text{NO}_3 + \text{NO}_2 + \text{NH}_4]$
- $[\text{NO}_3 + \text{NO}_2] \geq [\text{NO}_2]$
- Oxygen and Hydrogen sulphide do not co-exist at the same depth

Step 2. For a full cruise or series of cruises, carry out the following automated checks:

- Ship's speed between consecutive stations (checks reported position, date and time at these stations)
- Date/time increasing with increasing series/cast number

More sophisticated ways of identifying questionable data can of course be applied. It may for example be very useful to keep updated information on, for every regularly visited station, the mean value for each parameter and depth for every season, and check that any new data fall within plus/minus one standard deviation from this average. If not, a quality flag should be added to the deviating data. This procedure implies that a reasonably long time series exists.

Outcome

Automatic quality flags on identified data. In this step the added quality flags will consist of question marks.

Manual validation of the automatic screening

Aim

This will be the final check of the data, and will focus mainly on the data identified and flagged in the previous steps.

Procedure

All data is presented in, for example, transects of stations (sections), parameter by parameter, or in any other perspicuous way. The oxygen results are always presented both as concentration and saturation. The manual check will also include the supporting information (metadata), which hence will have to be presented together with the data. Automatically flagged data/metadata is marked with the appropriate flag (question marks from the automatic screening or other flags from the data entry). The reason for each flag to appear has to be listed separately or otherwise known.

The data can now be examined by experienced staff. It is necessary to use personnel with thorough knowledge of the local oceanographic conditions, and who are well acquainted with the analytical methods used. This manual screening will confirm or reject the quality flags set automatically, and will identify and flag any other data of questionable quality. For this work the persons carrying out the screening have to have access to documentation from the sampling and analysis (control charts, calibration information etc). It should be noted that access to discrete salinity data from each hydrographic sampling bottle is of utmost importance for the ability to identify sampling bottles that have closed at incorrect depth or that have been leaking.

The manual screening should thus include:

- Verification or rejection of existing quality flags (checks against control charts, calibration curves, sample storage information etc.)
- Verification of oxygen saturation at the surface, and the shape of the vertical profiles
- The relationship between the salinity/density profiles and the hydrochemistry
- Addition of new quality flags if necessary
- Identification of series of data that suffer from poor calibration, sample treatment, contamination or inadequate storage/storage time.
- Verification that all metadata is available

Outcome

Confirmation, rejection or substitution of the automatically set quality flags. Quality flags on dubious or bad data that was not identified by the automated procedures. Feedback to the analysts or sampling staff to improve methods and future actions. The data should now be ready for delivery to any monitoring data bank.

References

Manual of quality control procedures for validation of oceanographic data. Manuals and Guidelines 26, UNESCO, 1993.

Quality control and processing of historical oceanographic nutrient data. NOAA Technical report NESDIS 79, US Department of Commerce, Washington DC, 1994.

Quality control and processing of historical oceanographic temperature, salinity and oxygen data. NOAA Technical report NESDIS 81, US Department of Commerce, Washington DC, 1994

Annex 1: Quality Flags

The following quality flags should be applied on hydrographical data. Note that apparently good (“normal”) data remain unflagged.

Flags that can be set by the analyst

? Questionable data

The question mark is used as a general quality flag on data that appears to be wrong, but where no obvious reason is found. It is normally applied as a general warning.

I Interpolated manually

Used on data that has not been measured, but calculated manually from other data.

Z Zero by definition

Used where no measurement has been made, for example of oxygen or nitrate in the presence of hydrogen sulphide, but where the concentration has to be zero.

M Missing value

Used when a sample has been taken but no data has been reported, usually due to analytical problems.

< Below the detection limit of the analytical method

Example: Data given as < 0.5, where 0.5 is the detection limit

> Above the range of the analytical method

Example: >100, where 100 is the upper limit of the method

Flags that will be set by the automated procedure

? Questionable data

The question mark is used as a general quality flag on data that appears to be wrong, but where no obvious reason is found. It is normally applied as a general warning.

Flags that can be set at the manual validation

? Questionable data

The question mark is used as a general quality flag on data that appears to be wrong, but where no obvious reason is found. It is normally applied as a general warning.

I Interpolated manually

Used on data that has not been measured, but calculated manually from other data.

Corrected value

Used on data that has been recalculated due to e.g. recalibration

B Bad data

This flag is used on obviously bad data, or data which has been proven wrong

Z Zero by definition

Used where no measurement has been made, for example of oxygen or nitrate in the presence of hydrogen sulphide, but where the concentration has to be zero.

- ! Exceptional, but should be correct
This flag is used on data that at a first glance appears to be very dubious, but which has been checked and verified. Often this data has first been flagged with a question mark.
- M Missing value
Used when a sample has been taken but no data has been reported, usually due to analytical problems.
- < Below the detection limit of the analytical method
Example: Data given as < 0.5, where 0.5 is the detection limit
- > Above the range of the analytical method
Example: >100, where 100 is the upper limit of the method
- N Not quality controlled
Mainly used to flag old data that has not gone through the quality checks

Annex 2: Weather Codes

Weather

- 0 - Clear (no clouds at any level)
- 1 - Partly clouded (scattered or broken)
- 2 - Continuous layer(s) of cloud(s)
- 3 - Sand storm, dust storm or storm of drifting snow
- 4 - Fog, thick dust or haze
- 5 - Drizzle
- 6 - Rain
- 7 - Snow, or rain and snow mixed
- 8 - Shower(s)
- 9 - Not observed

Note: Code figure 2 is used when the total amount of clouds is 7/8 or 8/8

Clouds

- 0 - No clouds
- 1 - 1/8 or less, but not zero
- 2 - 2/8
- 3 - 3/8
- 4 - 4/8
- 5 - 5/8
- 6 - 6/8
- 7 - 7/8 or more, but not 8/8
- 8 - 8/8
- 9 - Not observed

Sea

- | | | |
|-----------------------|------|--------|
| 0 - Calm (glassy) | 0 | metres |
| 1 - Calm (rippled) | 0 | - 0.1 |
| 2 - Smooth (wavelets) | 0.1 | - 0.5 |
| 3 - Slight | 0.5 | - 1.25 |
| 4 - Moderate | 1.25 | - 2.5 |
| 5 - Rough | 2.5 | - 4 |
| 6 - Very rough | 4 | - 6 |
| 7 - High | 6 | - 9 |
| 8 - Very high | 9 | - 14 |
| 9 - Not observed | | |

Ice

- 0 - No ice
- 1 - Ice present in vicinity, but not identified as to type or amount (sighted visually or by radar)
- 2 - Few bergs (10 or less)
- 3 - Many bergs (more than 10)
- 4 - Very open or open pack ice (6/10 coverage or less), more than one nautical mile distant from the station
- 5 - Close or very close pack ice (coverage more than 6/10), more than one nautical mile distant from the station
- 6 - Very open or open pack ice (6/10 coverage or less); station within ice pack or less than one nautical mile distant from the station
- 7 - Close or very close pack ice (coverage more than 6/10); station within ice pack or less than one nautical mile distant from the station
- 8 - Station actually within very heavy concentration of pack ice, polar pack, fast ice etc. (observations made from 'ice islands', drifting pack, beset vessels, fast ice or similar cases)
- 9 - Not observed

Wind

Calm	00
Varying directions	99
N	36
NNE	02
NE	05
ENE	07
E	09
ESE	11
SE	14
SSE	16
S	18
SSW	21
SW	23
WSW	25
W	27
WNW	30
NW	32
NNW	34

ANNEX 11: OVERVIEW AND RECOMMENDATIONS FOR THE DETERMINATION OF CHLOROPHYLL *a* BY SPECTROSCOPIC METHODS

1 INTRODUCTION

Chlorophyll *a* is the principal pigment in plants. In converting light energy to chemical energy, it allows photosynthesis, i.e., light-induced carbon fixation (primary production) to take place. As a biomass indicator of aquatic micro-algae that supports food webs in the sea, it is probably the most frequently measured biochemical parameter in oceanography (Jeffrey and Mantoura, 1997).

Whatever the method used for the determination of algal pigments, the measure itself relies on their spectroscopic characteristics: light absorption or fluorescence. In discrete samples, photosynthetic pigments can be measured either by the traditional non-separative spectroscopic methods or after chromatographic separation, using HPLC. Detection by either remote sensing or *in situ* probes is also used, but these relative data must be calibrated against discrete 'chemical' measurements on samples.

As chlorophyll *a* determination is complex but non-specific, traceability and quality controls are difficult to establish. QA relies strongly on rigorous application, at each step, of recommended protocols checked by specialists, and good appraisal of the limits of validity of the method. This paper is not intended as a cook-book approach, but aims to draw attention to critical points of chlorophyll *a* determination for adequate QA/QC procedures. Specific publications from international bodies have reviewed the procedures and/or proposed guidelines and recommendations (SCOR-UNESCO, 1966; BMB, 1979). However, an updated UNESCO publication, entitled 'Phytoplankton pigments in oceanography: guidelines to modern methods', presents a very detailed review on phytoplankton pigments issued by the SCOR Working Group 78 on Determination of photosynthetic pigments in seawater (Jeffrey *et al.*, 1997). As this book contains the latest methodological developments and recommendations, it provides the benchmark for pigment studies. The present paper will therefore briefly review problems of chlorophyll *a* determination and recommendations when it is used as a biomass marker. It is a synthesis of specific information as summarized from the UNESCO monograph (Jeffrey *et al.*, 1997) and several other sources referred to below.

A standard procedure for chlorophyll *a* determination has been elaborated by the Working Group on Phytoplankton Ecology (WGPE) in conjunction with the Marine Chemistry Working Group (MCWG). This procedure appears in Annex 4.

2 CONTEXT AND DIFFICULTIES OF CHLOROPHYLL *A* DETERMINATION

Measurement of chlorophyll *a* requires its extraction from planktonic cells, which involves filtering the water as the first step, then extracting the filter with an appropriate solvent. Once the extracts are obtained, chlorophyll *a* can be measured using single or multi-wavelength spectrophotometric or fluorometric procedures. These procedures overcome some of the interferences from other pigments extracted together with chlorophyll *a* and having similar spectroscopic properties. Since pigments are light-sensitive molecules, protection from light should be a constant concern throughout all analytical steps.

2.1 Interfering Chlorophylls and Degradation Products

Three types of chlorophylls have been identified: *a*, *b*, and *c* (there are six known types of chlorophyll *c*).

The basic structure of chlorophylls is a tetrapyrrole macrocycle chelating a magnesium ion. Differing radicals characterize the three types of chlorophylls. Chlorophylls *a* and *b* have a side phytol chain, unlike chlorophylls *c*. When the chlorophyll (*a*, *b*, or *c*) molecule loses its magnesium ion, the resulting product is a pheophytin (*a*, *b*, or *c*) respectively). Dephytylation produces chlorophyllides. Pheophorbides are both dephytylated and magnesium-free. Pheophytins and pheophorbides constitute the pheopigments.

2.2 Occurrence and Significance of the Chlorophyll Group Pigments

Degradation of chlorophylls can occur either naturally in the medium or within the analytical chain. Table A3.1 shows the natural occurrence of the main pigments.

Table A3.1. Natural occurrence of the main pigments of the chlorophyll group.

Pigment	Occurrence
Chlorophyll <i>a</i>	All photosynthetic algae (except prochlorophytes) and higher plants
Chlorophyll <i>b</i>	Higher plants, green algae, symbiotic prochlorophytes
Chlorophylls <i>c</i>	Chromophyte algae, brown seaweeds
Chlorophyllide <i>a</i>	Senescent tissue, damaged centric diatoms, zooplankton faecal pellets
Chlorophyllide <i>b</i>	Senescent tissue, zooplankton faecal pellets
Pheophytin <i>a</i>	Photosynthetic reaction centres of higher plants, plant and algal detritus
Pheophytin <i>b</i>	Terrestrial plant detritus, protozoan faecal pellets
Pheophorbide <i>a</i>	Marine detritus, zooplankton and protozoan faecal pellets
Pheophorbide <i>b</i>	Terrestrial plant detritus, protozoan faecal pellets

From Table A3.1, it is clear that several pigments and degradation products may be found simultaneously in a sample. For research studies, analysis of the detailed pigment composition may significantly improve knowledge of plankton composition and physiology. Although this is not necessary for routine use of chlorophyll *a* as a biomass indicator, the following should be kept in mind:

- as the only pigment present in all microalgae, chlorophyll *a* is currently the right biomass indicator (the chlorophyll *a* derivative found in prochlorophytes is measured as chlorophyll *a*);
- in marine samples, pheopigments result from grazing and are, consequently, inactive pigments, thus determination of pheopigments *a* together with chlorophyll *a* may be useful;
- in turbid estuaries, higher plant detritus may contribute pigment concentrations (pheophytin *a* being known as an active plant pigment, misinterpretation may occur); this contribution, however, is assumed to be minor in comparison with river phytoplankton inputs;
- chlorophyllides, not spectroscopically distinct from chlorophyll *a*, lead to an overestimation of chlorophyll *a*.

2.3 Spectroscopic Characteristics and Resulting Measurement Methods

2.3.1 Spectrophotometry

Chlorophylls exhibit two major light absorption bands, one on the blue side of the visible spectrum (< 460 nm) and one in the red (630–670 nm). As carotenoids, co-extracted with chlorophylls, have also strong absorption maxima in the blue, spectrophotometric measurements are limited to the red absorption bands. Because of overlapping of the main absorption bands and of secondary maxima in the range 630–670 nm, several spectrophotometric procedures have been developed to determine the three chlorophylls in the same extract. They are based on measurement of absorbances at three wavelengths, then computation of chlorophylls using three equations (called ‘trichromatic equations’).

Unfortunately, degradation products have spectroscopic characteristics close to those of their parent chlorophyll. The spectra of chlorophyllides in the red wavelengths are so close to those of their parent chlorophylls that there is no way of differentiating the forms spectrophotometrically. Pheopigments *a* and *b* (no data available for *c*) also show spectra similar to those of the corresponding chlorophylls, but with a slight red shift and a decrease of the molar extinction coefficients to about 0.6 times those of chlorophylls.

Although methods, that take into account pheopigments in the extracts, have been developed for chlorophyll *a*, none of the spectrophotometric methods is quite accurate in the presence of degradation products.

2.3.2 Fluorometry

Fluorescence assays are one or two orders of magnitude more sensitive than spectrophotometric methods. This makes fluorometry more attractive for oligotrophic areas.

Excitation maxima for the pigments of the chlorophyll group are very close to their wavelengths of the blue absorption maximum, while emission maxima occur close to the strong red absorption maxima. As is the case for spectrophotometry, fluorometric methods for the measurement of chlorophyll *a*, with corrections for pheopigments,

have been developed. However, also in this case, chlorophyllide cannot be differentiated from chlorophyll. Multi-wavelength methods exist for the determination of the three chlorophylls and their pheopigments, but they require high performance fluorometers and complicated calibration procedures and consequently are not suitable for routine work.

3 CRITICAL VIEW OF THE PREPARATION OF PIGMENT EXTRACTS

3.1 Sampling and Sub-sampling

Water samples can be collected using any sampling bottle (preferably opaque) or a pump (up to 50 m). Sub-samples should be collected in opaque bottles, protected from warming, and filtered without delay. As zooplankton contains chlorophyll pigments, its presence may induce greater variability in the results. Pre-filtering through a nylon net of 100 µm to 150 µm mesh size eliminates most of the problems, but cannot be applied if large or colonial phytoplankton dominate. Later removal of large zooplankton from the filter forceps is also suggested.

3.2 Filtration

3.2.1 Filter material and pore size

Glass-fibre filters are widely used thanks to their large filtration capacity and flow rate. In addition, they are inert towards extracting solvents. Membrane filters, in particular those in cellulose esters, were often preferred for fluorometric determination since they dissolve in the extracting solvent. However, both types of filters may alter the analytical blank (see Section 4.2.4). Pore size should be small enough to prevent loss of picoplankton (0.2–2 µm), especially in the open ocean. Comparison of filter retention yields concluded that the 'depth' Whatman GF/F glass-fibre filter (0.7 µm nominal pore size) lead to concentrations of chlorophyll *a* that were indistinguishable from those obtained using Millipore 0.45 µm membranes. GF/F filters even recovered > 94 % of picoplanktonic chlorophyll *a*. Therefore, GF/F filters (or an equivalent) can be recommended for spectroscopic determination of chlorophyll *a*.

3.2.2 Magnesium carbonate

Magnesium carbonate has often been added on the filters, with the idea of preventing acid degradation of chlorophyll. Experiments show that it has no positive effect but, on the contrary, adsorbs the degradation pigments. Its use is now discouraged.

3.2.3 Vacuum pressure

To avoid damaging cells during filtration, *vacuum* pressure should be limited. While Jeffrey *et al.* (1997) mention keeping residual pressure under the filter not lower than 0.5 atm, most users recommend that it be kept higher than 0.7 atm.

3.3 Storage of the Filters

Storage temperature and time are critical points, with chilling being of obvious importance. Storage at room temperature, even after freeze-drying, is not recommended because it results in extensive degradation of pigments.

With the availability of deepfreezers, storage at –18 °C to –20 °C is a very convenient, widespread practice that has been recommended in several handbooks. An increasing proportion of marine scientists now use a lower storage temperature for phytoplankton samples.

A systematic study by the SCOR Working Group 78 checked storage conditions for up to 11 months at various temperatures (+22 °C, –20 °C, –90 °C, and –196 °C). Pigment composition was assessed using HPLC. The main findings are summarized as follows:

- the lower the temperature, the longer the storage time can be; usual deep-freezing conditions (about –20 °C) are above the eutectic point of the cell fluid, allowing biochemical reaction to proceed in the concentrated residual medium;
- degradation products of chlorophyll *a* were always dominated by chlorophyllide *a* and chlorophyll *a*-allomers, but after 11 months they accounted for only a quarter of the chlorophyll decline; the resulting decrease in total pigment suggested production of colourless degradation end-products;
- pheopigments *a* were never produced during storage;

- a 'bound' pool of pigments (up to 20 %), not extracted by methanol in fresh filters, was freed by extended freezing.

Consequences of the above findings about storage of filters for subsequent spectroscopic measurement of chlorophyll *a* are essential. Indeed, since early degradation products have spectral characteristics close to those of chlorophyll *a*, the original value of chlorophyll *a* in the sample will not be severely affected. This condition can be met for short storage times. However, if further degradation occurs, predominantly colourless products may be formed and erroneous data will be obtained.

The SCOR Working Group 78 recommended that storage of pigments for periods up to one year was done by freezing at the temperature of liquid nitrogen (−196 °C). Storage at −18 °C to −20 °C was acceptable only up to one week. However, when considering chlorophyll *a* alone, experiments with a natural phytoplankton community yielded ~100 % recovery over at least 1 month. This agrees with the findings of several authors that chlorophyll *a* decreased by less than 5–10 % in a deepfreezer for up to eight weeks (see Mantoura *et al.*, 1997b).

Finally, for storage not exceeding several weeks, it may be recommended that filters for chlorophyll *a* and pheopigments *a* be stored at −20 °C. Use of ultracold freezers allows extended storage times.

3.4 Extraction of the Filters

Extraction of pigments from planktonic diatoms and naked flagellates is easy, but some algae are difficult to extract (e.g., armoured dinoflagellates, heavily silicified benthic diatoms, cyanobacteria, thick-walled green algae). Extraction of pigments from filters has given rise to numerous tests and procedures published in the literature. Various solvents have been used, with or without mechanical action (sonication or grinding), at various temperatures, and for various lengths of time. Not all of these extraction parameters are independent. It must be noted that the extracting solvent is necessarily the solvent in which spectroscopic measurements will be made.

The SCOR Working Group 78 considered six criteria for the extraction technique applied to phytoplankton:

- 1) extractability: extraction of all pigments should be complete, irrespective of the algae;
- 2) fidelity: the pigments should not be altered by the process (stability up to one day);
- 3) compatibility: the solvent must be compatible with the materials (especially for HPLC);
- 4) precision: replication should be satisfactory;
- 5) simplicity: the technique should be rapid, with few handling steps;
- 6) safety: solvent should have low toxicity and flammability; few transfers.

The SCOR Working Group 78 performed extensive trials (using HPLC for identifying the pigments) with four micro-algae extracted using seven solvents (in particular, acetone, methanol, dimethylformamide, and dimethylsulfoxide) and various treatments (soaking, grinding, sonication). They showed that complex interactions between solvent and treatment precluded a simple step-by-step optimization of the process.

For a detailed HPLC analysis of the pigments, it appeared that sonication in dimethylformamide (DMF) should be regarded as a reference extraction method, since it gave the best pigment recovery of all protocols, and fulfilled criteria 1)–5), above. Sonication in methanol appeared to be a satisfactory alternative. Therefore, the SCOR Group recommended methanol for routine HPLC measurements of field samples, considering that it is less harmful than DMF (this last assertion is somewhat questionable). Acetone was significantly less effective on the algae tested.

In the context of the determination of chlorophyll *a* and pheopigments as bio-indicators for natural communities of phytoplankton, a comparative assessment of the entire set of protocols, using HPLC as a reference method, was developed by the SCOR Group (Mantoura *et al.*, 1997a). Results obtained with protocols using grinding of filters in 90 % acetone (Holm-Hansen *et al.*, 1965; Lorenzen, 1967) matched those of HPLC for chlorophyll *a* and pheopigments *a*. This solvent was therefore validated for these pigments as biomarkers in routine field work. Moreover, in this solvent absorption peaks are narrower and extinction coefficients are larger and precisely determined. In addition, 90 % acetone has little toxicity.

Note that, if acetone is used, it is strongly recommended to grind the filters instead of sonicating or soaking overnight. In a glass homogenizer with a motor-driven teflon pestle, complete disruption of the filter is obtained in about 1 minute. Extraction time may be prolonged to 30–60 minutes after transfer into the centrifuge tubes kept tightly closed and protected from heat and light (Lorenzen, 1967).

4 SPECTROSCOPIC MEASUREMENTS

4.1 Choice of the Method

Spectrophotometry and fluorometry can be equally used for chlorophyll *a* and pheopigments *a* determination. However, spectrophotometry is less sensitive and therefore requires the filtering of a much larger volume of sample in oligotrophic areas. Modern high performance spectrophotometers measure low absorbances with a 10^{-4} resolution, which allows chlorophyll *a* determination down to $\sim 0.1 \text{ mg m}^{-3}$ in samples of about 1 litre, with a 5 cm light-path cuvette. Fluorometry must be used when the available volume of water is insufficient for reliable absorbance measurement. It should be noted that, unlike spectrophotometers, fluorometers have to be calibrated with chlorophyll standards.

There are two types of spectrophotometric methods suitable for routine use: trichromatic and monochromatic. *Trichromatic methods* have been developed in order to determine the three types of chlorophyll (*a*, *b*, and *c*) in the absence of degradation products. Absorbances must be measured at the three maximum wavelengths of the three chlorophylls, plus a blank wavelength, then a set of three equations is used to calculate the concentrations. *Monochromatic methods* have been developed to correct chlorophyll *a* for pheopigment *a*. Absorbances are measured at the red maximum (plus a blank wavelength) before and after acidification. It is assumed that acidification degrades all chlorophyll-like pigments into pheopigments by eliminating the magnesium ion from the tetrapyrrole complex. The drop in absorbance allows both chlorophyll *a* and pheopigment *a* to be calculated.

The classic fluorometric method for routine work is similar, in its principle, to the spectrophotometric monochromatic method. Fluorescence of the extract is measured at a unique wavelength before and after acidification, then concentrations of chlorophyll *a* and pheopigments *a* can be calculated.

A reminder that none of the spectroscopic methods corrects for chlorophyllide *a*. However, from method comparisons (see Section 3.4) and field data available in the literature, such interference does not appear to be a serious problem. Overestimating chlorophyll *a* by trichromatic equations, due to the presence of pheopigments, is certainly the major problem encountered in coastal and estuarine waters. Pheopigment-correcting methods can therefore be recommended in these areas. Using fluorometry, the presence of chlorophyll *b* may result, if a standard lamp is used, in significant overestimation of pheopigments *a*, thus underestimating chlorophyll *a* (this is due to the wavelength shift of chlorophyll *b*, under acidification, into a band of strong energy of the lamp). As a quality control rule, in order to validate data obtained with pheopigment-correcting methods, it is suggested to perform occasional controls using the trichromatic spectrophotometric equations (or even multi-wavelength spectrofluorimetry).

4.2 Spectrophotometry

4.2.1 Instrumental characteristics

Since the determination of chlorophyll relies on absolute absorbance values (no calibration), it requires high performance spectrophotometers. The bandwidth should not exceed 2 nm. Significant underestimation of chlorophyll *a* occurs with large bandwidths (Brown *et al.*, 1980). As long-path cuvettes are generally required to increase sensitivity, operators must make sure that the entire light beam passes through the extract. Low volume (thick-wall) cuvettes may produce erroneous data in spectrophotometers having very converging beams.

4.2.2 Trichromatic method

Four sets of trichromatic equations have been published, following improvements in the values of maximum absorption wavelengths and extinction coefficients. Coefficients are determined for pigments dissolved in 90 % acetone. Equations of Richards and Thompson (1952) are obsolete and should not be used. Those of Parsons and Strickland (1963) and SCOR-UNESCO (1966) can be used for chlorophyll *a* only. The equations of Jeffrey and Humphrey (1975) are the only ones recommended for the three chlorophylls.

Trichromatic measurements allow the presence of chlorophyll *b* to be detected, hence, its possible interference in the measurement of chlorophyll *a* using monochromatic methods. When chlorophyll *b* is low, one should obtain: $[\text{trichromatic chlorophyll } a] \cong [\text{monochromatic chlorophyll } a] + 0.6 \times [\text{pheopigments}]$.

4.2.3 Monochromatic (pheopigment-correcting) method

Monochromatic methods are recommended for chlorophyll *a* in coastal and estuarine waters. The correction equations for pheopigments have been published by Lorenzen (1967). They are suitable for pigments dissolved in 90 % acetone. A derived set of equations was subsequently established by Holm-Hansen and Rieman (1978) for methanol.

4.2.4 Specific points of the spectrophotometric procedure

The blank should be determined with care. It is intended to correct for background absorption and/or turbidity produced by the filters and any particulate matter. With soluble membrane filters, the contribution of the filter to the blank must be accurately determined. With glass fibre filters, centrifugation is critical for avoiding the transfer of fibres into the optical cuvette. The blank (750 nm) should be checked for stability over the time required for measuring the sample. Decreasing blanks denote the presence of particles. Transfer of the extract in the cuvette should not be done by pouring but by slow pipetting. Closed cuvettes reduce cooling due to evaporation, hence absorbance variability due to the Schlieren effect.

In terms of acidification methods, it has been shown (Moed and Hallegraeff, 1978) that the acid concentration should be well controlled, i.e., in the extract $[H^+] = 3$ millimole per litre, according to the procedure of Holm-Hansen and Rieman (1978). A very important point in acidification methods is to ensure that any acid residue has been thoroughly rinsed out of the optical cuvette before the next sample extract is introduced into it (otherwise, chlorophyll would be degraded and underestimated; any suspect excess of pheopigment may indicate such an eventuality).

4.3 Fluorometric Measurement

4.3.1 Fluorometer characteristics

Characteristics equivalent to those of the popular Turner, Sequoia model 111, model 112, or Designs model 10 filter fluorometers are suitable with red sensitive photomultiplier R446, light source F4T5BL (preferably to the standard F4T5B or F4T5D), excitation filter 430–450 nm (e.g., Corning CS-5-60), emission filter 650–680 nm (e.g., Corning CS-2-64).

It is important to note that any new setting or change to the optical design of the fluorometer will involve re-calibrating the instrument.

4.3.2 Fluorometric equations

Equations for chlorophyll *a* and pheopigments have been proposed by Holm-Hansen *et al.* (1965).

4.3.3 Specific points of the fluorometric procedure

Blank problems are similar to those encountered in spectrophotometry. The filter fluorescence blank must be evaluated when solvent-soluble membranes are used.

Calibration of the fluorometer is easily done with a solution of pure chlorophyll *a*. The true concentration is determined spectrophotometrically at 664 nm in 90 % acetone, using an extinction coefficient of $87.67 \text{ l g}^{-1} \text{ cm}^{-1}$ (Jeffrey and Humphrey, 1975). Calibration with algal extracts can also be done provided their chlorophyll *a* concentration is known. However, as the solution should be free of pheopigments, chlorophyll *b* and preferably chlorophyll *c*, this calibration is less reliable and not recommended for routine use.

Acidification conditions and precautions defined for spectrophotometry are also valid for fluorometry.

5 SUMMARY OF PRACTICAL CONDITIONS

OPERATION	MATERIAL	CONDITIONS
Sampling	opaque sampling bottle	
Sub-sampling	opaque bottle	optional: pre-filtration 100–150 µm
Temporary storage of water		protected from heat and light; max. one hour
Filtration	0.7 µm glass fibre filter (e.g., Whatman GF/F)	> 0.7 atm residual pressure; subdued light; remove large zooplankton from filter with forceps
Storage of filter	deepfreezer	–20 °C; maximum two months
Extraction of the filter	solvent: 90 % acetone; homogenizer with teflon pestle	chill; subdued light; grinding: ~1 minute; until analysis (within 1 hour), keep the chill extract in darkness
Centrifugation or filtration of the extract	graduated, stoppered tubes	
Measurement	- spectrophotometer (bandwidth ≤ 2 nm) - fluorometer - both	Lorenzen (1967); Holm-Hansen <i>et al.</i> (1965); calibration with pure chlorophyll <i>a</i> test (spectrophotometry): Jeffrey and Humphrey (1975)

6 ALTERNATIVE PROCEDURES

Extraction by soaking in 96 % ethanol instead of 90 % acetone has been recommended by HELCOM (Baltic Monitoring Programme, 1998). Unfortunately few papers on this procedure have been published in the international literature, and ethanol extraction was not tested by the SCOR Group 78. Therefore, ethanol cannot be generally recommended at present.

Direct fluorometric determination of chlorophyll *a*, after 90 % acetone extraction but without acidification, has been developed by Welschmeyer (1994); interference from chlorophyll *b* and pheopigments is eliminated but the latter are not measured. The method uses a classic filter fluorometer equipped with a specific combination of lamp and interference filters. The SCOR Group 78 did not test this method, but it is mentioned as an interesting development for routine assays after the recommended acetone extraction.

7 ACKNOWLEDGEMENT

This report was prepared by A. Aminot (IFREMER-Brest, BP 70, 29280 Plouzané, France) with contributions from the Chemical Oceanography Sub-Group of the Marine Chemistry Working Group.

8 REFERENCES

- Baltic Monitoring Programme. 1998. Manual of the Baltic Monitoring Programme, HELCOM.
- Brown, J.M.A., Dromgoole, F.I., and Guest, P.M. 1980. The effect of spectrophotometer characteristics on the measurement of chlorophylls. *Aquatic Botany* 9: 173–178.
- Edler, L. 1979. Recommendations for marine biological studies in the Baltic sea: Phytoplankton and chlorophyll. Working Group 9, The Baltic Marine Biologists publication No. 5. 38 pp.
- Holm-Hansen, O., and Rieman, B. 1978. Chlorophyll *a* determination: improvement in methodology. *Oikos*, 30: 438–447.
- Holm-Hansen, O., Lorenzen, C.J., Holmes, R.W., and Strickland, J.D.H. 1965. Fluorometric determination of chlorophyll. *Conseil International pour l'Exploration de la Mer, Journal du Conseil*, 301: 3–15.

- Jeffrey, S.W., and Humphrey, G.F. 1975. New spectrophotometric equations for determining chlorophylls *a*, *b*, *c*₁ and *c*₂ in higher plants, algae and natural phytoplankton. *Biochemie und Physiologie der Pflanzen*, 167: 191–194.
- Jeffrey, S.W., and Mantoura, R.F.C. 1997. Development of pigment methods for oceanography: SCOR-supported Working Groups and objectives. *In* *Phytoplankton pigments in oceanography: guidelines to modern methods*, pp. 19–36. Ed. by S.W. Jeffrey, R.F.C. Mantoura, and S.W. Wright. UNESCO, Paris, France.
- Jeffrey, S.W., Mantoura, R.F.C., and Wright, S.W. 1997. *Phytoplankton pigments in oceanography: guidelines to modern methods*. UNESCO, Paris, France. 661 pp.
- Lorenzen, C.J. 1967. Determination of chlorophyll and pheopigments: spectrophotometric equations. *Limnology and Oceanography*, 12: 343–346.
- Mantoura, R.F.C., Jeffrey, S.W., Llewellyn, C.A., Claustre, H., and Morales, C.E. 1997a. Comparison between spectrophotometric, fluorometric and HPLC methods for chlorophyll analysis. *In* *Phytoplankton pigments in oceanography: guidelines to modern methods*, pp. 361–380. Ed. by S.W. Jeffrey, R.F.C. Mantoura, and S.W. Wright. UNESCO, Paris, France.
- Mantoura, R.F.C., Wright, S.W., Jeffrey, S.W., Barlow, R.G., and Cummings, D.E. 1997b. Filtration and storage of pigments from microalgae. *In* *Phytoplankton pigments in oceanography: guidelines to modern methods*, pp. 283–306. Ed. by S.W. Jeffrey, R.F.C. Mantoura, and S.W. Wright. UNESCO, Paris, France.
- Moed, J.R., and Hallegraeff, G.M. 1978. Some problems in the estimation of chlorophyll *a* and pheopigments from pre- and post-acidification spectrophotometric measurements. *Internationale Revue der gesamten Hydrobiologie*, 63 (6): 787–800.
- Parsons, T.R., and Strickland, J.D.H. 1963. Discussion of spectrophotometric determination of marine plant pigments, with revised equations for ascertaining chlorophylls and carotenoids. *Journal of Marine Research*, 21: 155–163.
- Richards, F.A., and Thompson, T.G. 1952. The estimation and characterisation of plankton populations by pigments analyses. II. A spectrophotometric method for the estimation of plankton pigments. *Journal of Marine Research*, 21: 155–172.
- SCOR-UNESCO. 1966. Determination of photosynthetic pigments in sea water. UNESCO Monographs on Oceanographic Methodology, 1. Paris, France. 69 pp.
- Welschmeyer, N.A. 1994. A method for the determination of chlorophyll *a* in the presence of chlorophyll *b* and pheopigments. *Limnology and Oceanography*, 39: 1985–1992.

ANNEX 12: ACTION LIST

E. McGovern	Update the list of relevant certified reference materials for organic compounds for use in marine monitoring in advance of MCWG 2000.
D. Wells	Update the list of contaminants which can be monitored routinely based on a selection of OSPAR/ICES laboratories in advance of the MCWG 2000 meeting
G. Asmund	Act intersessionally as Chair of Trace Metals Sub-Group and for MCWG 2000.
J. de Boer	Act as Chair of the Organics Sub-Group for MCWG 2000 and in the intersessional period.
S. Carlberg	Act as Chair of the Chemical Oceanography Sub-Group for MCWG 2000 and in the intersessional period.
B. Jansson	Present a list of priority contaminants to be critically evaluated at the 2000 MCWG meeting and provide refs. of such lists available through the Internet.
P. Roose and M. Cleenman	Present a discussion paper on information on marine monitoring programmes
M. Leermakers, J.F. Chiffolleau + members of the Trace Metals Sub-Group	M. Leermakers to send information on estuarine transport of trace elements to J.F. Chiffolleau and other members of the group to enquire whether relevant information exists in their countries and if so send it to J.F. Chiffolleau who will present an updated note on the subject at the next MCWG meeting.
B. Pedersen	Invite an expert on information on estuarine transport of trace elements to give a presentation at the next year's MCWG meeting
D. Wells	Provide approx. 5 lots of two different fish samples through QUASIMEME to be used in a 2 nd round of interlaboratory study on TCPM and TCPMe
J. de Boer, P. Roose, M. Lebeuf and M. Haarich	Analyse these two fish samples for TCPM and TCPMe and deliver data to J. de Boer before 1 January 2000 for presentation at the 2000 MCWG meeting.
M. Lebeuf	Update 1998 paper on TCPM and TCPMe on fish and present information on TCPM and TCPMe in marine mammals from eastern Canada.
M. Lebeuf and M. Haarich	Analyse the sediment sample which was provided in 1998 for TCPM and TCPMe and report to J. de Boer before 1 January 2000.
J. de Boer	Present the results of the TCPM and TCPMe interlaboratory study.
D. Wells	Inform MCWG at its 2000 meeting about progress in the European project on the certification of PAH metabolites in bile.
J. de Boer, J. Klungsøyr and E. McGovern	Present the final results of the European MATT project
E. Evers and all members of MCWG	All members to send additional information on TBT to E. Evers by 10 April; E. Evers to review the note on TBT and submit it to ICES with a copy to the chair of MCWG
P. Roose and B. Jansson	Present results of a study on volatile organics in biota at the 2000 MCWG meeting
E. Evers	Present results of a Dutch study on the use of membrane systems

All members of the Trace Metals Sub-Group, Martin Bloxham	Send examples of the use of contaminant concentrations in biological media as environmental indicators to detect trends to Martin Bloxham, who will collate the data and prepare a discussion paper on the subject to the next MCWG meeting, including any relevant information on seabird egg monitoring in UK and Ireland.
Gert Asmund and G. Audunsson	Gert Asmund to contact Jørgen Nørrevang Jensen at the ICES Secretariat concerning permission to use ICES data and with the view of writing a paper on the supplementary work to the Icelandic cod study together with J. Nørrevang Jensen and G. Audunsson.
All MCWG members	Send any available information on contaminants in deep-water fish to Martin Bloxham, who presently is preparing a report on the subject
Mikael Krysell and Stig Carlberg (nutrients) and J. Klungsøyr, P. Roose, P. Woitke and M. Cleemann (organics and trace metals)	Prepare a discussion paper on the QA methods used in laboratories involved in marine monitoring for the next meeting.
Chair of the COSG	Invite a person to give a plenary presentation on ecological modelling at the next MCWG meeting and together with the Chair of MCWG investigate the possibilities to arrange a joint session with the WGSSO to discuss the use of chemical data in numerical modelling and possible implications for future work in modelling and field sampling programmes

ANNEX 13: RECOMMENDATIONS

MCWG recommends that the regulatory authorities look for resources to carryout studies on 'new' contaminants or seriously consider to restructure their monitoring programmes in order to make resources available for studies on 'new' contaminants.

Recommendation 2

MCWG recommends that the paper on polycyclic musk compounds by G. Rimkus should be forwarded to ACME after minor technical revisions and appended to its report.

Recommendation 3

MCWG recommends that the paper on PBBs and PBDEs by J. de Boer, K. de Boer and J. Boon, after minor technical revisions, should be forwarded to ACME for information.

Recommendation 4

MCWG recommends that the paper on TBT by R. Law and E. Evers, after minor technical revisions, should be forwarded to ACME for information and appended to its report

Recommendation 5

MCWG recommends that the revised QA technical notes on dissolved oxygen, hydrogen sulphide, pH and alkalinity should be reviewed by ACME with a view to accepting them for transmission to HELCOM with a recommendation that they be published in the COMBINE QA guidelines of HELCOM.

Recommendation 6

MCWG recommends that the paper on chlorophyll determination should be forwarded to ACME for information and appended to its report with the possible inclusion of new information.

Recommendation 7

The Chair of the MCWG (B. Pedersen) should made the necessary preparations to hold the next MCWG meeting at ICES Headquarters. The meeting is scheduled to take place from 28 February to 3 March 2000 to:

- a) review and endorse the updated list of contaminants which can be monitored on a routine basis;
- b) review information on QA systems used in laboratories involved in marine monitoring and report the outcome;
- c) review progress on the application of high temperature techniques for the determination of total nitrogen in sea water ;
- d) review information on experience in the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables;
- e) review a comparison of spectrophotometric and volumetric alternatives for quantification in the Winkler method for the determination of dissolved oxygen in sea water and report on the outcome;
- f) review the use of chemical data in numerical modelling and the possible implications for future work in modelling and in field sampling programmes (requires a joint session with the WGSSO);
- g) review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring;
- h) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations;
- i) review information on marine monitoring programmes;
- j) review information on estuarine transport of trace metals and report on the outcome;
- k) review new information on TCPM and TCPMe in fish and in marine mammals from eastern Canada;
- l) review information on the results of the TCPM and TCPMe interlaboratory study, second phase;
- m) review information on volatile organic contaminants in biota;

- n) review new information on the analysis of PAH metabolites in bile and critically review the robustness of the techniques available and the comparability of their results;
- o) review information on the use of membrane systems;
- p) review new information on the use of contaminant concentrations in biological media as environmental indicators to detect trends;
- q) review a paper on supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various cofactors;
- r) review new information on the EU-MATT programme on monitoring, analysis and toxicity of toxaphene.