Marine Habitat Committee

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REPORT OF THE

MARINE CHEMISTRY WORKING GROUP

Stockholm, Sweden
2–6 March 1998

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1 OPENING OF THE MEETING

The Chairman, Dr B. Pedersen, opened the meeting of the Marine Chemistry Working Group (MCWG) at 10.00 hrs on 2 March 1998. Mr Stig Carlberg from SMHI and Mrs Ulla Britta Fallenius, Head of the Department at the Swedish Environmental Protection Agency, welcomed the Working Group on behalf of the Institute and the Agency, respectively.

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

2 ADOPTION OF THE AGENDA

The terms of reference for this meeting of the Marine Chemistry Working Group [ICES C.Res.1997/2:12:2] were to:

a) finalise guidelines for monitoring PAHs in biota, in relation also to the guidelines for sediments agreed in 1997 [OSPAR 1998/1.1];

b) review and assess data on concentrations of CBs, especially non-*ortho* and mono-*ortho* CBs, in marine mammals, as a contribution to the OSPAR Quality Status Report (with WGBEC, WGMMHA, and WGEAMS) [OSPAR 1998/3];

c) review the outcome of the Icelandic study on the influence of parameters such as fish size, liver size and fat content of the liver on the concentration of trace metals;

d) review the report on the new ICES data collection system covering not only analytical information but also sampling, sample handling and storage information;

e) review and report on an updated paper on organotins;

f) review the updated list of contaminants that can be monitored on a routine basis and transmit the list to ACME;

g) review and report on the progress of the second phase of the joint study on PCBs in fish eating mammals;

h) review and report on the progress on intersessional work on variance components in seabird egg analysis and the use of seabird eggs in national programmes (with WGSAEM);

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

j) review the report on synthetic musk compounds in the marine environment;

k) review information on the problems and limitations in the analysis of dissolved concentrations of highly hydrophobic compounds and bioconcentration in mussels from the Dutch Mussel Watch monitoring programmes;

l) review information on modelling PCB accumulation in the Seine estuary;

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

n) review the information on the fate of nutrients in estuaries and on experience in the use of automated in situ chemical oceanographic systems for observation of chemical variables;

o) review quality assessment procedures for nutrient and oxygen data in use in individual institutes;

p) advise on the need to standardise nutrient and oxygen units to $\mu mol\ kg^{-1}$.

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

MCWG was asked at the meeting by the Chairman of ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), if it was possible for MCWG to review some technical notes/annexes to the guidelines prepared by SGQAC. MCWG agreed to incorporate this item in their agenda.

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

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

Chemical Oceanography Subgroup: S. Carlberg (Chairman), A. Aminot, L. Føyn, M. Krysell, D. Mackey, K. Mäkelä, K. Nagel, J. Ólafsson, O. Vagn Olsen.

Trace Metals Subgroup: G. Asmund (Chairman), G. Audunsson, M.Bloxham J.F. Chiffoleau, J.R. Larsen (also in Organics and Chemical Oceanography Subgroup), K. Parmentier, B. Pedersen, P. Woitke.

Organics Subgroup: J. Klungsøyr (Chairman), E. Andrulewicz, A. Bignert A. J. Biscaya, J. de Boer, M. Cleemann, E. H.G. Evers, M.Haarich, B. Jansson, R.J. Law, M. Lebeuf, E. McGovern, T. Nunes, P. Roose, D.Schulz-Bull, D. Wells.

3 REPORT OF THE 85TH ICES STATUTORY MEETING

The Chairman informed the participants that all of the tasks requested for consideration by MCWG at the 1997 ICES Annual Science Conference (85th Statutory Meeting) had been incorporated into the draft agenda. MCWG was informed by the ACME Chairman, Stig Carlberg, about the new structure of ICES. The reorganization of the parent Committees of the working groups was one of the important changes. Almost all working groups should in the future belong/refer to one of the ICES scientific committees. There were several reasons for the restructuring, one was to strengthen the scientific side of the work of the working groups.

In future, MCWG will report to the Marine Habitat Committee instead of to the Advisory Committee on the Marine Environment as in previous years.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR and HELCOM

Official requests from the regulatory Commissions have been included in the agenda.

For OSPAR, guidelines for monitoring PAHs in biota and data assessment on concentrations of CBs, especially non-*ortho* and mono-*ortho* CBs, in marine mammals, are requested.

4.2 Intergovernmental Oceanographic Commission (IOC)

MCWG discussed different initiatives to improve the contacts between ICES MCWG and the IOC, as there was a general feeling that the two organizations had several areas of interest in common. It was decided, that all members should try to seek information about IOC and report back at the next MCWG meeting. Already at the meeting possible information about activities of common interest were investigated through the web. Among the IOC programmes that could be relevant to MCWG, at least the Marine Pollution Research and Monitoring (GIPME/MARPOLMON) seems to be particularly interesting. The objectives of GIPME are:

1) authoritative evaluations of the state of the marine environment at both regional and global levels;
2) identification of the requirements for measures to prevent, or correct, marine pollution;
3) procedures for assessing and improving compliance and surveillance monitoring of conditions and effects in the marine environment.

The Programme is developed by a Scientific Committee and is conducted by three Expert Scientific Groups. These groups are the Group of Experts on Methods, Standards and Intercalibration (GEMSI), the Group of Experts on the Effects of Pollutants (GEEP) and the Group of Experts on Standards and Reference Materials (GESREM). As several of these activities overlap what is going on in MCWG, further information on the activities within GIPME has been requested from Dr G. Kullenberg, the Executive Secretary of IOC.

4.3 QUASIMEME

Dr D. Wells briefly informed about QUASIMEME II, the successor of QUASIMEME I. For details about the QUASIMEME II project, see Annex 3.

The QUASIMEME Laboratory Performance Studies (LPS) became available to all laboratories worldwide from June 1996 and has been open to all organizations making chemical measurements in the marine environment. The programme

for the first year of QUASIMEME, from June 1996 to May 1997, was designed specifically to support those chemical measurements required for the international marine monitoring programmes of the Oslo and Paris Commission (OSPAR), the Helsinki Commission (HELCOM) and the Mediterranean Pollution Monitoring and Research Programme (MEDPOL) and national programmes, the National Monitoring Programme (NMP) of the United Kingdom Marine Pollution Management and Monitoring Group (UKMPMMG). In doing so, the needs of many other national and individual programmes were also served.

During the first year, there were four rounds. Each assessment has been completed and all participants have received a personal report with their own data from each round.

The majority of sediment and biota samples were provided as natural or processed unspiked homogeneous samples.

The seawater samples for each group of determinands were prepared to cover the range and concentrations of estuarine, coastal and open water sites.

The LP Studies were designed to support the quality management of participating chemical laboratories and assist in the improvement of the quality of measurements. The assessments provided by QUASIMEME also complement internal laboratory QA, and provide a support to laboratory accreditation in addition to the QA support to the environmental monitoring programmes. QUASIMEME now has a presence in 27 countries.

The new scheme for the second year is now ready. Leaflets as well as a poster about the programme are available and could be ordered by contacting Dr D. Wells.

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

The status of the QUASH project was presented by the coordinators 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. At present many of the guidelines or recommendations for a QA/QC programme related to sample handling or cofactors have not been verified and documented by interlaboratory trials.

The programme consists of six work packages (WP):

1) sampling and preservation of nutrients in sea water [Coordinator: Mr Stig Carlberg (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: Dr Spyros Kornilios (IMBC, Crete)];
5) preparation of test material, laboratory and field performance studies [Coordinator: Dr Wim Cofino/Freek Ariase (IVM, NL)];
6) laboratory and field performance studies [Coordinator: Dr David Wells (Aberdeen, UK)].

WP1: The present status of sampling and preservation of nutrients in sea water has been evaluated through a questionnaire sent to the National Coordination Centers (NCCs) which participate in the programme and some other relevant laboratories, and also through a literature study on preservation methods. A practical workshop has been held at the Spanish Oceanographic Institute in Tenerife with participants from the NCCs. The workshop included the following critical steps: Sampling of sea water, cleaning of bottles for subsampling, subsampling from the hydrocast bottles, pretreatment (filtration/centrifugation), preservation, storage, and transportation of sea water samples. A verification study of preservation methods has been initiated.

WP2: An interlaboratory study on the determination of total lipids has been organized. In this study, a new method for the determination of total lipid content is compared with existing methods. The study will be evaluated and the results presented at a Workshop for WP2 and 3, on lipid determination and sampling in October in Galway, Ireland.

WP3: The present status of sampling and sample handling has been evaluated through a questionnaire sent to the NCCs. Samples for an interlaboratory study, especially designed to determine the main sources of error due to differences in

homogenisation procedures, have been sent to the NCCs. The results are planned to be presented at the workshop in Ireland, where also other critical steps in sampling and sample handling will be covered.

WP4: The present status of sample handling and cofactors in relation to normalization procedures for sediments has been evaluated through a questionnaire sent to the NCCs. An interlaboratory study, using wet sediments, has been organized to study the sample handling and sieving procedures. A workshop is planned to be held at IMBC, Crete, where the outcome of the interlaboratory study will be discussed, as well as other relevant topics.

WP5/WP6: Relevant test material has been prepared and tested and QUASH database has been developed to support the other WPs. A QUASH Launch workshop has been held in Groningen, NL in 1997.

4.5 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.

Mr Stig Carlberg, the Chairman of ACME, gave a short presentation under this agenda point of the work of ACME and the important role of the working groups. He especially raised a problem concerning the future work of ACME. A lot of important material is generated to the marine community thorough the work of ACME and/or the working groups, which is not especially asked for and paid by the OSPAR and Helsinki Commissions. This can in the long term generate a financial problem for ACME/ICES. If, however, ACME only dealt with questions raised (and paid for) by the Commissions, this would naturally limit the agenda/work of ACME, but could at the same time make it less attractive for scientists to participate in the work of ACME including the WGs in the future. The members of the MCWG thought it could be useful to contact their national delegates to ICES to make them understand that it is a good idea that ACME also in the future handles other tasks than those given by the Commissions.

7 PLENARY TOPICS

7.1 Outcome of the AMAP Programme (Arctic Monitoring and Assessment Programme)

Marianne Cleemann, Gert Asmund and Jarle Klungsøyr gave presentations on the outcome of the first period of AMAP. After a short presentation of the AMAP programme, Marianne Cleemann concentrated her presentation on the persistent organic pollutants found in sediments and biota in Greenland. 484 samples of mussels, fish, birds and seals were collected in 1994 and 1995 at four different locations in Greenland, three at the west coast and one at the east coast. The analyses performed included PCBs, HCB, HCHs, Dieldrin, DDTs, chlordanes, toxaphenes and PAHs, determined in all samples or in a part of them. The results showed levels comparable to or slightly lower than values reported from other Arctic regions. For all species analyzed, PCB and DDT levels were found higher at the east coast compared to the west coast of Greenland. Organochlorines were found to concentrate in animals of higher trophic levels to different degrees, while PAHs showed the highest levels in shorthorn sculpin, the lowest in seal blubber.

Gert Asmund presented new information concerning mercury (Hg) in the Greenland environment. The Hg concentration in blood from inhabitants living in East Greenland was up to ca. 12 times higher than the concentration of Hg in blood from people living in Denmark. There was also a clear correlation between the blood concentration and the number of seal meals per week. Especially alarming was the high concentrations found in new-born children. The Hg concentration has also been measured in fish livers, blue mussels, reindeers and marine sediments.

The conclusion was that Hg tends to increase towards the north in slow-growing organisms and decrease towards the north in items influenced by rain water. Hg also accumulates from "normal" values in fish to very high values in mammals including man. Anthropogenic inputs might be seen in marine sediments.

Jarle Klungsøyr concentrated his presentation on PAHs in Barents Sea sediments. The samples were collected in 1992–1993 from a total of 206 stations using a box corer. PAHs were analysed by GC/MS in two separate grab samples from each of 139 locations together with GS and TOC for characterizing the sediment. A principal component analysis of the PAH concentration data was done and it was found that the main features could be described by three components. The conclusion was that the highest levels of petrogenic PAHs were found around Svalbard and the highest levels of combustion PAHs were found in the central parts of the Barents Sea. The perylene concentrations were quite high in some of the samples, probably caused by both natural and anthropogenic sources.

The AMAP programme will continue in the coming years.

7.2 Use of Seabird Eggs in Monitoring Programmes

Anders Bignert gave a presentation on the use of seabird eggs in monitoring programmes. Bird eggs seem to be an appropriate matrix for temporal trend analysis of mercury and organochlorine contaminants and possibly other organic compounds, provided that they can be collected from a more or less stationary population. Bird eggs in themselves represent rather well-defined sampling units, relative to other biological matrices, in that sex, physiological, nutritional and reproductive status are known. They reflect the status of the mother, and evidently the mothers are healthy, active, reproductive females. Some organic compounds are present at low concentrations in bird eggs, while others are degraded either by the birds themselves or by their prey. This may apply for instance to PAHs, for which fish have a well-developed capacity for metabolism. The bioconcentration factor for mercury in guillemot eggs is fifteen times higher than in herring but the same as for other metals such as chromium, copper nickel and lead. For contaminants which are found at elevated concentrations, such as chlorobiphenyls, the within- and between-year variances seem to be low compared to other biological matrices as demonstrated in the time-series based upon guillemot eggs from St. Karlsö in the Baltic Sea. Additional advantages include the fact that birds' eggs are sufficiently large to permit individual analyses, have a relatively high and stable fat content, and that they allow integrated bio-effect monitoring of shell parameters (in relation to phenomena such as eggshell-thinning due to DDT). Experience with spatial studies based upon the analysis of birds' eggs is sparse, and it may prove difficult to find bird populations in all areas which do not migrate and so are representative of a well-defined area. The target bird population must also be dense and stable, thereby allowing repeated sampling without depleting the population. A recent development in this area is the trilateral monitoring to be undertaken by Denmark, Germany and the Netherlands involving the analysis of common tern eggs from the Wadden Sea, and this will provide further useful information on the utility and practicality of this approach.

7.3 Impact of the 1995 Rhine Overflow on the Skagerrak and Kattegat

Mikael Krysell gave a presentation the impact of the 1995 Rhine overflow on the Skagerrak and Kattegat.

In late 1994 and early 1995 central Europe was exposed to unusually high precipitation. As a result of this, the flow of surface water became much higher than average in many parts of the continent. In January 1995 the flow in the Rhine and Meuse system peaked at around five times the average flow for the season, consequently transporting more particles and potentially more contaminants, nutrients, etc., to the sea than usual.

The first indications of large-scale impact on the sea were observed at the German island of Sylt in early February. The river water (RW) was then transported northwards along the western Jutland coast of Denmark with the Southern Jutland Current. Approximately two months after the flow peak in January, the water reached the Skagerrak/Kattegat area.

The fate of the RW when entering the Skagerrak/Kattegat was followed during several cruises with Swedish, Danish and Norwegian vessels. Apart from the regular monitoring cruises in the area, a few additional major cruises were carried out to follow the RW. The main stream of RW entered the Skagerrak cyclonic gyre, but approximately 20 % entered the Kattegat as intermediate or deep water. The salinity of the RW entering the Kattegat was 30–32, whereas the surface salinity of the Kattegat is 21–28, hence the penetration of the RW into the underlying water layers.

During the investigations some very high nutrient concentrations were observed in the RW. For example, in the period 14–17 March, nitrate concentrations of 71 µM were observed outside Thyborøn (S = 28), and 50 µM was found at Skagen (S = 29.5). These are the highest concentrations ever observed in these areas. During the two months of transport from the southern North Sea to the Skagerrak only physical processes (dilution) affected the nutrients. Due to the very high turbidity of the water (Secchi depths normally < 1 m) no measurable production took place in the RW. In the Jutland current the low visibility was maintained by high flow velocity (25–20 cm sec^{-1}), shallow depth and

closeness to sandy sea bottoms and shores. When the water entered the much deeper Skagerrak the flow velocity decreased rapidly, the water cleared, and the production could start.

In mid-April the inflow had ceased, and there were virtually no signs of RW in the surface of the Skagerrak/Kattegat. However, the deeper water layers were affected, and some of the intermediate water had penetrated into fjords in the region. Calculations show that the annual nutrient supply to the Skagerrak/Kattegat increased by approximately 15 % due to a two-week overflow of the river systems in the southern North Sea. At normal flow conditions, the transportation time to the Skagerrak/Kattegat is approximately 6 months, now it took only 2 months to reach this area. The extra supply of nutrients had some, but no major, impact on primary production and chlorophyll *a* concentrations.

7.4 Skeidararhlaup Glacial Outburst, November 1996

In early October 1996 a volcanic eruption broke out under the Vatnajökull glacier in Iceland. Melt water accumulated in the Grimsvötn subglacial Calder and burst out on 5 November flowing across a glacial sand plain out to the sea. In about 30 hours, 3.6 km^3 of mud-loaded water entered the sea and the plume advanced more than 30 km offshore. Jon Olafsson described this event and oceanographic work, the distribution of freshwater and suspended matter and results from studies of nutrient concentrations. The flood water had about 100 times higher silicate concentrations than the coastal sea water but the concentration of oxidized nitrogen species was practically 0 and the phosphate concentration was lower than that of the coastal sea water. No adverse biological effects of the flood have been observed.

7.5 ICES Environmental Data Centre: Past, Present, and Future

Jan René Larsen, the ICES Environmental Data Scientist, gave a short presentation on the structure of the present ICES Environmental Data Centre. He also gave the historical background for its creation as well as some ideas of what could be done in the future. The present database contains data sets from many areas, such as contaminant concentration data in sediment, sea water and biota samples; oceanographic data such as salinity, temperature, oxygen and nutrient data (the first data in the Oceanographic Database are from 1902); and biological and biological effects data sets. The database is constantly improved, e.g., through the development of data reporting formats and data entry/data screening software programs.

The data have been used in many assessments of the marine environment, especially for the OSPAR and Helsinki Commissions.

More information about the ICES Environmental Data Centre and a demonstration of the database are presented on the ICES website (http//www.ices.dk/env).

7.6 Sea Empress Oil Spill: Impact on Fisheries and Marine Life Revisited

In 1997 Robin Law presented the results of the monitoring undertaken during the first year following the oil spill from the *Sea Empress* in Wales in 1996. At MCWG98 he presented an update of the final phase of the study, as assessment of the shellfish monitoring data had revealed aspects of particular relevance to other PAH monitoring studies and so of general interest to the members. Principal component analysis of the PAH data for bivalve molluscs (cockles, mussels and oysters) had revealed the presence of a seasonal cycle in combustion-derived PAH concentrations unrelated to the effects of the oil spill. Concentrations of benzo[*a*]pyrene, for example, showed minimum concentrations in summer (August) and maxima in winter (March). This seemed to result from a combination of increased inputs during winter, and progressive storage of lipids within the animals during the autumn as they prepared for spawning in the spring. As PAHs are lipophilic then they would be expected to be stored with the lipids (as the capacity of molluscs to metabolise them is poor) and released with the gametes at spawning. Rapid growth in the post-spawning period would reinforce the fall in concentrations, leading to the summer minimum. In order to make temporal and spatial comparisons in monitoring studies it is therefore of paramount importance that all samples are collected at the same time of year, preferably in the first two months of the year before animals spawn. The study reported that at two sites in Milford Haven the concentrations of benzo[*a*]pyrene ranged from essentially zero to 20–50 $\mu g\ kg^{-1}$ wet weight—hardly a trivial difference. Similar cycles could occur for other lipophilic contaminants, but they have not been investigated so far.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

For the sake of clarity, the outcome of the discussions on topics requested by ACME will be presented in Section 8.1. Then, additional items discussed in the Subgroups will be dealt with in Sections 8.2 to 8.4, below.

8.1 Topics Requested by ACME

8.1.1 Finalise guidelines for monitoring PAHs in biota, in relation also to the guidelines for sediments agreed in 1997 [OSPAR 1998/1.1]

The Organics Subgroup considered the draft paper 'Guidelines for the determination of polycyclic aromatic hydrocarbons (PAHs) in biota' prepared by Jarle Klungsøyr and Robin Law. Following a short presentation of the paper by Jarle Klungsøyr, the subgroup discussed various aspects of the document. The comments provided to the authors were mainly on the incorporation of more detailed technical information and the addition of the advantages and drawbacks of the methods or techniques that were reported.

Jarle Klungsøyr agreed to prepare by the end of March 1998 a revised version of the draft paper which incorporates the recommendations of the Organics Subgroup. The document will be circulated by e-mail to the members of the Organics Subgroup, and they agreed to return comments within 14 days of receipt of the revised draft (i.e., by mid-April).

MCWG recommended that the final version incorporating all of the comments be forwarded to ACME 1998 and included as an annex to the 1998 ACME report. It is appended as Annex 4.

8.1.2 Review and assess data on concentrations of CBs, especially non-*ortho* and mono-*ortho* CBs, in marine mammals, as a contribution to the OSPAR Quality Status Report (with WGBEC, WGMMHA, and WGEAMS) [OSPAR 1998/3]

This request relates to a number of issues and questions regarding environmental problems raised within the framework of the OSPAR Joint Assessment and Monitoring Program (JAMP). One of these questions related to the potential harm caused by non-*ortho* and mono-*ortho* CBs to marine living resources. Norway volunteered to act as lead country for this task, and to send a questionnaire to the participating countries requesting information about levels of these compounds. However, only a limited amount of information was gathered via the questionnaire and it was assumed that more information could be obtained. ICES was contacted for this purpose, which resulted in an e-mail message sent by R. Law (via the MCWG mailbox) prior to this meeting asking MCWG members to forward information concerning CBs in marine mammals to the ICES Environmental Data Scientist for compilation. Although this has yielded some additional information, the group still feels that additional data are available. An action was therefore formulated for all members of the group to send additional data to the Data Manager at ICES by 1 April 1998. M. Haarich volunteered to conduct a literature search of the ASFA database, and to make this reference list available to ICES. M. Lebeuf agreed to contact colleagues in North America for additional information, as currently few data are available from this region although it is known that many studies have been conducted.

8.1.3 Review the outcome of the Icelandic study on the influence of parameters such as fish size, liver size, and fat content of the liver on the concentration of trace metals

G. Audunson presented a preliminary paper containing many new and interesting observations about cod liver. The paper describes a three-year study on trace elements in Icelandic cod liver. 454 cod were analysed for several trace elements, liver size, fat and water content, and nitrogen and phosphorus levels in the liver. The main conclusions were:

Fat and water content and trace element concentrations are very much dependent on liver size up to 100 grams. Livers heavier than 100 grams are relatively uniform in composition with respect to macro constituents and many trace elements. Fish size does not influence the composition of cod liver.

The Icelandic study shows how to perform the trace element normalization for Icelandic cods. For other areas and fish, it must be checked as to whether the same normalization procedures can be applied.

The subgroup decided to revise the paper by e-mail between its members during the last 3 weeks of March, so the revised paper could be appended to the MCWG report as Annex 5.

8.1.4 Review the report on the new ICES data collection system covering not only analytical information but also sampling, sample handling and storage information

A draft paper was provided by Gert Asmund including a list of additional information that it would be desirable to collect in the new ICES data collection system. The paper was discussed and some amendments were made by the subgroups, including:

1 analysis of reference materials: space is available to allow laboratories to insert information on the means and standard deviations of results of more than one laboratory and certified reference material;

2 detection limits: the term 'detection limit' will be changed to 'limit of determination', and space will be created so that laboratories can enter their own definition of their limit of determination;

3 lipid determination: three specifications were given for lipid determinations;

   3.1 total lipid determination according to Bligh and Dyer or based on a Bligh and Dyer method,

   3.2 extractable lipid determination (Soxhlet), and

   3.3 other method (to be specified);

4 analytical methods used: it was agreed that the method codes from the QUASIMEME data collector should be copied so that they can be used in the present document;

5 should be possible to specify more than one intercomparison exercise, all results from an intercomparison should be reported with submitted data.

The ICES Environmental Data Scientist, J.R. Larsen, took note of the comments made by the Subgroups at the meeting and will modify the draft paper accordingly. The modified paper is attached as Annex 6.

8.1.5 Review and report on revised organotins paper

At the 1996 MCWG meeting in Lisbon a paper on organotins prepared by The Netherlands was presented. As a follow-up to that paper, it was the intention to prepare an updated version which also contained information from other countries. This suggestion was discussed, but it was felt that to expand the Dutch text in this way would make it too unwieldy. Instead it was agreed that MCWG should prepare a review note summarizing current knowledge about concentrations of butyltins, any apparent trends and effects, with particular emphasis on aspects related to their continued use in antifoulants on large vessels. The note would concentrate, therefore, on harbours, ports and shipping lanes. Robin Law agreed to prepare this review note for MCWG99, and Erik Evers kindly offered to assist in this task. R. Law will also contact J. Boon of WGBEC for relevant information. All Subgroup members are asked to forward relevant information to R. Law before 1 June 1998, so that as much information as possible can be incorporated in the review note.

8.1.6 Review the updated list of contaminants that can be monitored on a routine basis

The overall performance within the QUASIMEME 2 programme for given parameters was used as an indicator of the ability of laboratories to perform routine monitoring. A graphical and tabular presentation prepared by D. Wells outlined the performance of laboratories which participated in the QUASIMEME scheme in the exercises between June 1996 and December 1997 for analysis of CBs, organochlorine pesticides and metals in biota, metals, PCBs, OCPs and PAHs in sediments, and trace metals and nutrients in sea-water.

The three Subgroups used the information presented in slightly different ways when evaluating the performance of the laboratories.

Nutrients

In the period mentioned above, a total of six intercomparison samples, covering a range of concentrations, had been distributed for the analysis of dissolved ammonia, nitrite, phosphate, silicate, total nitrogen, total phosphorus, and total oxidized nitrogen (nitrate + nitrite). The intercomparison samples had covered both low salinity (estuarine) water and oceanic water. For either group, up to 40–50 laboratories had returned results. The overall assessment of these groups of laboratories can be taken as an indication of their capacity to monitor nutrients. It must also be realised that these groups do not represent the ICES community as a whole, for which comparable material is not available.

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 6 at the most. It indicates that for nitrite, silicate and total oxidized nitrogen there were only a few problems encountered, although some individual laboratories may have returned unsatisfactory results. Similarly, it indicates that for total phosphorus and total nitrogen problems were more frequent, although some laboratories may have returned satisfactory results.

The laboratory performance with respect to the nutrients can be regarded as encouraging, as it must be realised that a situation where all laboratories show simultaneously good performance is unlikely to materialize.

Table 1. Summary assessment of laboratory group performance in QUASIMEME nutrient exercises, June 1996–December 1997.

Determinand	Medium	[1]Range of assigned values (µmol l^{-1})	[2]Range of ± Target Bias (%)	[3]Range of between-lab. CVs (%)	[4]Range for % No. obs. with |Z| < 2	[5]Satisfactory performances/ total rounds
Ammonia	low salinity water	5.56–24.29	7.03–10.5	11–16	71–92	5/6
Ammonia	saline water	0.90–22.1	7.13–33.88	13–64	34–84	4/6
Nitrite	low salinity water	1.02–6.37	6.39–8.52	5–8	89–94	6/6
Nitrite	saline water	0.42–1.77	7.42–11.97	4–16	80–92	6/6
Phosphate	low salinity water	1.56–6.54	6.38–7.60	4–16	62–92	5/6
Phosphate	saline water	0.05–1.65	7.52–60.59	5–76	67–93	5/6
Silicate	low salinity water	4.83–21.86	6.46–7.15	7–10	78–92	6/6
Silicate	saline water	1.79–17.20	6.58–11.59	7–21	65–89	6/6
Total-N	low salinity water	24.73–65.05	6.38–7.01	8–22	76–88	5/6
Total-N	saline water	8.76–51.60	6.48–7.21	9–23	53–85	3/6
Total-P	low salinity water	1.56–6.62	6.38–7.61	6–21	48–89	4/6
Total-P	saline water	0.20–1.78	7.41–18.76	7–44	63–92	4/6
Total oxN	low salinity water	15.86–36.27	6.69–7.58	5–7	60–89	6/6
Total oxN	saline water	1.19–22.41	7.12–27.06	3–16	83–95	6/6

[1]Range of assigned values for six rounds of the QUASIMEME scheme. The determined assigned values are only indicative.
[2]Target 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.
[3]Range of between-laboratory coefficients of variance (CVs) (%) over six rounds.
[4]Range of the number of laboratories achieving the set QUASIMEME standard of |Z| < 2 (expressed as %).
[5]Number 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 × 2) > 0.

Trace Metals

The QUASIMEME data represent six concentration levels of trace metals in sediments and in biota tissues (cod muscle, cod liver, mussel). Unfortunately, there was not enough data to evaluate the outcome of intercomparison exercises of trace metals in sea water.

The table below gives the minimum trace metal concentrations in sediments and biota for which the majority of the laboratories achieved |Z|-scores < 2. Generally, most of the laboratories participating in QUASIMEME LPS do not have problems to analyse concentrations down to the values in the table and, therefore, are able to analyse trace metals in sediments and biota on a routine basis. However, the QUASIMEME results demonstrate that only a limited number of laboratories can be expected to produce comparable data for sandy sediments containing low amounts of trace metals, as one needs special experience to analyse the very low concentrations. The Trace Metals Subgroup recommends the inclusion of additional elements in the QUASIMEME LPS, as mentioned in the MCWG-Report 1997 (Si, Be, Tl, Sn, Sb, Ag, Se, MMHg, and organotin compounds in sediments; Ag, Se, Sb, Fe, MMHg, As compounds and organotin compounds in biota). For trace metal determinations in biota, the laboratory performance for some metals seems to be dependent on the tissue type.

Table 2. Lowest concentrations of trace metals in sediments and biota which can be monitored on a routine basis by the majority of laboratories (outcome of QUASIMEME LPS, Round 6, 8, and 10).

Metal	Sediments	Biota
Zn	75 mg kg^{-1}	≤ 4.6 mg kg^{-1}
Cd	340 µg kg^{-1}	depends on the tissue for cod muscle 5.2 µg kg^{-1} for cod liver 12 µg kg^{-1}
Pb	40 mg kg^{-1}	problems for the majority of the labs, even at 1 mg kg^{-1}
Cu	21 mg kg^{-1}	≤ 0.3 mg kg^{-1}
Cr	28 mg kg^{-1}	problems for the majority of the labs, even at 2 mg kg^{-1}
Ni	23 mg kg^{-1}	depends on the tissue, for cod liver and cod muscle 0.1 mg kg^{-1}
As	6 mg kg^{-1}	≤ 1.3 mg kg^{-1}
Hg	120 µg kg^{-1}	≤ 8 µg kg^{-1}
Al	- no concentration dependence of the percentage of successful labs	-
Mn	≤ 850 mg kg^{-1}	-
Fe	≤ 2.8 %	
Li	≤ 35 mg kg^{-1} (5 labs only)	
Sc	≤ 7.6 mg kg^{-1}	

'≤' means that only a less than concentration can be given and not a minimum concentration for which the majority of the laboratories is able to analyse; the minimum concentration could not be calculated from the results of the QUASIMEME LPS, Round 6, 8, and 10, as the concentrations of the samples used were not low enough.

Organic Compounds

The following points were noted:

- a number of laboratories do not perform to the standard as defined by the QUASIMEME criteria (|z| score < 2);
- the performance for CBs in sediments was better than that for CBs in biota;
- the performance for most OCPs was poor;
- the tables were extracted from the QUASIMEME database, and while they should include all of the laboratories submitting monitoring data to ICES, additional laboratories were also included (this is because some laboratories subscribing to QUASIMEME are not involved in analysis for routine monitoring purposes and so do not submit data to ICES);
- different laboratories may have different analytical performance criteria depending on the purpose of their analyses (as more laboratories that are not involved in ICES monitoring join QUASIMEME, an assessment of the overall performance of laboratories within QUASIMEME may no longer reflect the performance of laboratories engaged in routine monitoring programmes);
- these are difficult analyses and a substantial investment in resources (time and money) is required to produce consistently good quality results;
- the importance of including data from other pertinent sources, such as other intercalibration studies, was recognised, and particularly from those schemes involving North American laboratories;
- information on PCDD/F, TBT, toxaphene, non-*ortho* CBs, and PAH in shellfish is not currently available. Some information for these parameters derived from the QUASIMEME programme will be available for MCWG 1999.

Table 3. Summary assessment of laboratory group performance in QUASIMEME organic contaminant exercises, June 1996–December 1997.

Determinand	[1]Range of assigned values	[2]Range of ± Target Bias (%)	[3]Range of between-lab CVs (%)	[4]Range for % No. obs. with |Z| < 2	[5]Satisfactory performances/total rounds
CBs in biota	**μg kg^{-1}**				
CB28	0.31–12.09	12.91–28.52	44–90	42–79	2/6
CB52	0.53–28.12	12.68–22.01	29–68	40–70	0/6
CB101	1.47–102.01	12.55–15.90	17–55	45–74	2/6
CB105	0.38–40.79	12.62–25.58	33–58	44–65	1/6
CB118	1.05–147.29	12.53–17.25	32–39	52–68	0/6
CB138	2.32–286.91	12.52–14.65	24–36	48–79	1/6
CB153	3.20–391.95	12.51–14.06	27–41	48–68	0/6
CB156	0.15–16.41	12.80–44.90	31–82	53–82	3/6
CB180	0.43–85.93	12.56–24.08	23–45	52–79	4/6
OCPs in biota	**μg kg^{-1}**				
HCB	0.07–12.93	12.89–82.43	30–68	48–63	0/3
pp–DDE	0.58–160.20	12.53–21.07	27–57	52–71	0/6
α–HCH	0.16–2.58	14.44–43.75	41–114	50–71	0/3
γ–HCH	0.07–3.07	14.13–89.42	49–122	48–58	0/2
pp–DDD	0.25–46.28	12.61–32.23	22–82	46–75	2/6
pp–DDT	0.58–26.28	12.69–21.12	50–114	45	0/1
op–DDT	0.09–17.71	12.78–68.06	103–161	38	0/1
Trans-Nonachlor	0.14–22.27	12.72–48.47	26–94	65–90	4/6
Dieldrin	0.53–48.67	12.60–22.00	47–67	19–67	0/6
Lipids in biota	**%**				
lipid total	1.14–58.34	12.59–16.90	8–40	64–100	3/4
lipid extr.	1.07–56.15	12.59–17.15	6–35	72–100	4/4
CBs in sediments	**μg kg^{-1}**				
CB28	0.15–2.05	14.94–45.83	30–52	39–94	4/6
CB52	0.19–1.24	15.54–38.54	28–73	54–81	4/6
CB101	0.50–1.98	15.02–22.50	17–47	60–86	2/6
CB105	0.14–1.42	16.01–47.34	25–112	61–100	4/6
CB118	0.36–2.75	14.32–26.43	23–58	63–78	3/6
CB138	1.03–3.73	13.84–17.35	25–43	52–77	3/6
CB153	0.94–3.75	13.83–17.81	22–44	52–83	2/6
CB156	0.10–0.47	23.04–62.50	28–72	47–78	4/5
CB180	0.59–2.89	14.23–20.97	35–75	42–75	1/6
OCPs in sediments	**μg kg^{-1}**				
HCB	0.12–1.19	16.71–55.86	24–55	70–89	2/4
p,p'–DDE	0.40–2.49	14.51–24.89	28–65	55–89	4/6
α–HCH	0.08–0.21	36.13–71.68	56–87	80	2/2
γ–HCH	0.14–0.54	21.84–42.47	40–119	59–83	4/6
p,p'–DDD	0.49–11.52	12.93–22.70	35–60	40–63	0/6
p,p'–DDT	0.25–3.74	13.84–32.50	48–97	36–73	0/6
o,p–DDT	0.08–0.44	23.91–76.78	41–122	67–89	2/3
Trans-Nonachlor	0.05–0.19	39.22–123.61	61–115	-	-
dieldrin	0.17–1.58	15.70–41.08	38–86	50–90	2/6
PAHs in sediments	**mg kg^{-1}**				
benz[*a*]anthracene	0.26–1.18	12.58–12.89	25–36	56–77	2/6
benzo[*a*]pyrene	0.18–1.17	12.59–13.06	22–37	56–77	2/6
benzo[*a*]fluoranthene	0.27–1.42	12.57–12.88	28–48	44–68	0/6
benzo[*e*]pyrene	0.18–1.34	12.54–12.78	16–43	41–88	2/6
benzo[*ghi*]perylene	0.18–1.22	12.91–15.21	26–51	56–73	1/6
chrysene	0.31–1.48	12.50–12.50	28–47	36–73	0/6
fluoranthene	0.81–2.46	12.54–12.62	17–32	60–82	5/6
indeno[123-*cd*]pyrene	0.18–1.16	12.93–15.23	28–46	43–70	1/6
phenanthrene	0.49–1.39	12.86–13.52	21–35	56–77	3/6
pyrene	0.55–2.16	12.55–12.68	17–30	68–77	3/6

[1]Range of assigned values for six rounds of the QUASIMEME scheme. The determined assigned values are only indicative.
[2]Target 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.
[3]Range of between-laboratory coefficients of variance (CVs) (%) over six rounds.
[4]Range of the number of laboratories achieving the set QUASIMEME standard of $|Z| < 2$ (expressed as %).
[5]Number 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 × 2) > 0.

8.1.7 Review and report on the progress of the second phase of the joint study on PCBs in fish-eating mammals

There has been no meeting of the Marine Mammal Study Group during 1997/8, for the following reasons:

1) The Study Group agreed that the paper which resulted from the first collaborative study should be finalised and published prior to commencing with the next stage. This paper has now been published, and copies were made available at this meeting.
2) Within a number of the collaborating institutes, marine mammal data are being produced for submission as components of scientists' Ph.D. studies. It has been agreed that these research groups would be able to complete their work and prepare their own publications before the data were pooled for further collaborative analysis.
3) Additional essential data on other marine mammal species and data on the prey of these species were also being collected and would be required for the collaborative study. Some of this work has now been completed and will be available for the Study Group during 1998/1999.

It was felt that sufficient progress had been made within each institute that the Study Group could now be reconvened with a view to progressing the second stage of the study. This second stage would entail the collation of a common data set, which would then be analysed by different multivariate techniques to identify the strengths and weaknesses of each analytical approach, and to compare the information provided by them and the ways in which they aid interpretation of the combined dataset.

D. Wells will contact the members of the original Study Group and other members of MCWG with relevant data with a view to arranging a workshop and taking this work forward.

8.1.8 Review and report on the progress on intersessional work on variance components in seabird egg analysis and the use of seabird eggs in national programmes (with WGSAEM)

More information is given under Section 7.2, above, where there is the summary of the presentation given by Anders Bignert on this topic.

There was a round-table review to establish which countries currently used seabird eggs in a monitoring programme for contaminants.

There were no active monitoring programmes which would use seabird eggs within the following countries:

Belgium, Norway, Spain, Portugal, Ireland (one-off surveys only), Poland, UK.

Canada, Sweden and Finland have programmes.

Germany, The Netherlands and Denmark have a trilateral monitoring programme for the Wadden Sea using the common tern.

Eggs can be used to indicate local sources of contamination. However, this does depend on the feeding habits of the birds studied. Good ornithological information is therefore required to identify strictly marine feeding species with limited or well-defined migratory patterns. The habitat and nesting behaviour also need to be examined before a monitoring programme using eggs can be established.

For some contaminants which occur at relatively high concentrations, the within-year and between-year variations seem to be low compared to those for other biological matrices, thus making birds' eggs particularly suitable for time-trend monitoring.

The variability in the population, between and within clutches, and the analytical variability need to be established. Knowledge of the ecology of the coastal birds to be used needs to be well understood before designing the programme. However, there was clearly more detailed information available for birds relative to that for to fish.

The group agreed that the use of seabird eggs was appropriate for time trend studies which were undertaken by a single institute, as the key variables could then be kept under control. Dense, viable populations of clearly identified species are however required.

With the information available at the meeting it was difficult to suggest a single approach for the whole Convention area, but the approach was good for specific smaller areas.

Any monitoring of seabird eggs should be undertaken in addition to the usual monitoring work including fish and shellfish, sediments, and marine mammals, i.e., to complement this monitoring rather than supplant it.

8.1.9 Review the progress in the collaborative study on TCPM and TCPMe

A review presented in 1996 on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) suggested that these compounds might be distributed globally, and indicated that data from the North Atlantic and the North Sea were scarce. A small group of laboratories within MCWG agreed to implement analyses of TCPM and TCPMe and to investigate the concentration levels in different species within this area.

Results from this collaborative group, involving members from Belgium, Canada, Germany, the Netherlands and Norway, were presented, and showed that TCPM and TCPMe are also found in fish, shellfish, marine mammal and sediment samples from the North Sea, the St. Lawrence estuary and the Gulf of St. Lawrence. Their possible world-wide distribution is therefore confirmed, but differences in ratios between TCPM and TCPMe suggest some difficulties with the analytical procedure in the participating laboratories. An interlaboratory study will be conducted using samples from QUASIMEME in order to improve the comparability of the analytical results. Meanwhile the participating laboratories will continue to analyse different species and seek additional information on the toxicology of these compounds.

8.1.10 Review the report on synthetic musk compounds in the marine environment

Gerhard Rimkus was unable to attend MCWG, but expressed his intention to present his report at next year's meeting. The new chairman of the Organics Subgroup, J. de Boer, will contact G. Rimkus to make the necessary arrangements.

8.1.11 Review information on the problems and limitations in the analysis of dissolved concentrations of highly hydrophobic compounds and bioconcentration in mussels from the Dutch Mussel Watch monitoring programmes

Erik Evers presented an overview of techniques and limitations in sampling and analysing (highly) hydrophobic organics in estuarine and marine waters. The results that were presented have been derived from the work of Foppe Smedes. The results were found to be very relevant in relation to the SGQAC 'Technical notes on the analysis of chlorinated biphenyls and organochlorine pesticides in sea water', which were discussed at the meeting (see Section 8.3, below) and should therefore also be incorporated here as far as possible.

When setting up a monitoring programme for highly hydrophobic organic compounds, such as PCBs, PAHs, PCDDs and PCDFs, the objectives should be well defined. To quantify, for example, the effectiveness of reduction measures agreed upon in the North Sea Action Plan, fluxes of these types of contaminants to the sea have to be determined properly (Smedes, 1994). Assessing the impact of human activities in the coastal zone (e.g., dredging, sediment disposal) by using calibrated water quality models, demands information on speciation/partitioning of organic contaminants over various phases.

Most pitfalls in methodology of sampling and the determination of partition coefficients appear to originate from adsorption. For low to medium hydrophobic compounds (e.g., log $K_{ow} < 4$), the truly dissolved phase can be determined by simply sampling the aqueous phase. For more hydrophobic contaminants, sampling of the suspended particulate matter (e.g., by flow-through centrifuges) is preferred for flux-determinations, as this method is hardly affected by adsorption.

Most methods used to determine the bound and freely dissolved phases of hydrophobic compounds are based on physical separation of the particulate and aqueous phases. Filtration of water samples with membrane or glassfibre filters severely suffers from adsorption of compounds onto the filter (Hermans *et al.*, 1992). Additionally, the filtering performance will decrease during filtration by clogging of material. Techniques using direct dialysis may result in extremely low concentrations that have to be determined, next to adsorption problems. Retention of organic contaminants on adsorption columns (Landrum *et al.*, 1984) applied in the field may be disturbed by sorption of dissolved organic material onto the column and by desorption of less hydrophobic compounds from the column. Gas purge techniques can only be used for the measurement of contaminants with high Henry constants (e.g., not for 2–3 ring PAHs). Furthermore, the yield is temperature dependent, the water flows must be high in relation to the gas-flow to prevent exhausting of the aqueous phase, and purge times needed may be extremely long (e.g., days to weeks). The use

of fluorescence quenching (Gauthier *et al.*, 1986) is limited to fluorescent compounds (e.g., PAHs) only. Problems may arise from fluorescent dissolved organic matter and light absorption of DOC.

Promising new techniques, such as cosolvent techniques (Rao *et al.*, 1992) and semipermeable membrane devices (Södergren, 1987; Huckins *et al.*, 1993), probably applied without organic solvent fillings, have to be studied in more detail and applied in marine field studies.

It can be concluded that a direct measurement of the truly dissolved content of highly hydrophobic organics (log $K_{OW} > 6$) is not yet really possible.

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8.1.12 Review information on modelling PCB accumulation in the Seine estuary

Alain Abarnou was unable to attend MCWG, but expressed his intention to make this presentation at next year's meeting. J. de Boer will contact A. Abarnou about this item.

8.1.13 Review a report on progress a) in the application of high temperature techniques for the determination of total nitrogen in sea water, b) a discussion paper on statistical tools to demonstrate the reliability of old nutrient data, c) a paper on particulate carbon (POC) in anoxic water and d) a paper on quality assurance aspects in the determination of chlorophyll in sea water

8.1.13.1 Report on the progress in the application of high temperature techniques for the determination of total nitrogen in sea water

The determination of total nitrogen (TN) in sea water is one of the key parameters for the evaluation of the nitrogen cycle—and related to this cycles of carbon and phosphorus—in any marine ecosystem. Species in which nitrogen occurs in these systems are:

1) particulate (organic) nitrogen (PON);
2) dissolved inorganic nitrogen (DIN) ('nutrient salts');

3) dissolved organic nitrogen (DON);
4) volatile nitrogen compounds.

For routine analyses, methods including the aspects of quality assurance are available for DIN and—with some limitations—for PON. At present, volatile nitrogen compounds are of minor interest and their contribution to TN should not be considered here.

One nitrogen species which is of great interest for many kinds of investigations is the nitrogen bound in organic material. As particulate inorganic nitrogen compounds are generally rare in aquatic systems, the particulate part of this fraction can be determined by CHN-analysis with established methods and with acceptable accuracy and precision.

For the determination of DON problems arise from the fact that in nearly all methods the amount of DON is calculated as the difference of total dissolved nitrogen (TDN) and DIN. Therefore the accuracy of the DON determination directly depends on the accuracy available for the determinations of TDN and DIN. Only a few efforts are documented describing the direct determination of DON. Main problems for direct DON determination arise from the complex and unknown structure of the organic material.

Methods commonly used for the routine analysis of TN or TDN are basing on wet oxidation of the sample, either with persulfate or by UV treatment. Many modifications of these methods have been described and compared in several intercalibration exercises. Generally the precision and accuracy of these methods for the determination of TDN or TN are in the range of 5–10 %.

In 1985 methods were introduced for the analysis of DOC and TDN or TN based on a high temperature combustion of the sample. The first results obtained attracted great interest because values found for DOC as well as for TN were much higher than those reported from measurements using wet oxidation methods. However, these high values could not be reproduced later and they were probably associated with problems in calibration and in blank determinations. In some direct comparisons, it had been shown that the differences between values obtained by wet oxidation and high temperature combustion are comparable. However, the use of high temperature combustion methods may become attractive because a simultaneous determination of TDN and DOC from the same sample is considered to be possible.

The actual and most comprehensive overview on methods for the determination of TDN by high temperature oxidation is found in a special issue of Marine Chemistry (Marine Chemistry, 49, 1993), where the results of a workshop on the measurement of dissolved organic carbon and nitrogen in natural waters is summarised (NSF/NOAA/DOE Workshop, Seattle, WA, USA, 15–19 July 1991). Although there are a number of reports giving examples for the determination of TDN by high temperature combustion methods, there is no evidence that they have started to displace the wet oxidation procedures as yet.

The basic principle of high temperature combustion methods is the conversion of all nitrogen compounds in the sample to NO with subsequent quantification of the NO gas. There are several modifications of this basic method described which mainly differ in combustion conditions and in the quantification of the reaction products. For the combustion, two principle methods can be distinguished:

- HTO methods: high temperature oxidation (without using a catalyst)
  combustion temperatures used are between 1000 °C and 1100 °C
- HTCO methods: high temperature catalytic oxidation
  combustion temperatures used vary between 680 °C and 1000 °C; catalysts applied are Pt (in different forms), MnO_2, Al_2O_3, CuO or some others.

Independent from the use of a special catalyst, additional problems in this step arose from the decomposition of NaCl at higher temperatures producing Cl_2. For most methods available Cl_2 interferes with the quantification of the NO produced in the combustion step and therefore has to be removed from the gaseous oxidation products. In some cases, the choice of a combustion temperature of 680 °C seems to be a compromise between minimal production of Cl_2 and sufficient oxidation of the sample.

The most commonly used detector systems are in-line chemiluminescence and chromogenic trapping. For the in-line chemiluminescence detection, two types of detectors are available: ozone-based 'NO_x' boxes and luminol-based NO_2 detectors. As direct comparisons between different types of detectors are very rare, no general statement for the use of one of the mentioned methods can be given at the moment.

As result of the workshop mentioned above, a number of questions were identified that have to be clarified before HTO or HTCO methods may be recommended for the determination of TDN. Some of these open questions are:

- What are the optimal procedures for standardisation, calibration and blank determination in DON analysis?
- What procedures are applicable for the determination of oxidation efficiency in routine analysis?
- What can be done to improve the precision and accuracy of the TDN or TN determination?
- How do structural characteristics and biological liability of DON affect its determination using HTO or HTCO methods?

These questions—which in some aspects are also valid for the wet oxidation methods—have been open for several years, but no analytical protocol and method for the determination of TDN or TN by high temperature combustion has yet been generally accepted. Besides several technical problems, the lack of appropriate reference samples or certified reference standards may be one of the reasons why HTO or HTCO methods are not used in many laboratories.

From the information available at the moment it not clear whether HTO or HTCO methods for the determination of TN or TDN are generally applicable to all areas of the marine environment. The Chemical Oceanography (CO) Subgroup therefore encouraged interested institutes to perform direct comparisons between wet oxidation methods and high temperature combustion using samples from different areas of the sea and sampled during different seasons of the year.

Members of the Subgroup offered to co-operate on this by sending samples to Klaus Nagel, who will prepare a report for the 1999 MCWG meeting.

8.1.13.2 On the reliability of historical nutrient data

Last year Ole Vagn Olsen presented a paper in which he tried to analyse nutrient data from samples originating from the deep parts of the Faeroe-Shetland Channel and from the deep areas of the North Sea. The Faeroe-Shetland data, from the 1960s and the 1970s, showed that there were small but significant differences in the nitrate values determined by two laboratories, one in Scotland and one in Denmark. For the other nutrients there was good agreement. Occasional data from other laboratories seemed to be of poor quality. The conclusions on the North Sea data were rather weak and involved only a few laboratories. The group decided that he should try further investigations on an extended data set. The only additional data found were from the Baltic Sea including the Kattegat. Chemical conditions are far from constant in the Baltic Sea. This in itself would not influence the analyses if the laboratories were represented with large numbers of datasets, and if the data sets were large, and if the observations were randomized in time and space. However, most data came from ship cruises sampling sporadically: many observations covered a period of one or two weeks followed by many months without any sampling. Furthermore, most laboratories sampled relatively densely near their own coasts. The resulting bias could have been compensated by models if relevant parameters reacted in a simple manner. But nutrient concentrations in the Baltic Sea do not obey simple rules: the models will introduce too many degrees of freedom and the deviations will hide any possible differences arising from analytical practices. The conclusion must be that it is not possible to fulfil the task given with the available statistical tools.

8.1.13.3 Review a paper particulate organic carbon (POC) in anoxic water

Mikael Krysell reported that no progress had been made on this item since the last meeting of the MCWG. Due to a financial cut-back with staff consequences at SMHI, the monitoring of POC/PON had been discontinued for some time. However, the monitoring will soon be started again, and the agenda point should stay on for a possible contribution at the next year's meeting. Klaus Nagel reported briefly on organic carbon monitoring carried out by IOW in Warnemünde. Mikael Krysell and Klaus Nagel promised to scrutinize their existing and new data with a view of producing a common report for the 1999 MCWG meeting.

8.1.13.4 Quality assurance aspects in the determination of chlorophyll *a* in sea water

At the meeting held in 1997, the Chemical Oceanography Subgroup agreed to produce a paper recommending a method for the routine determination of chlorophyll *a* as a biomass marker. A. Aminot was in charge of the preparation of this paper.

The paper was not intended to be an analytical manual, but was meant to i) summarize the background on the ecological importance of chlorophyll *a*, ii) summarize the analytical principles and the procedures for its determination, and iii) point out the critical and controversial aspects of the protocol.

In parallel, the Working Group on Phytoplankton Ecology (WGPE) undertook a similar task at its 1997 meeting,. The report of the WGPE was available this year for the CO Subgroup discussion of Aminot's draft. Both documents benefited from the recent (early 1997) publication of the SCOR Working Group 78 report, under the auspices of UNESCO ('Phytoplankton pigments in oceanography' by Jeffrey *et al.*). This monograph served as a reference for the recommendations given in the two documents although they were produced independently.

Two additional external contributions were available: the HELCOM recommended procedure (Manual of the Baltic Monitoring Programme, 1998) and comments on Aminot's draft from Lars Edler (biological oceanographer, SMHI, Sweden).

Very similar advice and recommendations were given in the WPGE report and in the MCWG CO Subgroup draft. The main difference concerned the time of storage of the filtered samples at a temperature of –20 °C. The WGPE retained the recommendation of the SCOR group, i.e., a few days, although this applied to all the carotenoid and chlorophyll pigments tested. However, for the routine spectrophotometric or fluorometric determination of chlorophyll *a* only, Table 10.4 in the UNESCO monograph showed that recovery after 60 days was 100 ± 10 % of the initial concentration, for both artificial mixtures of microalgae and natural populations. Consequently, it was considered that a storage time of up to 2 months at –20 °C could reasonably be recommended. Note that the HELCOM procedure recommends that the filters not be stored, or, if this is not possible, that they be kept in a desiccator at –20 °C for no more than 24 hours.

A main point of discussion concerned the extraction solvent. Although the SCOR work showed that 90 % acetone does not completely extract chlorophyll *a* from a few specific algae, tests on natural populations gave satisfactory results when compared with the reference solvent (dimethylformamide). Therefore, given that extinction coefficients are well established in 90 % acetone, and that this solvent has a low toxicity, the SCOR group recommended it (with grinding of the filter) for routine spectrophotometric and fluorometric determinations. This recommendation is followed by the two ICES WGs (WGPE and MCWG). The HELCOM procedure recommends the use of 96 % ethanol. However, despite potential advantages of that method, it cannot presently be recommended for the ICES community since the complete methodology using this solvent is not available in the international literature.

When the ethanol method is finally documented, MCWG recommends that further work be undertaken to compare the relative merits of the two extraction procedures.

However, the two papers from WGPE and Aminot have a different focus. The papers are overlapping but yet they are also unique because they both have unique parts. The main basic difference is that Aminot's paper focuses on chlorophyll-*a* only. MCWG thinks that there is a prospect that the two documents could be merged into one. If so, this is something that could be done intersessionally by some experts from both WGs. If not, they are still useful for the ICES community in their own right but require careful reading since at some points they would seem as contradicting each other. The Chemical Oceanography Subgroup therefore suggested that Aminot's paper should be sent to the Chairman of WGPE to seek the view of that working group at its meeting in late March.

8.1.14 Review information on the fate of nutrients in estuaries and experience in the use of *in situ* chemical oceanographic systems for observation of chemical variables

8.1.14.1 Review the information on the fate of nutrients in estuaries

As estuaries can be main sources of nutrients for coastal waters, this matter was considered an important discussion item for the Subgroup. A. Aminot prepared a paper dealing with nitrogen in the macrotidal estuaries. The paper focused on the problem of the determination of the nitrogen flux into the coastal zone, since reduction of the nutrient inputs by 50 % was considered essential by the North Sea Conference Ministerial Declaration to reduce eutrophication events. The paper raised the question whether recommendations could be given for establishing a monitoring programme strategy for measuring the fluxes into the coastal waters.

The Subgroup produced some input to the discussion, and K. Mäkela distributed several interesting papers on the fate of nutrients in the marine environment. One of the main features seems to be the removal of nitrogen through the denitrification process (nitrate converted into dinitrogen).

The Subgroup agreed that work on this topic should be focused on trying to develop a strategy for monitoring inputs of nutrients to the coastal zone. This work will go on intersessionally with A. Aminot as coordinator, and this item will be again on the agenda for the Subgroup at the next year's meeting.

8.1.14.2 Review the information on experience in the use of automated *in situ* chemical oceanographic systems for observation of chemical variables

There was no written contribution to this agenda point, and therefore it was only briefly discussed. The Subgroup was informed that there have been two international workshops dealing with this topic within recent years. The most recent one was held in Brest, France, 17–19 November 1997. In the SeaNet organization there is a recently established working group dealing with this topic. As Lars Føyn is a member of that group, as well as of the MCWG, he agreed to prepare a written contribution on this topic for the next MCWG meeting.

8.1.15 Review quality assessment procedures for nutrient and oxygen data in use in individual institutes

The justification for this agenda point was that the ACME has noted a decline in the overall quality of nutrient and oxygen data being submitted to ICES. The problems seemed not to relate to the chemical analysis, but indicated that data are not being checked before being dispatched by the reporting institutes. MCWG had thus been requested to review the current state-of-the-art with a view to establishing guidelines together with the Working Group on Marine Data Management (WGMDM).

The presentation of the SMHI data screening system given by Mikael Krysell under Agenda Item 8.3.7 was taken as a background for further discussions in the Subgroup (cf. that agenda point). The view of the Subgroup members was that most institutes represented in the Subgroup use similar techniques to screen their own data before dispatching them to ICES, but that there was no reason to argue with the ACME view that practical guidelines for this important part of the quality control work would be of utmost importance. The existence of written guidelines would have two distinct advantages: it would show laboratories reporting to the ICES data bank how important it is to apply quality control procedures on the data, and it would provide ICES with data sets which are easier to handle and which have a documented QC history behind them.

Mikael Krysell undertook the task to look deeper into this matter and to contact the WGMDM to get their view. All members of the MCWG are asked to send information to him about the quality assessment procedures used in their institutes. The aim will be to present preliminary guidelines at next year's MCWG meeting.

8.1.16 Advise on the need to standardise nutrient and oxygen units to μmol kg^{-1}

Introduction

The *justification* for this agenda item is given by the Council as follows. "Many organizations, especially academic institutes, and a number of global projects such as GEOSECS and WOCE, have unilaterally adopted the unit μmol/kg for most chemical parameters. The trend for using this unit is increasing and an explanation for the scientific grounds for this, as well as advice to the data management community, is required. In particular, advice to the data community should take into account the fact that historical databases hold data only in μmol/l or equivalent. MCWG should also consider to recommend the adoption of this unit by the ICES community in general, and if the unit is adopted by ICES, to prepare a case for its formal adoption by UNESCO."

The Chemical Oceanography Subgroup is aware that the term 'concentration' is officially defined only as related to volume. However, for the discussion of the task given to the group, the term 'concentration' is here also used related to mass since there is no alternative universal term that is defined in relation to mass.

For a very long time chemical data reported to the ICES Oceanographic Data Centre have been expressed in volumetric concentrations (as μmol l^{-1} for nutrients and ml l^{-1} for oxygen). In recent years, some institutes have reported data as mass concentration (e.g., μmol kg^{-1}) rather than volume concentration (e.g., μmol l^{-1}). This is due to participation in, e.g., WOCE and JGOFS programmes where the requirement is to report data as mass concentration.

The current practice in ICES is to convert these data to volume concentration using the density of the standard ocean since this is the practice of the World Oceanographic Data Centres. This is not satisfactory, especially as in the case of oxygen the temperature at which the pickling took place is important for the volume determination of the sample and this temperature is usually not known or at least not reported with the data. The group expressed great concern about this practice since it can introduce errors as well as compromise the integrity of the original data if they are no longer stored in their original form.

It is essential to recognize that in producing, reporting and using data there are at least four discrete steps:

Chemist ===> Data reporter ===> Database manager ===> User/Assessor

In each of these steps, scientists may have their own views on what is the most suitable way of reporting/handling the data. However, in principle, the requirements of the user are the most important ones because if he cannot rely on the data and use them for his purpose all the work in the previous steps may be done in vain.

Certainly, for every set of chemical data produced in the first step there is identified at least one specific use in the last step. In the case of, e.g.. a contaminants programme of a regulatory commission, the use can be an assessment of trends of metals in biota. This use defines a number of conditions and constraints on sampling, chemical analysis as well as on reporting of the data in a certain way, e.g., on a wet weight basis, dry weight basis or lipid basis (or a combination thereof) and the reporting of the corresponding metadata makes possible the conversion of data from one reporting basis to the other.

The ICES Oceanographic Data Centre/database represents a much more difficult case to handle for a very obvious reason. The data centre is there to store the oceanographic data reported by institutes in the member countries and to make the data available to them on certain conditions, but also to use the data to serve member institutes or cooperating regulatory commissions with data products (subject to certain conditions).

Quite obviously, in comparison, this makes the role of the ICES Oceanographic Data Centre much more difficult since member institutes are reporting data collected in various national and international programmes (e.g., WOCE) without necessarily knowing when their data will be requested by others or how they will be used. It is therefore essential that a data centre has the flexibility to receive, store and convert data from several sources and for a great variety of uses. This raises some questions, for example:

- has the data centre received all the metadata to describe the quality level of the data reported?
- has the data centre received all the data and/or other information required for the conversion of, e.g., volume concentration to mass concentration?

Usefulness of using mass concentration in oceanic/marine studies

Introduction

It has for many years been customary to express concentrations of minor elements in sea water on a volume basis, e.g., mg l^{-1}. But the concentrations of the major constituents of the salinity have, however, been expressed on a mass basis, e.g., g kg^{-1}, as it was realized that the specific volume of sea water changes sufficiently with temperature, salinity and depth to introduce significant uncertainty to results on these constituents when expressed on a volume basis.

However, treating the volumetric concentration has certain disadvantages in these circumstances. The concentration, as used in the advection-diffusion equation for dissolved substances, is the amount of dissolved substance per volume of sea water under *in situ* circumstances. This implies that the volumetric concentration may change when a water sample is brought to the sea surface.

Heating and cooling, or compression and expansion, and all the things that can happen when a water sample is brought from the cold abyss to the sea surface, will not change the numerical value of concentrations expressed on a per mass basis.

Chemists are aware of this problem and specify the concentration of a dissolved substance as the volumetric concentration at some specific laboratory conditions but the corresponding metadata are not always reported. Moreover, people in different laboratories use different laboratory conditions when reporting their volume concentrations.

In the Operations Manual of the international WOCE Hydrographic Programme, the general rule is to record concentrations of dissolved nutrients, inorganic carbon, and dissolved gases on a mass basis.

The issue

When one wants to use the volumetric concentrations in the advection-diffusion equation, a set of corrections has to be made to transform the concentration to the *in situ* values. Since it is not always clear what standard laboratory conditions are the standard requirements for reporting oceanographic data expressed on a volume basis, there are several possibilities of erroneous corrections. When reporting the concentrations as mass concentration there is no need to worry any more about the specific laboratory conditions or *in situ* conditions to which the concentrations refer. Errors only can be made when the data originator transforms the volumetric concentrations to mass concentrations. And when for whatever reason or condition the *in situ* concentration is required, one simply multiplies the mass concentration by the *in situ* density of the sea water.

Many outstanding issues in chemical oceanography relate to biogeochemical processes and the cycles of carbon and nutrients. One example is the question of the ocean carbon system response to rising atmospheric CO_2. Here the task lies in resolving and explaining space- and time-related concentration variations which are small in comparison with a large background. The time dimension may span a season or decades and the space dimension may be depth or long horizontal distances. Analytical procedures in carbon chemistry work are designed to reach a high precision, typically 0.05 % or 1 part in 2000, and systematic errors are controlled, e.g., by the use of certified reference materials. It is equally important that the results are expressed, documented and stored in an unambiguous fashion. That can be achieved by relating concentration to mass rather than volume.

Calibration at sea

During oceanic cruises, most chemical species are measured on board the research vessel. For producing satisfactory data, these measurements require frequent calibration using working standard solutions. However, for nutrients, for instance, the working standards are known to be unstable, so they should be prepared on board, shortly before use. As gravimetry is not reliable on board ships, only volumetry can be used to prepare working standards. Consequently, *concentrations are not directly determined per mass of sea water* (as required) but per litre.

Concentrations on a mass basis can then be arrived at by different routes:

1) Analysing a sample weighed (in vacuo) and standardizing with standards expressed on a mass basis.
2) Analysing a sample on a volume basis and converting to a mass basis using the equation of state for sea water. For this, precisely volume-calibrated glassware must be used and the salinity and temperature of the sample at the time of analysis must be known.
3) Convert data, expressed on a volume basis, e.g., from a compilation or a data centre, to a mass basis. To do this accurately one needs either (i) the salinity and the temperature of the sample when it was measured, or (ii) one may use a single conversion factor and assume the same salinity and the same temperature for all samples, e.g., a density of 1025 kg m^{-3} as practised at ICES (S = 35, t = 20 °C).

Routes 1 and 2 are reliable and either one can be selected by the investigator. Route 3(i) is troublesome since the temperature of measurement usually does not accompany the data. Route 3(ii) implies two assumptions, that the measurement temperature has been near 20 °C and that the salinity has been near 35. The magnitude of the error introduced by assuming constant density therefore varies as the sample salinity departs from 35 and as the measurement temperature departs from 20 °C.

Consequence in terms of precision

Sea water (of salinity 35) has a density of 1.0248 kg dm^{-3} at 20 °C. This means that the value of a concentration expressed in µmol/kg is ~2.5 % lower than when expressed in µmol l^{-1}. A temperature difference of about ± 4 °C generates a density difference of ± 0.1 %, i.e., a rather low error which usually may be neglected. A salinity change as high as ± 1.3 (range 33.7–36.3) leads to a change in the final value by only ± 0.1 %.

Problems for coastal and estuarine studies

For coastal and estuarine studies, the problem is different from oceanic studies. These areas are under strong continental influence, therefore salinity (hence density) varies significantly in space and time. For that reason, if calibration of the methods is done, as usual, on a volumetric basis, each sample may have to be treated individually for density correction.

This is obviously more complicated than in the case of oceanic studies. Generally, the more the data that have to be corrected, the greater the risk of errors in final values.

What will happen if the salinity data are missing? Such data contributions should not be accepted in the first place. On the other hand, errors will never exceed about 2.5 % for an uncorrected concentration, i.e., maintained in 'per litre' instead of converted to 'per kilogram'. An estimated correction can be done if the salinity is known approximately. Is this error acceptable while QA is developing to increase the reliability of data?

Should the standard solutions be prepared gravimetrically?

Until now, all the papers dealing with measurement methods for marine and estuarine waters used concentration data expressed per volume of water. Salt effects, in particular, were calculated using standards prepared on a volumetric basis. It must be clear that if 'per mass' concentrations are used instead of 'per volume', salt effects have to be recomputed accordingly! Even if standards are prepared gravimetrically, many of the analytical procedures and measurements can only be done on a volumetric basis.

Because of the problems induced by the use of concentrations expressed per mass of water, instead of per volume, in estuaries and coastal areas, it seems preferable not to recommend calibration in 'per kilogram' of water.

Conclusions

In case the unit $\mu mol\ kg^{-1}$ would, however, be generally accepted, the whole measurement procedure (including calibration) should be done as usual on the volumetric basis. Concentrations of the samples have to be converted after the measurement, either by the chemist or by the database manager. This is done by dividing by the density of the water at the nominal temperature of the calibration solutions, assumed to be 20 °C when not otherwise reported.

After considerable discussion, the Working Group agreed that:

- It is essential that laboratories be allowed to report their data to the ICES Oceanographic Data Centre either on a volume basis or a mass basis depending on their normal practice and/or the requirements of special programmes (e.g., WOCE or JGOFS) they may be participating in.
- It is also essential that metadata (supporting information) are reported so that conversion from a volume basis to a mass basis is possible.
- This reporting should be supported by the data reporting format (amended as might be needed).
- It is essential that data are stored in the data centre in their original form (either volume basis or mass basis) so that the integrity of the original data is not compromised.
- Any conversion of data is performed either by the data user or by the data centre on a direct and specific request by the user.
- While converting the data, the user should be responsible to ascertain that the original as well as the converted data have/will have the quality needed for the particular purpose for which the conversion is performed.

8.2 Other Issues: Trace Metals Subgroup

8.2.1 Review on the updated paper on mercury speciation

The updated paper titled 'Mercury in the Marine Environment—A Review' by Martine Leermarkers was considered by the Trace Metals Subgroup. The paper describes the global Hg cycle with particular reference to anthropogenic influences, the distribution of mercury in the marine environment, the biogeochemical behaviour of mercury, bioaccumulation pathways, concentrations and trends of mercury in the North Sea and northern Atlantic and concludes by summarising uncertainties and gaps in the information on mercury in the marine environment.

The Trace Metals Subgroup found this excellent paper very informative and MCWG recommended that it should be forwarded to ACME for incorporation in the 1998 report after minor technical and typographical revisions to be carried out intersessionally. The final paper is attached as Annex 7.

8.2.2 Review the guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea

The Trace Metals Subgroup was asked to review the revised Annex H (Technical Notes on the Determination of Trace Metals including Mercury in Sea Water) and the 'Technical Notes on the Determination of Total Mercury in Marine Biota by Cold Vapour Atomic Absorption Spectrometry'. The Subgroup found both documents very informative and technically concise. Some minor comments and some suggestions for improvements are given in Annex 8.

8.2.3 Any other business

8.2.3.1 Suggestions for plenary presentations

The Subgroup suggested the following presentations for the next MCWG meeting:

- the influence of fish size, liver size, fat and water content of the liver on the concentration of minor and trace elements in cod liver (to be presented by Gudjon Audunsson);
- the latest TBT research in France (to be presented by Jean François Chiffoleau);
- shellfish toxins in the waters around Ireland (to be presented by an Irish scientist);
- the QUASH programme (to be presented by the coordinators).

8.2.3.2 Election of a Subgroup Chairman

The Trace Metals Subgroup re-elected with acclamation Gert Asmund as chairman for the intersessional period and for the next meeting.

8.3 Other Issues: Organics Subgroup

8.3.1 Assessment of the draft paper 'Determination of polycyclic aromatic hydrocarbons (PAHs) in sea water and biota'— technical annex to guidelines on QA of Chemical Measurements in the Baltic Sea

The Organics Subgroup considered that many details were missing in the present document. MCWG recommended that both JAMP and the Baltic Monitoring Programme used the same guidelines for the determination of PAHs in biota which is being prepared (see Section 8.1.1, above).

Regarding the determination of PAHs in sea water, the Organics Subgroup agreed that an extensive revision of the document was required. However, nobody within the Subgroup was familiar enough with the needs to prepare such a guideline. It was recommended that such a task should be forwarded to people involved in the Baltic Monitoring Programme through the chairman of SGQAC, Mikael Krysell.

8.3.2 Technical notes on the analysis of chlorinated biphenyls (CBs) and organochlorine pesticides (OCPs) in sea water (prepared by SGQAC)

The Subgroup took note of this paper but decided not to make any revision of it. As the paper is obviously incomplete and lacks fundamental information, it was recommended that those familiar with seawater analysis of chlorobiphenyls should prepare a revised version.

8.3.3 Draft Guidelines on the Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments— Analytical Methods (prepared by WGMS 1997)

Questions were raised about the current guidelines for the determination of PAHs in sediments (Annex 4 of the 1997 WGMS Report). After discussion, the following proposals were made for some improvements to the guidelines:

- Under sampling: storage materials which have been tested and demonstrated to be appropriate for this purpose should be mentioned explicitly.
- Under extraction: in some cases (e.g., clay sediments) the use of Soxhlet extraction could lead to problems and the efficiency of extraction should be carefully monitored. Alternative methods should be mentioned, such as the commonly-used alkaline saponification technique.

- Under storage: storage of samples at temperatures as high as 25 °C for even a short time period is not appropriate for samples which are to be analysed for PAHs.
- Under quantification: MS detection is presented in the guidelines as being inherently non-linear, and this is incorrect. The linearity and linear range of an MS-detector depends *inter alia* on the type of mass spectrometer. This text should be modified.

It was recommended that the comments should be forwarded by the MCWG Chairman to the Chairman of WGMS, with the recommendation that the present guidelines should be revised at their 1998 meeting.

8.3.4 Comments on list of reference materials (CRMs) available for routine monitoring of organic contaminants in the marine environment

Tables of information on certified reference materials (CRMs) available for use in marine monitoring were prepared for the 1998 MCWG meeting by Evin McGovern. The tables, which are presented in Annex 9, contain an overview of information on reference materials that are currently available for routine monitoring of organic contaminants in the marine environment. The collated information covers sediments and fish and shellfish tissue (marine and freshwater).

The author made the following comments to the tables:

- values preceded by an asterisk (*) are non-certified, all others are certified;
- certified calibration materials and standards were not included;
- the list does not purport to be a complete list and all CRMs listed may not be commercially available;
- users of CRMs should consult vendors for full and accurate information relating to individual CRMs;
- methyl mercury is not considered as an organic contaminant for this list.

The tables were discussed at the meeting and there were a number of comments to the tables from the Subgroup:

1) There is a lack of CRMs for some determinands in marine matrices.
2) While marine matrices are preferred as CRMs for marine monitoring programmes, freshwater sediments and biota may be suitable in the absence of appropriate marine-based materials.
3) This table is incomplete and will be updated for MCWG 1999.
4) There is sometimes a lack of information on CRMs. It can be difficult to compare CRMs used for routine monitoring due to a lack of information being presented on the method(s) used for the determination of assigned values, acceptable ranges and the associated uncertainty.
5) Although there is a whale blubber reference material for organochlorine compounds (SRM - 1945) available from NIST (USA), it was not clear as to whether this material is available to purchasers outside the USA.

Information was also given about materials in preparation, see below:

Materials in preparation

Code	Producer	Country	Analyte/matrix
LGC6114	LGC	UK	PCBs in marine sediment
LGC6156	LGC	UK	TBT (& metals) in marine sediment
HS-4B	NRC	Canada	PAHs in marine sediment
HS-3B	NRC	Canada	PAHs in marine sediment

MCWG agreed that the list of reference materials should be updated annually and E. McGovern volunteered to take the lead.

8.3.5 Review of the report on chlorinated paraffins

Bo Jansson presented information on a very complex group of contaminants, the chlorinated paraffins (CPs). The world production of these compounds is estimated to be 300,000 tonnes per annum (IPCS EHC181, 1996). The technical

products are divided into six different classes depending on the carbon chain length (short, medium or long) and the degree of chlorination (low or high). The theoretical number of possible congeners is almost infinite, and there are no prospects for congener-specific analysis in the foreseeable future. Very few pure substances have been synthesized and the technical products must be used as reference materials for the analysis of CPs.

Most analytical methods are based on gas chromatography after clean-up using mainly HPLC or GPC techniques. Mass spectrometric detection (NCI) is sensitive and can be specific, especially at high MS resolution. If less specific detection techniques are utilized then extensive clean-up is essential if interference from other compounds eluting within the broad band of GC peaks due to CPs is to be avoided.

The available database for environmental levels of CPs is very limited, and most of the samples which have been analysed are from the vicinity of point sources. There are some data from the marine environment indicating sediment concentrations in UK waters in the range 50 to 500 $\mu g\ kg^{-1}$ wet weight. Concentrations in biota have been estimated to be in the range from 30 to more than 3,000 $\mu g\ kg^{-1}$ wet weight. One study, including samples from both the aquatic and terrestrial environments, suggested that CPs may occur at higher concentrations in terrestrial animals.

Copies of the overheads from this presentation are attached as an Annex 10 to this report.

8.3.6 Any other business

8.3.6.1 Topics for the Subgroup meeting at MCWG 1999

New Contaminants

The Subgroup considered how to proceed, and how to identify topics under 'New Contaminants and their Relevance to the Marine Environment' for MCWG.

As a general approach it was agreed that existing lists of hazardous and toxic compounds which have been prioritized within working groups of the HELCOM and OSPAR Commissions and other relevant bodies should be collated. Prof. Bo Jansson agreed to collect information and prepare a proposal for MCWG99. It was agreed that P. Roose, J. Klungsøyr and other MCWG members should send information on national priorities to B. Jansson.

Polybrominated Diphenylethers (PBDEs) and Polybrominated Biphenyls (PBBs)

Jacob de Boer will prepare an update of his earlier review paper on these compounds for MCWG 1999.

Suggestions for Plenary Lectures and Other Presentations

a) The Subgroup would like to have a presentation concerning the status of research and monitoring activities relating to Atmospheric Inputs of Organic Contaminants to the Marine Environment. The Subgroup asked E. Andrulewicz and D. Schulz-Bull to contact relevant colleagues, and to inform the Subgroup Chairman of their response.

b) Erik Evers agreed to approach G.M. Suijlen (NL) with a view to requesting that he consider presenting a lecture on the use of organic compounds in riverine waters as tracers.

c) A note will be prepared by E McGovern and J. de Boer for information concerning the MATT project (Monitoring, Analysis and Toxicity of Toxaphenes) which began in June 1997 under the FAIR programme.

8.3.6.2 Miscellaneous

The Subgroup noted two recent papers: one by F. Smedes and J. de Boer on the 'Determination of Chlorobiphenyls in Sediments - Analytical Methods', published in Trends in Analytical Chemistry, 16: 503–517 (1997). This work was initiated within MCWG some years ago, and the authors were thanked for their worthwhile efforts. The paper was felt to be most useful, and provides a good example of the way in which the group can give guidance to outside bodies. The second is by J.P. Boon, J. van der Meer, C.R. Allchin, R.J. Law, J. Klungsøyr, P.E.G Leonards, H. Spliid, E. Storr-Hansen, C. McKenzie and D. E. Wells on the 'Concentration-dependent changes of PCB patterns in fish-eating mammals: structural evidence for induction of cytochrome P450', 33: 298–311 (1997). This paper arose from the work

of the study group on fish-eating mammals, and illustrated the successful partnerships which could be built within MCWG.

8.3.6.3 Election of a Subgroup Chairman

The Subgroup appointed Jacob de Boer (NL) as chairman for the next year's and for the intersessional period before MCWG1999 unanimously by acclamation. The Subgroup thanked Jarle Klungsøyr for his firm and effective chairmanship over the past three years.

8.4 Other Issues: Chemical Oceanography Subgroup

8.4.1 Discuss quality assurance procedures of data to be loaded into a database, and prepare a general guideline for this activity

Mikael Krysell demonstrated the procedures used at SMHI for quality control and quality checks of the data to be loaded into the SMHI database. At SMHI, the quality control is divided into two different parts, in addition to the internal and external quality control carried out in connection with the analysis of the sample. When data are loaded into the preliminary database, certain automatic checking is carried out by the software. For example, the data are checked to ensure that they are within the concentration range of the laboratory's accreditation and that the expected number of decimals are given. Before the data are moved from the preliminary to the official data bank, a more thorough check is carried out. In the end, more than 50 different characteristics, like the expected concentration range within the sea area, the fact that the sum of inorganic nitrogen species cannot be larger than the value for total nitrogen and that the supporting data (position, time, weather conditions, bottom depth, etc.) make sense, have been checked. Some of these characteristics depend on the examined sea area (local conditions), and some, like measurable concentration range, depend on the known performance of the laboratory in question. At the same time, the data are printed out in different ways, as hydrographic sections, time series, etc., to facilitate a manual data screening by experienced oceanographers and chemists at the laboratory. Any questionable data are flagged, which means that they always remain in the database, but that they will not be extracted if the normal procedures for data extraction are followed. Data are never deleted from the data bank at this stage, unless it is possible to prove that they are wrong, and why they are wrong. It is also important to point out that data identified by the automated procedures as questionable are not automatically flagged as questionable in the official data bank, but this is done only after manual screening.

The conclusion is that the use of certain automatic procedures give good support in trying to identify questionable data. Still, the success of the data screening is to a very large extent dependent on manual labour by experienced persons, and it is important to leave the actual decisions concerning the flagging of data to these persons (cf. item 8.1.15 of the 1997 MCWG report). The development of more advanced statistical tools would be of high value for the monitoring laboratories in their efforts to identify and explain questionable data.

8.4.2 Any other business

Future work programme

At this meeting, the use of chemical data was raised again. It was pointed out in the discussion that the datasets transferred to databases came from different sources and are produced for different purposes (see also Section 8.3.6, above).

Since many of the databases are accessible to the whole community of marine scientists, it was felt there was a problem in that chemical data are sometimes used in a manner that they were not originally designed for.

The CO Subgroup agreed that there should be more discussion within the oceanographic community on the widespread use of chemical oceanographic data. This discussion must address the different requirements of the end users with regard to precision, resolution in time and space, etc. It was therefore agreed that the Working Group on Shelf Seas Oceanography (WGSSO) and the Working Group on Oceanic Hydrography (WGOH) should be asked to consider their demands for chemical data in relation to what is available from data centres and what is currently being produced. On the basis of these statements, MCWG should discuss to what extent the data produced will fulfil these requirements and, if additional requirements are necessary, to what extent they can be fulfilled.

Plenary presentations in 1999

Stig Carlberg and Mikael Krysell offered to contribute a plenary presentation of the results of the nutrients part of the QUASH Project.

Election of chairman

The CO Subgroup re-elected Stig Carlberg as chairman for the intersessional period and for the next meeting.

9 PLENARY DISCUSSION OF SUBGROUP 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

Different ways to improve the communication within MCWG were discussed under this agenda item, such as:

- use the ICES/MCWG mailbox for an easy and fast communication (please notify ICES if your e-mail address is changed in order to keep the mailing list up to date by contacting melodie@ices.dk);
- use a more humble form and not the latest form/version of a program when sending a file to your colleagues, e.g., through the MCWG mailbox (not all members have access to the most modern version of a software);
- PC-working groups are very suitable for producing draft documents;
- e-mail is fast but remember ... **do not use it as an excuse for sending late documents!**

11 RECOMMENDATIONS AND ACTION LIST

The Action List and Recommendations are given in Annexes 11 and 12, respectively.

12 DATE AND VENUE OF THE NEXT MEETING

MCWG discussed the venue and dates of the next meeting. The Irish member offered to host the 1999 meeting of the MCWG in Dublin, Ireland. MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for 8–12 March 1999.

13 CLOSURE OF THE MEETING

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

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

The Chairman then closed the meeting at 14 hrs on 6 March 1998.

ANNEX 1

LIST OF PARTICIPANTS

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ANNEX 2

AGENDA

1 OPENING OF THE MEETING

2 ADOPTION OF THE AGENDA

3 REPORT OF THE 85TH ICES STATUTORY MEETING

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPARCOM AND HELCOM
Official requests have been included in the agenda.

4.2 Intergovernmental Oceanographic Commission (IOC)

4.3 Laboratory Performance Study 'QUASIMEME II'
Dr Wells has been requested to provide an update.

4.4 EU-BCR QA project 'QUASH'
The co-ordinators of the project have been requested to inform about the programme

4.5 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 the 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 Marianne Cleemann (and other members of the MCWG)
'The outcome of the first year of the Arctic Monitoring and Assessment Programme (AMAP)'

7.2 Anders Bignet
'The use of seabird eggs in monitoring programmes'

7.3 Mikael Krysell
'The impact of the 1995 Rhine overflow on the Skagerrak and the Kattegatt'

7.4 Jon Olafsson
'The Skeidararhlaup glacial outburst, November 1996, as it entered the sea'

7.5 Jan René Larsen
'The ICES Environmental Data Centre: Building the bridge to the 21st century'

7.6 Robin Law
'Sea Empress Oil Spill: Impact on Fisheries and Marine Life, 2nd year'

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

8.1 Trace Metal Subgroup

8.1.1 (C.Res. 1997/2:12:2 c) Review the outcome of the Icelandic study on the influence of parameters such as fish size, liver size and fat content of the liver on the concentration of trace metals; (*In Oostende, it was agreed that G. Audunson would make information available from an Icelandic study on associations between metals and relevant co-variables*)

8.1.2 (C.Res. 1997/2:12:2 d) Review the report on the new ICES data collection system covering not only analytical information but also sampling, sample handling and storage information; (*In Oostende, a small working group consisting of J.R. Larsen (Chairman), G. Asmund, J. Klungsøyr, S. Carlberg, and D. Wells volunteered to work intersessionally on the item and report back at the next MCWG meeting*)

8.1.3 (C.Res. 1997/2:12:2 e) Review and report on an updated paper on organotins

8.1.4 (C.Res. 1997/2:12:2 f) Review the updated list of contaminants that can be monitored on a routine basis and transmit the list to ACME (*In Oostende, it was decided that tables for organic compounds, trace metals, and nutrients should be prepared by a small group prior to the MCWG meeting and circulated to Subgroup members by e-mail*)

8.1.5 (C.Res. 1997/2:12:2 h) Review and report on the progress on intersessional work on variance components in seabird egg analysis and the use of seabird eggs in national programmes (with WGSAEM) (*In Oostende it was agreed that A. Bignert should be asked to present a plenary lecture concerning the Swedish seabird monitoring programme utilising guillemot eggs at MCWG 1998, and all members of the organic Subgroup to send information on national monitoring programmes involving seabird eggs to Professor Bo Jansson intersessionally, for discussion at MCWG 1998*)

8.1.6 Review the updated paper on mercury speciation prepared by M. Leermakers (I*n Oostende, it was agreed that M. Leermakers should supplement her revised review on mercury speciation by including more information of mercury concentrations in biota from different areas, which was to be sent to her by the other members of the group*)

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

8.2 Organic Subgroup

8.2.1 (C.Res. 1997/2:12:2 a) Finalise guidelines for monitoring PAHs in biota, in relation also to the guidelines for sediments agreed in 1997 [OSPAR 1998/1.1] *(In Oostende, it was agreed that a revised draft of the guidelines for monitoring PAHs in biota would be prepared in order to meet the needs of OSPAR*)

8.2.2 (C.Res. 1997/2:12:2 b) Review and assess data on concentrations of CBs, especially non-*ortho* and mono-*ortho* CBs, in marine mammals, as a contribution to the OSPAR Quality Status Report (with WGBEC, WGMMHA, and WGEAMS) [OSPAR 1998/3]

8.2.3 (C.Res. 1997/2:12:2 d) Review the report on the new ICES data collection system covering not only analytical information but also sampling, sample handling and storage information (*In Oostende, a small working group consisting of J.R. Larsen (Chairman), G. Asmund, J.Klungsøyr, S. Carlberg, and D. Wells volunteered to work intersessionally on the item and report back at the next MCWG meeting*)

8.2.4 (C.Res. 1997/2:12:2 e) Review and report on an updated paper on organotins

8.2.5 (C.Res. 1997/2:12:2 f) Review the updated list of contaminants that can be monitored on a routine basis and transmit the list to ACME (*In Oostende, it was decided that tables for organic compounds, trace metals, and nutrients should be prepared by a small group prior to the MCWG meeting and circulated to Subgroup members by e-mail*)

8.2.6 (C.Res. 1997/2:12:2 g) review and report on the progress of the second phase of the joint study on PCBs in fish eating mammals. (*In Oostende, it was agreed that D. Wells should prepare a note on the progress of the second phase for MCWG 1998*)

8.2.7 (C.Res. 1997/2:12:2 h) Review and report on the progress on intersessional work on variance components in seabird egg analysis and the use of seabird eggs in national programmes (with WGSAEM) (*In Oostende it was agreed that A. Bignert should be asked to present a plenary lecture concerning the Swedish seabird monitoring programme utilising guillemot eggs at MCWG 1998, and all members of the organic Subgroup to send information on national monitoring programmes involving seabird eggs to Professor Bo Jansson intersessionally, for discussion at MCWG 1998*)

8.2.8 (C.Res. 1997/2:12:2 I) Review the progress in the collaborative study on TCPM and TCPMe (*It was recommended in Oostende, that the laboratories involved in this study should continue to work intersessionally and report any new data to J. de Boer before the end of 1997*)

8.2.9 (C.Res. 1997/2:12:2 j) Review the report on synthetic musk compounds in the marine environment (*In Oostende G. Rimkus agreed to prepare a review note on synthetic musk compounds in the marine environment for MCWG 1998*)

8.2.10 Review the report on chlorinated paraffins compounds in the environment (*In Oostende B. Jansson agreed to prepare a review note on chlorinated paraffins compounds in the (marine) environment for MCWG 1998*)

8.2.11 (C.Res. 1997/2:12:2 k) Review information on the problems and limitations in the analysis of dissolved concentrations of highly hydrophobic compounds and bioconcentration in mussels from the Dutch Mussel Watch monitoring programmes. (*In Oostende, it was agreed that A. van der Zande should present the Dutch results at the next MCWG*)

8.2.12 (C.Res. 1997/2:12:2 l) Review information on modelling PCB accumulation in the Seine estuary (*In Oostende, it was recommended that A. Abarnou should present information on the subject at MCWG 1998*)

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 Subgroup

8.3.1 (C.Res. 1997/2:12:2 d) Review the report on the new ICES data collection system covering not only analytical information but also sampling, sample handling and storage information; (*In Oostende, a small working group consisting of J.R. Larsen (Chairman), G. Asmund, J. Klungsøyr, S. Carlberg, and D. Wells volunteered to work intersessionally on the item and report back at the next MCWG meeting)*

8.3.2 (C.Res. 1997/2:12:2 f) Review the updated list of contaminants that can be monitored on a routine basis and transmit the list to ACME *(In Oostende, it was agreed that tables for organic compounds, trace metals, and nutrients should be prepared by a small group prior to the MCWG meeting and circulated to Subgroup members by e-mail)*

8.3.3 (C.Res. 1997/2:12:2 m) Review a report on progress in the application of high temperature techniques for the determination of total nitrogen in sea water, a discussion paper on statistical tools to demonstrate the reliability of old nutrient data, a paper on particulate carbon (POC) in anoxic water and a paper on quality assurance aspects in the determination of chlorophyll in sea water. *(In Oostende, the following was recommended; K. Nagel to report on progress in the application of high*

temperature techniques for the determination of total nitrogen in sea water, O.Vagn Olsen to prepare a discussion paper on statistical tools to demonstrate the reliability of old nutrient data., M. Krysell to review a paper on particulate organic carbon (POC) in anoxic water and A. Aminot to review a paper on quality assurance aspects in the determination of chlorophyll in sea water. at the MCWG 1998)

8.3.4 (C.Res. 1997/2:12:2 n) Review the information on the fate of nutrients in estuaries and on experience in the use of automated in situ chemical oceanographic systems for observation of chemical variables. *(In Oostende, it was recommended that Chemical Oceanographic Subgroup should collate and review information on the experience of the use of automated in situ systems for observation of chemical variables)*

8.3.5 (C.Res. 1997/2:12:2 o) Review quality assessment procedures for nutrient and oxygen data in use in individual institutes

8.3.6 (C.Res. 1997/2:12:2 p). Advise on the need to standardise nutrient and oxygen units to µmol kg^{-1}

8.3.7 Discuss quality assurance procedures of data to be loaded in a database, and prepare a general guideline for this activity. *(In Oostende, it was agreed that Mikaell Krysell should demonstrate at the MCWG 1998, one or more screening softwares for chemical data to be entered into data bases)*

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

9 PLENARY DISCUSSION OF SUBGROUP WORK

10 ANY OTHER BUSINESS

11 RECOMMENDATIONS AND ACTION LIST

12 DATE AND VENUE OF THE NEXT MEETING

13 CLOSURE OF THE MEETING

ANNEX 3

QUASIMEME GOES WORLDWIDE

The QUASIMEME Laboratory Performance Studies became available to all laboratories Worldwide from June 1996 and has been open to all organisations making chemical measurements in the marine environment, particularly those institutes which provide data for national or international monitoring programmes, and for individual or collaborative research..

The programme for the first year of QUASIMEME, from June 1996 to May 1997 was designed specifically to support those chemical measurements required for the international marine monitoring programmes of the Oslo and Paris Commission (OSPAR), the Helsinki Commission (HELCOM) and the Mediterranean Pollution Monitoring and Research Programme (MEDPOL) and national programmes the National Monitoring Programme (NMP) of the United Kingdom Marine Pollution Management and Monitoring Group (UKMPMMG). In doing so the needs of may other national and individual programmes were also served. Formerly, this programme was the QUASIMEME Scientific Assessment Group (SAG) and the Advisory Board. The Scientific Assessment Group was primarily a continuation of the same group which directed the earlier EU programme and the Advisory Board was established to strengthen the links with the Commissions and the key Agencies which require this level of quality assurance for their monitoring programmes. A full list of the membership of these bodies are given on the back cover of this Bulletin.

The LP Studies were designed to support the quality management of participating chemical laboratories and the assist in the improvement of the quality of measurements where it is required, bearing in mind that for any analysis it should be fit for the purpose of the question being asked. The assessments provided by QUASIMEME also complement internal laboratory QA, and provide a support laboratory accreditation in addition to the QA support to the environmental monitoring programmes.

During the first year there were four rounds (Nos. 6–9) as a continuation from the initial EU project which concluded at round 5. Each assessment has been completed and all participants have received a personal report with their own data from each round. The preliminary assessment of the data is now made within one month of the deadline for the submission of data and all participants receive a preliminary data sheet of their performance. The full report usually follows within 6 weeks.

Participation

The participation of QUASIMEME has fluctuated over the first two years under the subscription scheme as the priorities of institutes settle after being used to the provision of samples without cost and the opportunity to attend workshops (which is coming again this year!). QUASIMEME now has a presence in 27 countries and will continue to build on this with the publicity programme for this year. We have an A4 three fold leaflet, an example of which is enclose, for distribution at major conferences and meetings.

Table 1 given below indicates participation in QUASIMEME for 1996–97 and 1997–98. Germany showed the most noticeable decrease in laboratories participating by country. The German participants located in Cuxhaven, Greifswald, Heide, Hamburg and Wilhelmshaven are apparently no longer involved in marine monitoring programmes because of changed tasks and responsibilities. Due to financial restrictions two German laboratories decided to participate in QUASIMEME every second round as this was still felt to fulfil their external quality assurance requirements. Two laboratories in the UK and one in Denmark combined to form one 'subscribing' institute. Despite this QUASIMEME has increase from 73 participants at the end of the EU project in March 1996 to 117 last year and now 126 in the current year.

In spite of an overall increase in the number of laboratories participating in round 8 compared to round 6 fewer data sets were assessed for round 8 (See table). The Scientific Assessment Group have designed a questionnaire which has gone to laboratories who did **not** to return data for round 8. Feedback from participants is essential if QUASIMEME is to continue to improve on the level of service this questionnaire offered to participants in the future.

There has also been a rationalisation of the number tests that any one laboratory is currently selecting. with most groups having one or two less participants. The main decline was for the nutrients, but this was primarily due to the changes of responsibility of some of our German colleagues (Table 2).

Test Materials

Test materials for the first year from June 1996 to May 1997 were distributed by the Water Research Centre (WRc), Medmenham, UK under the control and supervision of Dr Mike Gardner. At the end of the year WRc felt unable to continue this work and so all of the test materials were shipped to Aberdeen for storage and subsequent despatch. Since June 1997, the distribution of all test materials was undertaken by FRS Marine Laboratory Aberdeen under the supervision of Kieren Smith. All of the aqueous samples are now prepared at the Marine Laboratory in Aberdeen. The sediment test materials were supplied by the Institute for Environmental Studies, Vrije Universiteit, Amsterdam, The Netherlands under the control of Dr Wim Cofino and the biological tissues were supplied by The Netherlands Institute for Fisheries Research, IJmuiden, The Netherlands under the direction of Dr Jacob de Boer.

The samples for each group of determinands were prepared to cover the range and concentration of estuarine, coastal and open water sites. At least one sample in each pair contained the determinands at concentrations expected in estuarine or coastal region. Where possible the number of samples containing very low concentrations was limited to reduce the number of analyses reporting 'less than' values.

Aqueous samples were in some cases supplied as sea water with an accompanying spike material. This was the case for the organophosphorus compounds which are unstable for long periods in sea water. In some samples the raw, unfiltered sea water was provided while in other cases the sea water was filtered.

The majority of sediment and biota samples were provided as natural or processed unspiked homogeneous samples. Spiked samples in the development exercises were notified to the participants. Test materials designed for the development exercises to examine different parts of the analytical methodology covered calibration solutions, raw and cleaned-up extracts or digests in addition to the complete matrix. Spiked materials were also included.

Test materials were despatched by courier within one month of the commencement of each round of testing. Participants were able to request test material at any time, however, the project office could not guarantee the timely arrival of the test material if it was ordered after the normal despatch date for that round. All participants were notified of the despatch of all test materials either by fax or more recently via the QUASIMEME II newsletter.

Matrices and Determinands

Four test materials for each group of determinands were issued during the year as a split level test approximately every six months. One set of test material was issued for the development exercises. Where participants selected the development exercises, QUASIMEME recommended that the routine group samples were also selected to give a comprehensive laboratory test. The content of the scheme for the past year of QUASIMEME was essentially very similar to that proposed for the new year starting in June, details of which are given elsewhere in this bulletin.

Database Development

The database used in the initial QUASIMEME I project was developed for the present programme. This has allowed the participants data to be entered into the central database by diskette or e-mail ensuring swift and accurate data entry. To date there have been no incidences of corrupt or incorrect entries and no data from any participant has been overlooked or missed out in a assessment. Let's hope QUASIMEME can keep up the 100 % record.

The database has been updated to allow for following improvements:

1) A record of the constant and proportional error associated with the assigned values.
2) An automatic generation of additional tables for new determinand groups, e.g., volatile organic compounds, organophosphorus compounds and triazines.
3) Update of report format for participants data sheets.
4) Labels for sample delivery and airway bills.

The main addition to the database has been the inclusion of a financial database. This was developed so that the entry of a participants request will generate the acknowledgement of application and invoice. It also provides an automatic entry into the participant list, and generation of the appropriate data collector and request for samples. This automation of the finances has provided greater control and an auditable trail for the whole system.

The final update for 1996–97 has been to change the indexing system which will provide a much more reliable way of cross linking the data tables to improve the overall robustness and speed of the system. The next database up-date will be the long awaited move to a Windows based data collector which will (hopefully) be more appreciated than the first DOS version. All database updates have been undertaken by R and D Software under the direction of Dr Paul McKay.

Data Assessment

The assessment for each round was carried out by an internal team of assessors whose aim was to prepare detailed reports for each group of determinands within two months of the receipt of data. From Round 8 onwards, the individual laboratory performance page for each report was sent out ahead of the main report to inform participants of their performance within a month of submitting the data An overall summary of the data assessment of the four rounds of the QUASIMEME programme for 1996–7 are given in Tables 4 and 5. Rounds 6 and 8, and Rounds 7 and 9 which are similar are tabulated together. In general the data for the nutrients provide the best standard of performance with over 40 % of participants achieving a 100 % satisfactory performance for all determinands in the seawater samples with the performance measurement of nutrients in the estuarine water improving between the two rounds. It is important for laboratories to evaluate their data and to identify those areas of the analysis where the measurements can be improved. It is not possible to comment of the differences between just two rounds, particularly when additional details such as the concentration of the determinands plays such an important part in the overall performance of the laboratory. A detailed assessment of these data and for the current year will be made and presented to participants at the QUASIMEME Workshop to be held in Spring 1999.

Annual Summary of Data

Last year QUASIMEME offered a service to provide a summary report of all data submitted along with the Z score assessment on diskette, for a *small fee!* Although this service was requested by a number of laboratories, QUASIMEME has decided to offer this service to all participants as part of the overall support to the laboratories. Initially the data will be provided on diskette or as an attached e-mail file. The data on the file can be used for internal assessment, but more importantly these files can be used to froward the external QA data to the appropriate Agencies which collate the national or international environmental monitoring data. It is essential that al participants take the opportunity to provide these data to their respective monitoring organisations in order that they can evaluate the environmental data with the required level of assurance on the quality of information provided.

Table 1.

Participating laboratories, by country 1996–1997 and 1997–1998		
Country	QUASIMEME I I 1996–97	QUASIMEME I I 1997–98
Argentina	0	1
Australia	2	2
Belgium	4	7
Canada	2	6
Denmark	4	5
Faeroe Islands	1	1
Finland	4	3
France	6	5
Germany	22	18
Greece	4	2
Iceland	2	3
Italy	1	2
Latvia	1	2
Lithuania	1	0
Netherlands, The	4	5
Norway	7	10
Poland	4	2
Portugal	3	5
Republic of Ireland	2	2
Russia	2	1
Saudi Arabia	0	1
South Africa	1	2
Spain	11	8
Sweden	7	7
Turkey	1	1
United Kingdom	23	23
USA	0	12
Total	117	126

Table 2.

Participation by group 1996–1997 and 1997–1998		
Group no	1996–1997 No. labs/group	1997–1998 No. labs/group
AQ-1	71	59
AQ-2	49	42
AQ-3	56+	27
AQ-4	26	22
AQ-5	27	16
AQ-6	17	10
AQ-7	19	10
AQ-8	21	10
AQ-9/DE-4	9	8
MS-1	53	47
MS-2	37	34
MS-3	32	29
MS-4	24	N/A
MS-5	20	N/A
BT-1	47	42
BT-2	46	40
BT-3	9	8
BT-4	17 *	15#
DE-1	N/A	6
DE-2	N/A	18
DE-3	N/A	16
DE-4	N/A	8

+ this was an ICES I/C exercise to which QUASIMEME institutes which were not already ICES laboratories were invited to participants.
* CBs and OCPs - development exercise
# PAH shellfish
N/A not available for that year

ANNEX 4

PAH GUIDELINES

Guidelines for the Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Biota

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1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) consist of a variable number of fused aromatic rings. By definition, PAHs contain at least three fused rings, although in practice related compounds with two fused rings (such as naphthalene and its alkylated derivatives) are often determined and will be considered in these guidelines. PAHs arise from incomplete combustion processes and from both natural and anthropogenic sources, although the latter generally predominate. PAHs are also found in oil and oil products, and these include a wide range of alkylated PAHs formed as a result of diagenetic processes, whereas PAHs from combustion sources comprise mainly parent (non-alkylated) PAHs. PAHs are of concern in the marine environment for two main reasons: firstly, low-molecular weight (MW) PAHs can be directly toxic to marine animals; secondly, metabolites of some of the high-MW PAHs are potent animal and human carcinogens, benzo[*a*]pyrene is the prime example. Carcinogenic activity is closely related to structure, however, and benzo[*e*]pyrene and four benzofluoranthene isomers (all six compounds have a molecular weight of 252 Da) are much less potent. Some compounds (e.g., heterocyclic compounds containing sulphur, such as benzothiophenes and dibenzothiophenes) may also cause taint in commercially exploited fish and shellfish and render them unfit for sale. PAHs are readily taken up by marine animals both across gill surfaces and from their diet, and may bioaccumulate, particularly in shellfish. Filter-feeding organisms such as bivalve molluscs can accumulate high concentrations of PAHs, both from chronic discharges to the sea (e.g., of sewage) and following oil spills. Fish are exposed to PAHs both via uptake across gill surfaces and from their diet, but do not generally accumulate high concentrations of PAHs as they possess an effective mixed-function oxygenase (MFO) system which allows them to metabolize PAHs and to excrete them in bile. Assessment of exposure of fish to PAHs therefore requires also the determination of PAH-metabolite concentrations in bile samples, as turnover times can be extremely rapid. The analysis of PAHs in fish muscle tissue should normally only be undertaken for food quality assurance purposes (Law and Biscaya, 1994).

There are marked differences in the behaviour of PAHs in the aquatic environment between the low-MW compounds (such as naphthalene; 128 Da) and the high-MW compounds (such as benzo[*ghi*]perylene; 276 Da) as a consequence of their differing physico-chemical properties. The low-MW compounds are appreciably water soluble and can be bioaccumulated from the 'dissolved' phase by transfer across gill surfaces, whereas the high-MW compounds are relatively insoluble and hydrophobic, and can attach to both organic and inorganic particulates within the water column. PAHs derived from combustion sources may actually be deposited to the sea already adsorbed to atmospheric particulates, such as soot particles. The majority of PAHs in the water column will eventually be either taken up by biota or transported to the sediments, and deep-water depositional areas may generally be regarded as sinks for PAHs, particularly when they are anoxic.

2 APPROPRIATE SPECIES FOR ANALYSIS OF PAHs

2.1 Benthic Fish and Shellfish

All teleost fish have the capacity for rapid metabolism of PAHs, thereby limiting their usefulness for monitoring temporal or spatial trends of PAHs. Shellfish (particularly molluscs) generally have a lesser metabolic capacity towards PAHs, and so they are preferred because PAHs concentrations are generally higher in their tissues.

For the purposes of temporal trend monitoring, it is essential that long time series with either a single species or a limited number of species are obtained. Care should be taken that the sample is representative of the population and can be repeated annually. There are advantages in the use of molluscs for this purpose as they are sessile, and so reflect the degree of contamination in the local area to a greater degree than fish which are mobile. The analysis of fish tissues is often undertaken in conjunction with biomarker and disease studies, and associations have been shown between the incidence of some diseases (e.g., liver neoplasia) in flatfish and the concentrations of PAHs in the sediments over which they live and feed (Malins *et al.*, 1988; Vethaak and ap Rheinallt, 1992). The exposure of fish to PAHs can be assessed by the analysis of PAH-metabolites in bile, and by measuring the induction of mixed-function oxygenase enzymes which effect the formation of these metabolites. At offshore locations the collection of appropriate shellfish samples may be problematic if populations are absent, sparse or scattered, and the collection of fish samples may be simpler. Generally the analysis of PAHs in fish muscle tissue should only be considered for the purposes of food quality assurance.

2.2 First Choice Shellfish Species

Mytilus sp. (mussel)

The blue mussel (*Mytilus edulis*) occurs in shallow waters along almost all coasts of the Northeast Atlantic. It is therefore suitable for monitoring in nearshore waters. No distinction is made between *M. edulis* and *M. galloprovincialis* because the latter species, which may occur along Spanish and Portuguese coasts, fills a similar ecological niche. A sampling size range of 30–70 mm shell length is specified to ensure availability throughout the whole maritime area. In some areas (e.g., the Barents Sea), other species may be considered. Recent monitoring studies have indicated a seasonal cycle in PAH concentrations (particularly for combustion-derived PAHs) in mussels, with maximum concentrations in the winter prior to spawning and minimum concentrations in the summer. It is particularly important therefore that samples selected for trend monitoring and spatial comparisons are collected at the same time of year, and preferably in the first months of the year before spawning.

3 SAMPLING

3.1 Fish

Fish are not recommended for spatial or temporal trend monitoring of PAHs, but can be useful as part of biological effects studies or for food assurance purposes. The sampling strategy for biological effects monitoring is described in the JAMP Guidelines for Monitoring Contaminants in Biota.

3.2 Shellfish

For shellfish, the upper limit of shell length should be chosen in such a way that at least 20 mussels in the largest length interval can easily be found. The length stratification should be determined in such a way that it can be maintained over many years for the purposes of temporal trend monitoring. The length interval shall be at least 5 mm in size. The length range should be split into at least three length intervals (small, medium and large) which are of equal size after log transformation. For example, if the length range is 40–70 mm, then the interval boundaries could be as follows :

small: 40–48 mm shell length;
medium: 49–58 mm shell length;
large: 59–70 mm shell length.

4 TRANSPORTATION

Samples should be kept cool or frozen (at a temperature of –20 °C or lower) as soon as possible after collection. Live mussels should be transported in closed containers at temperatures between 5 and 15 °C, preferably below 10 °C. For

live animals it is important that the transport time is short and controlled (e.g., maximum of 24 hours). Frozen samples should be transported in closed containers at temperatures below –20 °C. If biomarker determinations are to be made, then it will be necessary to store tissue samples at lower temperatures, for example, in liquid nitrogen at –196 °C.

5 PRE-TREATMENT AND STORAGE

5.1 Contamination

Sample contamination may occur during sampling, sample handling, pre-treatment and analysis, due to the environment, the containers or packing materials used, the instruments used during sample preparation and from the solvents and reagents used during the analytical procedures. Controlled conditions are therefore required for all procedures, including the dissection of fish organs on-board ship. In the case of PAHs, particular care must be taken to avoid contamination at sea. On ships there are multiple sources of PAHs, such as the oils used for fuel and lubrication, and the exhaust from the ship's engines. It is important that the likely sources of contamination are identified and steps taken to preclude sample handling in areas where contamination can occur. A ship is a working vessel and there can always be procedures occurring as a result of the day-to-day operations (deck cleaning, automatic overboard bilge discharges, etc.) which could affect the sampling process. One way of minimizing the risk is to conduct dissection in a clean area, such as within a laminar-flow hood away from the deck areas of the vessel. It is also advisable to collect samples of the ship's fuel, bilge water, and oils and greases used on winches, etc., which can be used as fingerprinting samples at a later date, if there are suspicions of contamination in particular instances.

5.2 Fish

5.2.1 Dissection and storage

Ungutted fish should be wrapped separately in suitable material (e.g., aluminium foil) and frozen. If plastic bags or boxes are used, then they should be used as outer containers only, and should not come into contact with tissues. Organ samples (e.g., livers) should be stored in pre-cleaned containers made of glass, stainless steel or aluminium, or should be wrapped in pre-cleaned aluminium foil and shock-frozen quickly in liquid nitrogen or in a blast freezer. In the latter case, care should be taken that the capacity of the freezer is not exceeded (Law and de Boer, 1995). Cold air should be able to circulate between the samples in order that the minimum freezing time can be attained (maximum 12 hours). The individual samples should be clearly and indelibly labelled and stored together in a suitable container at a temperature of –20 °C until analysis. If the samples are to be transported during this period (e.g., from the ship to the laboratory), then arrangements must be made which ensure that the samples do not thaw out during transport. Subsamples for biomarker determinations should be collected immediately after death (maximum 1 hour) in order to minimize post-mortem changes in enzymatic and somatic activities, and stored in suitable vials in liquid nitrogen until analysis.

When samples are processed, both at sea and onshore, the dissection must be undertaken by trained personnel on a clean bench wearing clean gloves and using clean stainless steel knives and scalpels. Stainless steel tweezers are recommended for holding tissues during dissection. After each sample has been prepared, all tools and equipment (such as homogenizers) should be cleaned.

5.2.2 Subsampling

To sample fish muscle, care should be taken to avoid including any epidermis or subcutaneous fatty tissue in the sample. Samples should be taken underneath the red muscle layer. In order to ensure uniformity, the right side dorso-lateral muscle should be sampled. If possible, the entire right side dorsal lateral fillet should be homogenized and subsamples taken for replicate PAH determinations. If, however, the amount of material to be homogenized would be too large, a specific portion of the dorsal musculature should be chosen. It is recommended that the portion of the muscle lying directly under the first dorsal fin is used in this case.

When dissecting the liver, care should be taken to avoid contamination from the other organs. If bile samples are to be taken for PAH-metabolite determinations, then they should be collected first. If the whole liver is not to be homogenized, then a specific portion should be chosen in order to ensure comparability. Freeze-drying of tissue samples cannot be recommended for PAH determination, due to the contamination which may result from back-streaming of oil from the rotary pumps used to generate the vacuum.

When pooling of tissues is necessary, an equivalent quantity of tissue should be taken from each fish., e.g., 10 % from each whole fillet.

5.3 Shellfish

5.3.1 Depuration

Depending upon the situation, it may be desirable to depurate shellfish so as to void the gut contents and any associated contaminants before freezing or sample preparation. This is usually applied close to point sources, where the gut contents may contain significant quantities of PAHs associated with food and sediment particles which are not truly assimilated into the tissues of the mussels. Depuration should be undertaken in controlled conditions and in clean sea water; depuration over a period of 24 hours is usually sufficient. The aquarium should be aerated and, if possible, the temperature and salinity of the water should be similar to that from which the animals were removed.

5.3.2 Dissection and Storage

Mussels should be shucked live or after thawing if stored deep-frozen, and opened with minimum tissue damage by detaching the adductor muscles from the interior of at least one valve. The soft tissues should be removed, homogenized, and frozen in glass jars at –20 °C until analysis.

When samples are processed, both at sea and onshore, the dissection must be undertaken by trained personnel on a clean bench wearing clean gloves and using clean stainless steel knives and scalpels. Stainless steel tweezers are recommended for holding tissues during dissection. After each sample has been prepared, all tools and equipment (such as homogenizers) should be cleaned.

6 ANALYSIS

6.1 Preparation of Materials

Solvents, reagents and adsorptive materials must be free of PAHs and other interfering compounds. If not, then they must be purified using appropriate methods. Reagents and absorptive materials should be purified by solvent extraction and/or by heating in a muffle oven as appropriate. Glass fibre materials (e.g., Soxhlet thimbles) should be cleaned by solvent extraction, and filter papers should be thoroughly solvent-rinsed before use. It should be borne in mind that clean materials can be re-contaminated by exposure to laboratory air, particularly in urban locations, and so storage after cleaning is of critical importance. Ideally, materials should be prepared immediately before use, but if they are to be stored, then the conditions should be considered critically. All containers which come into contact with the sample should be made of glass, and should be pre-cleaned before use. Appropriate cleaning methods would include washing with detergents, rinsing with water, and finally solvent-rinsing immediately before use. Heating of glassware in an oven (e.g., at 400 °C for 24 hours) can also be useful in removing PAH contamination.

6.2 Lipid Determination

Although PAH data are not usually expressed on a lipid basis, the determination of the lipid content of tissues can be of use in characterizing the samples. The lipid content should be determined on a separate subsample of the tissue homogenate, as some of the extraction techniques used routinely for PAH determination (e.g., alkaline saponification) destroy lipid materials. The total fat weight should be determined using the method of Bligh and Dyer (1959) or an equivalent method.

6.3 Dry Weight Determination

Generally PAH data are expressed on a wet weight basis, but sometimes it can be desirable to consider them on a dry weight basis. Again, the dry weight determination should be conducted on a separate subsample of the tissue homogenate, which should be air-dried to constant weight at 105 °C.

6.4 Extraction and Clean-up

PAHs are lipophilic and so are concentrated in the lipids of an organism, and a number of methods have been described for PAH extraction. The preferred methods generally utilize either Soxhlet extraction, or alkaline digestion followed by liquid-liquid extraction with an organic solvent. In the case of Soxhlet extraction, the wet tissue must be dried by mixing with a chemical agent (e.g., anhydrous sodium sulphate), in which case a time period of several hours is required between mixing and extraction in order to allow complete binding of the water in the sample. Alkaline digestion is

conducted on wet tissue samples, so this procedure is unnecessary. In neither case can freeze-drying of tissue prior to extraction be recommended because of the danger of contamination from oil back-streaming from the rotary pump (which provides the vacuum) into the sample. Apolar solvents alone will not effectively extract all the PAHs from tissues when using Soxhlet extraction, and mixtures such as hexane/dichloromethane may be effective in place of solvents such as benzene and toluene, used historically for this purpose. Alkaline digestion has been extensively used in the determination of PAHs and hydrocarbons and is well documented. It is usually conducted in alcohol (methanol or ethanol) which should contain at least 10 % water, and combines disruption of the cellular matrix, lipid extraction and saponification within a single procedure, thereby reducing sample handling and treatment. For these reasons, it should be the method of choice. Solvents used for liquid-liquid extraction of the homogenate are usually apolar, such as pentane or hexane, and these will effectively extract all PAHs.

Tissue extracts will always contain many compounds other than PAHs, and a suitable clean-up is necessary to remove those compounds which may interfere with the subsequent analysis. Different techniques may be used both singly or in combination, and the choice will be influenced by the selectivity and sensitivity of the final measurement technique and also by the extraction method employed. If Soxhlet extraction was used, then there is a much greater quantity of residual lipid to be removed before the analytical determination can be made than in the case of alkaline digestion. An additional clean-up stage may therefore be necessary. The most commonly used clean-up methods involve the use of alumina or silica adsorption chromatography, but gel permeation chromatography and similar high performance liquid chromatography (HPLC)-based methods are also employed (Nondek *et al.*, 1993; Nyman *et al.*, 1993; Perfetti *et al.*, 1992). The major advantages of using HPLC-based clean-up methods are their ease of automation and reproducibility.

6.5 Pre-concentration

The sample volume should be 2 ml or greater to avoid errors when transferring solvents during the clean-up stages. Evaporation of solvents using a rotary-film evaporator should be performed at low temperature (water bath temperature of 30 °C or lower) and controlled pressure conditions, in order to prevent losses of the more volatile PAHs such as naphthalenes. For the same reasons, evaporation to dryness should be avoided at all costs. When reducing the sample to final volume, solvents can be removed by a stream of clean nitrogen gas. Suitable solvents for injection into the gas chromatrograph (GC) or GC-MS include pentane, hexane, heptane and *iso*-octane, whereas for HPLC analyses acetonitrile and methanol are commonly used.

6.6 Selection of PAHs to be Determined

Because PAHs have not previously been included in collaborative monitoring programmes, no agreed list of determinands exists at present. The choice of PAHs to be analysed is not straightforward, both because of differences in the range of PAH compounds resulting from combustion processes and from oil and oil products, and also because the aims of specific monitoring programmes can require the analysis of different representative groups of compounds. PAHs arising from combustion processes are predominantly parent (unsubstituted) compounds, whereas oil and its products contain a much wider range of alkylated compounds in addition to the parent PAHs. This has implications for the analytical determination, as both HPLC-based and GC-based techniques are adequate for the determination of a limited range of parent PAHs in samples influenced by combustion processes, whereas in areas of significant oil contamination and following oil spills only GC-MS has sufficient selectivity to determine the full range of PAHs present. The availability of pure individual PAHs for the preparation of standards is problematic and limits both the choice of determinands and, to some degree, the quantification procedures which can be used. The availability of reference materials certified for PAHs is also rather limited. A list of target parent and alkylated PAHs suitable for environmental monitoring is given in Table 1, and this differs both from the list previously developed within ICES specifically for intercomparison purposes, and the historic list of Borneff. In both cases, these were concentrated on a subset of parent (predominantly combustion-derived) PAHs due to analytical limitations. This approach completely neglects the determination of alkylated-PAHs, which allows the interpretation of PAH accumulation from multiple sources including those due to oil inputs. It will not be necessary for all of these PAH compounds and groups to be analysed in all cases, but an appropriate selection can be made from this list depending on the specific aims of the monitoring programme to be undertaken.

6.7 Instrumental Determination of PAHs

Unlike the situation for chlorobiphenyls (CBs) where GC techniques (particularly GC-ECD) are used exclusively, two major approaches based on GC and HPLC are followed to an equal extent in the analysis of PAHs. The greatest sensitivity and selectivity in routine analyses are achieved by combining HPLC with fluorescence detection (HPLC-UVF) and capillary gas chromatography with mass spectrometry (GC-MS). In terms of flexibility, GC-MS is the most capable technique, as in principle it does not limit the selection of determinands in any way, while HPLC is suited only

to the analysis of parent PAHs. In the past, analyses have also been conducted using HPLC with UV-absorption detection and GC with flame-ionization detection, but neither can be recommended because of their relatively poor selectivity. Both in terms of the initial capital cost of the instrumentation, and cost per sample analysed, HPLC-UVF is cheaper than GC-MS. With the advent of high-sensitivity benchtop GC-MS systems, however, this cost advantage is now not as marked as in the past, and the additional information regarding sources available makes GC-MS the method of choice.

Intercomparison exercises have demonstrated a serious lack of comparability between specific hydrocarbon concentrations measured in different laboratories and using both analytical approaches described above (Farrington *et al.*, 1986). An interlaboratory performance study has recently been carried out within the QUASIMEME laboratory testing scheme in order to assess the current level of comparability among laboratories conducting PAH analyses and to identify improvements in methodology, but samples of biota have not yet been distributed in this series of exercises (Law and Klungsøyr, 1996; Law *et al.*, 1998).

Limits of determination within the range of 0.1 to 0.5 $\mu g\ kg^{-1}$ wet weight for individual PAH compounds should be achievable by both GC-MS and HPLC-UVF techniques.

6.8 HPLC

Reversed-phase columns (e.g., octadecylsilane (RP–18) of 15–30 cm in length are used almost exclusively, in conjunction with gradient-elution using mixtures of acetonitrile/water or methanol/water. A typical gradient may start as a 50 % mixture, changing to 100 % acetonitrile or methanol in 40 minutes. This flow is maintained for 20 minutes, followed by a return to the original conditions in 5 minutes and 5–10 minutes equilibration before the next injection. The use of an automatic injector is strongly recommended. Also, the column should be maintained in a column oven heated to 10–30 8 °C. The systems yielding the best sensitivity and selectivity utilise fluorescence detection. As different PAH compounds yield their maximum fluorescence at different wavelengths then for optimum detection of PAHs the wavelengths of the detector should be programmed so that the excitation/emission wavelengths detected are changed at preset times during the analytical determination. For close-eluting peaks it may be necessary to use two detectors in series utilising different wavelength pairs, or to effect a compromise in the selected wavelengths if a single detector is used. As the fluorescence signals of some PAHs (e.g., pyrene) are quenched by oxygen, the eluents must be degassed thoroughly. This is usually achieved by continuously bubbling a gentle stream of helium through the eluent reservoirs, but a vacuum degasser can also be used. Polytetrafluorethylene (PTFE) tubing must not then be used downstream of the reservoirs as this material is permeable to oxygen—stainless steel or polyetheretherketone (PEEK) tubing is preferred.

6.9 GC-MS

The two injection modes commonly used are splitless and on-column injection. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. If splitless injection is used, the liner should be of sufficient capacity to contain the injected solvent volume after evaporation. For PAH analysis, the cleanliness of the liner is also very important if adsorption effects and discrimination are to be avoided, and the analytical column should not contain active sites to which PAHs can be adsorbed. Helium is the preferred carrier gas, and only capillary columns should be used. Because of the wide boiling range of the PAHs to be determined and the surface-active properties of the higher-PAHs, the preferred column length is 25–30 m, with an internal diameter of 0.15 to 0.3 mm. Film thicknesses of 0.3 to 1 μm are generally used; this choice has little impact on critical resolution, but thicker films are often used when one-ring aromatic compounds are to be determined alongside PAHs, or where a high sample loading is needed. No stationary phase has been found on which all PAH isomers can be resolved; the most commonly used stationary phase for PAH analysis is 5 % phenyl methylsilicone (DB-5 or equivalent). This will not, however, resolve critical isomers such as benzo[*b*], [*j*] and [*k*]fluoranthenes, or chrysene from triphenylene. These separations can be made on other columns if necessary. For PAHs there is no sensitivity gain from the use of chemical ionization (either positive or negative ion), so analyses are usually conducted in electron-impact mode at 70eV. The choice of full-scan or multiple-ion detection is usually made in terms of sensitivity. Some instruments such as ion-trap mass spectrometers exhibit the same sensitivity in both modes and so full-scan spectra are collected, whereas for quadrupole instruments greater sensitivity is obtained if the number of ions scanned is limited. In that case, the masses to be detected are programmed to change during the analysis as different PAHs elute from the capillary column.

7 CALIBRATION AND QUANTIFICATION

7.1 Standards

A range of fully-deuterated parent PAHs is available for use as standards in PAH analysis. The availability of pure PAH compounds is limited. Although most of the parent compounds can be purchased as pure compounds, the range of possible alkyl-substituted PAHs is vast and only a limited selection of them can be obtained. In HPLC where the resolving power of the columns is limited and the selectivity less than that which can be obtained using MS detection, only a single internal standard is normally used (e.g., phenanthrene-d_{10}) although fluoranthene-d_{10} and 6-methyl chrysene, among others, have also been used. If GC-MS is used, then a wider range of deuterated PAHs can be utilized, both because of the wide boiling range of PAHs present and because that allows the use of both recovery and quantification standards. Suitable standards could range from naphthalene-d_8 to perylene-d_{12}. Crystalline PAHs of known purity should be used for the preparation of calibration standards. If the quality of the standard materials is not guaranteed by the producer or supplier (as for certified reference materials), then it should be checked by GC-MS analysis. Solid standards should be weighed to a precision of 10^{-5} grams. Calibration standards should be stored in the dark as some PAHs are photosensitive, and ideally solutions to be stored should be sealed in amber glass ampoules. Otherwise, they can be stored in measuring cylinders in a refrigerator.

7.2 Calibration

Multi-level calibration with at least five calibration levels is preferred to adequately define the calibration curve. In general, GC-MS calibration is linear over a considerable concentration range but exhibits non-linear behaviour when the mass of a compound injected is low due to adsorption. Quantification should be conducted in the linear region of the calibration curve, or the non-linear region must be well characterized during the calibration procedure. For HPLC-UVF the linear range of the detection system should be large, and quantification should be made within the linear range. External standardization is often used with HPLC due to the relatively limited resolution obtainable with this technique as generally employed.

7.3 Recovery

The recovery of analytes should be checked and reported. Given the wide boiling range of PAHs to be determined, the recovery may vary with compound group, from the volatile PAHs of low molecular weight to the larger compounds. For GC-MS analysis, deuterated standards can be added in two groups: those to be used for quantification are added at the start of the analytical procedure, whilst those from which the absolute recovery will be assessed are added prior to GC-MS injection. This ensures that the calculated PAH concentrations are corrected for the recovery obtained in each case. In the case of HPLC, where only a single deuterated PAH standard is used, it is more common to assess recovery periodically by carrying a standard solution through the whole analytical procedure, then assessing recovery by reference to an external standard. This technique does not, however, correct for matrix effects, and so may be used in conjunction with the spiking of real samples.

8 ANALYTICAL QUALITY CONTROL

Further information on analytical quality control procedures for PAHs can be found elsewhere (Law and de Boer, 1995). A procedural blank should be measured with each sample batch, and should be prepared simultaneously using the same chemical reagents and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will result in errors in quantification. The procedural blank is also very important in the calculation of limits of detection and limits of quantification for the analytical method. In addition, a laboratory reference material (LRM) should be analysed within each sample batch. The LRM must be homogeneous and well-characterized for the determinands of interest within the analytical laboratory. Ideally, stability tests should have been undertaken to show that the LRM yields consistent results over time. The LRM should be of the same matrix type (e.g., liver, muscle, mussel tissue) as the samples, and the determinand concentrations should be in the same range as those in the samples. Realistically, and given the wide range of PAH concentrations encountered, particularly in oil spill investigations, this is bound to involve some compromise. The data produced for the LRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision, but a certified reference material (CRM) of a similar matrix should be analysed periodically in order to check the method bias. The availability of biota CRMs certified for PAHs is very limited, and in all cases the number of PAHs for which certified values are provided is small. At present, only NIST 1974a (a frozen wet mussel tissue) and NIST 2974 (a freeze dried mussel tissue) are available. At regular intervals, the laboratory should

participate in an intercomparison or proficiency exercise in which samples are circulated without knowledge of the determinand concentrations, in order to provide an independent check on performance.

9 DATA REPORTING

The calculation of results and the reporting of data can represent major sources of error, as has been shown in intercomparison studies for PAHs. Control procedures should be established in order to ensure that data are correct and to obviate transcription errors. Data stored on databases should be checked and validated, and checks are also necessary when data are transferred between databases. Data should be reported in accordance with the latest ICES reporting formats.

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Table 1. Target parent and alkylated PAHs (including some oil-derived sulphur heterocyclic compounds) for environmental monitoring.

Compound	MW	Compound	MW
Naphthalene	128	C_2 -Phenanthrenes/Anthracenes	206
C_1 -Naphthalenes	142	C_3 -Phenanthrenes/Anthracenes	220
C_2 -Naphthalenes	156	Fluoranthene	202
C_3 -Naphthalenes	170	Pyrene	202
C_4 -Naphthalenes	184	C_1 -Fluoranthenes/Pyrenes	216
Acenaphthylene	152	C_2 -Fluoranthenes/Pyrenes	230
Acenaphthene	154	Benz[*a*]anthracene	228
Biphenyl	154	Chrysene	228
Fluorene	166	2,3-Benzanthracene	228
C_1 -Fluorenes	180	Benzo[*a*]fluoranthene	252
C_2 -Fluorenes	194	Benzo[*b*]fluoranthene	252
C_3 -Fluorenes	208	Benzo[*j*]fluoranthene	252
Dibenzothiophene	184	Benzo[*k*]fluoranthene	252
C_1 -Dibenzothiophenes	198	Benzo[*e*]pyrene	252
C_2 -Dibenzothiophenes	212	Benzo[*a*]pyrene	252
C_3 -Dibenzothiophenes	226	Perylene	252
Phenanthrene	178	Indeno[1,2,3-*cd*]pyrene	276
Anthracene	178	Benzo[*ghi*]perylene	276
C_1 -Phenanthrenes/Anthracenes	192	Dibenz[*ah*]anthracene	278

ANNEX 5

STUDY ON THE BEHAVIOUR OF TRACE ELEMENTS IN COD LIVERS FROM ICELANDIC WATERS

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INTRODUCTION

Monitoring programmes deal with comparisons of concentrations of analytes in various compartments. For being able to do so, the laws governing the natural variation of the analytes in the compartment in question must be known. Cod livers are widely used for monitoring purposes, both for organic and inorganic analytes, where sampling is based on length of fish, usually 30–45 cm is selected for monitoring of spatial trends, and sampling of 25 individuals per sample is performed prior to spawning. However, it is well known that levels of trace elements may vary considerably in cod livers where factors of ten or more between the lowest and highest concentrations are not uncommon within a sample. This variability of trace element results have often been related to variation in the fat content of the livers. The fat content of cod livers may vary dramatically with season. In the North Atlantic, an increase in liver lipids is observed from autumn until the end of the year. When gonads start to develop in the beginning of the year, the liver lipids decrease and reach a minimum shortly after spawning in the springtime. This cyclical variation may be between 10 % and 70 % fat in the liver. However, great variability is found between individual fishes of similar sizes at the same ground and the same time. Differences are also observed in this cyclical behaviour from one year to another at the same fishing ground (affected by for example food availability and temperature). Higher fat content than 70–75 % is rarely found and lower fat than 10 % is uncommon. However, as low as 2 % fat has been found in liver of 40–70 cm cod during extreme starvation in the laboratory (livers weighing 4–10g) (R.M. Love, 1958, J. Sci. Fd. Agric., 9: 617–620). This cyclical change occurs both in mature and immature cod although the variability may be greater in mature cod. Finally, the fatty acid composition of the fat varies with amount of fat. In a study by K.D. Witt (1963, J. Sci. Fd. Agric., 14: 92–98) on cod liver oils from six fishing grounds (White Sea, Iceland, Bear Island, the Norwegian coast, Greenland, and the Faroes), a distinct increase was found for the iodine value (a measure of unsaturation) of the oil from August 1961 to January 1962. In a study of P.M. Jangaard *et al.* (1967a, J. Fish. Res. Bd. Canada, 24: 607–612 and 1967b, J. Fish. Res. Bd. Canada, 24: 613–627) on cod from Terence Bay, Nova Scotia, an increase was found of 20:1 and 22:1 (especially in female fish) with increased fat content of the livers, i.e., decreased unsaturation with fat content in contrast to the results for cod from the Northeast Atlantic. Thus, cod from different fishing grounds or different stocks of cod may show quite dissimilar behaviour.

The aim of the work here presented was to look into the data on trace elements in cod livers from Icelandic monitoring studies (1994–1996) for examining possible relations between element concentrations and various biological covariables. Possible ways to normalize trace element concentrations in cod livers have been looked into by working groups within ICES and date at least back to a paper by N.W. Green in 1987 (The importance of liver lipids in assessing cadmium and PCB trends in cod liver from the outer Oslofjord. ICES CM 1987/E:24, Annex 8, pp. 51–66). As late as 1996 this was an issue of the ICES Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM), that met in Stockholm 18–22 March 1996 (item 6.2). WGSAEM referred to much of earlier work by MCWG on the subject and came to the following conclusion: 'Lean (wet-fat) is the most appropriate basis for expressing zinc concentrations. Further corrections cannot be recommended based on these (Swedish and Norwegian) data. In particular, there seems to be no gain in correcting for water and expressing metals on a dry lean basis, possibly due to major analytical errors in the measurement of total dry %. For other metals (Cd, Cu) no clear picture could be obtained.'

Concentrations of inorganic and organic contaminants are generally low in cod livers from Icelandic waters and these waters may be considered unpolluted. However, direct comparison with data from other waters, e.g., those appearing in *ICES Cooperative Research Report* No. 176 (April 1991) and *ICES Cooperative Research Report* No. 151 (January 1988), cadmium levels are generally higher in Icelandic cod livers than in other areas of the Northeast Atlantic while the levels of copper and zinc are generally lower. These characteristics are most likely attributable to some natural processes, the nature of which is still not known.

MATERIALS

Sampling took place in the years 1994, 1995, and 1996. Most samples were taken off NW, NE, SE, S, and SW Iceland in March or the beginning of April each year. Each sample consisted of 25 individuals except the 30–45 cm cods off NE-Iceland, where 50 individuals were collected. In 1996, additional samples of length classes 15–30 cm, 45–60 cm, 60–75 cm, and 75–90 cm were collected off NE-Iceland and 45–60 cm and 60–75 cm in 1994. Furthermore, cod

samples of length class 30–45 cm were sampled off NE-Iceland in July and October 1994, January 1995, and June 1996. Altogether 17 samples were obtained, or 454 cod (8 samples in 1994, 1 sample in 1995, and 8 samples in 1996).

After selection in a length class, every fish was weighed, gutted, and the sex determined. Each liver was placed in a preweighed and precleaned glass jar. On arrival to the laboratory, the gutted fish was weighed, the length and age determined as well as the weight of the muscle tissue. The livers of each sample were pooled into five or more groups. The groups were chosen so as to have as homogeneous liver sizes as possible in each group. The number of livers in a group ranged from one to eight. When the subsamples were prepared, the livers were first homogenized by an Ultra-Turrax and then all the material from each glass jar was transferred and weighed into the pooled subsample. Losses upon this transfer were more or less a constant figure of about 0.1–0.25 g independent of liver size. Subsamples from each group were taken after thorough homogenisation of the pooled sample. A total of 110 groups were prepared from the 17 samples.

PARAMETERS STUDIED

The parameters analysed in the grouped samples are shown in Table A5.1 together with ranges of values they took. The higher ranges of the chemical constituents were most often found for cod livers of fish in the length class 30–45 cm sampled in March.

Table A5.1. Parameters analysed with ranges of values.

Parameter	Minimum for a group	Maximum for a group	Ratio
Length, cm	18.1	79.8	4.4
Weight, g	57.3	5239	91.4
Liver size, g	0.87	721.3	829
Age, +year	2	8	4
Moisture, mg/g	193.2	710.7	3.7
Fat, mg/g	91.0	749.6	8.2
Nitrogen, mg/g	5.70	26.25	4.6
Phosphorus, mg/g	0.88	3.16	3.6
Total ash, mg/g	3.65	14.85	4.1
Ca*, µg/g	20.7	403.2	19.5
Mg*, µg/g	41.6	255.6	6.1
Na*, µg/g	373	1876	5.0
K*, µg/g	779	3733	4.8
Zn, µg/g	6.10	66.8	11.0
Fe, µg/g	7.3	86.9	11.9
Mn, µg/g	0.34	2.67	7.8
Cu, µg/g	1.6	22.2	13.9
As*, µg/g	1.26	19.2	15.2
Se, µg/g	0.24	2.80	11.7
Pb, ng/g		<50	
Cd, ng/g	26	842	32.4

*Only analysed for samples from 1996.

RESULTS

Macroconstituents of cod livers

The weight fraction of fat, X_f, and the weight fraction of mosture, X_{aq}, are linearly related in the cod livers as shown in Figure A5.1., i.e., $X_{aq} = a - bX_f$. This relation prevails coherently for the whole range of data here presented. Additionally, several other studies at this laboratory dating back to 1965, show the same behaviour and it has been found that a and b in this equation are insignificantly different (95 % confidence level). Thus, the relation may be written as:

$X_{aq} = b \times (1 - X_f) = (0.7736 \pm 0.0033) \times (1 - X_f)$

(n = 110; r^2 = 0.994; 95 % confidence interval)

implying that on extrapolation to zero fat content ($X_f = 0$), the moisture content becomes b (77.4 %), and extrapolation to 100 % fat ($X_f = 1$), the moisture content becomes zero. However, these extreme values of fat in cod livers will not be found in nature.

By this way other macroconstituents may be evaluated in terms of fat or, for practical reasons, moisture, since moisture may be determined easily and accurately, e.g.,

weight fraction of dry matter: $X_{DM} = 1 - X_{aq} = 1 - b(1 - X_f)$

weight fraction of fat-free dry matter: $X_{ffDM} = X_{DM} - X_f = (1 - b) \times (1 - X_f) = [(1 - b)/b] \times X_{aq}$

weight fraction of fat-free liver or lean fraction: $X_l = 1 - X_f = (1/b) \times X_{aq}$

From the relation for X_{ffDM} it is seen that the ratio of fat-free dry matter and moisture in cod livers is given by $(1 - b)/b$ for all liver sizes, resulting in the well-known figure of about 1/4 (b = 0.8).

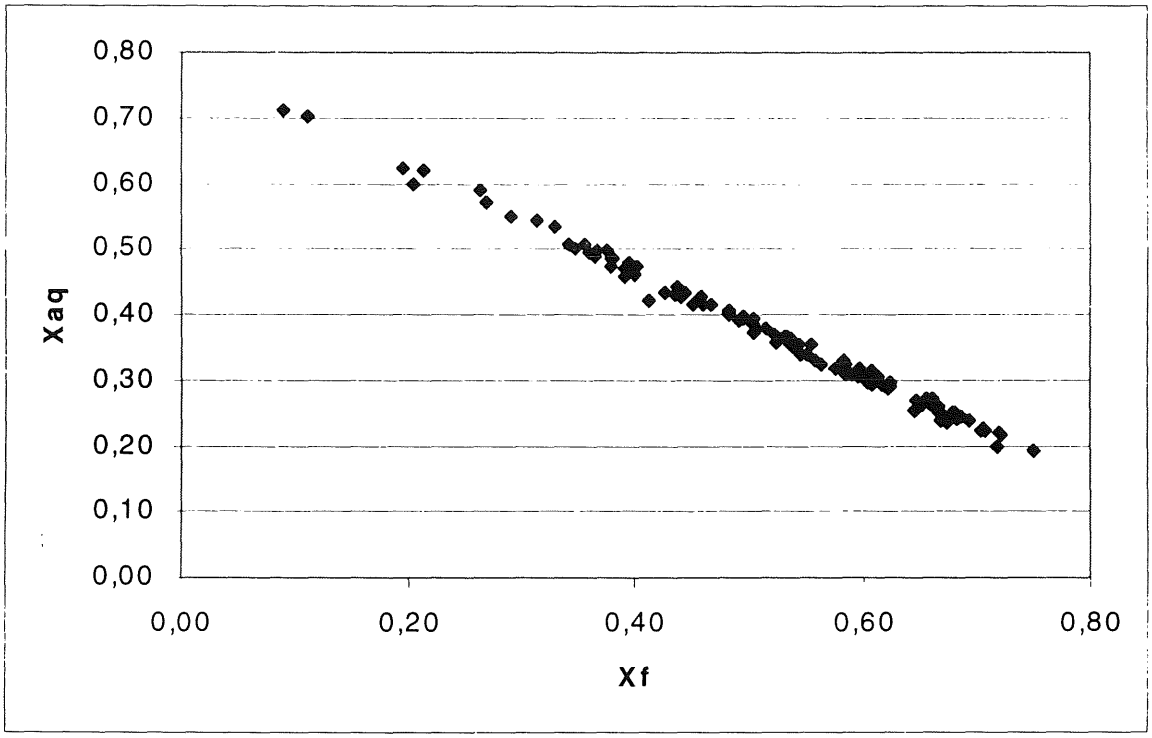

Figure A5.1. Relationship between weight fraction of fat and moisture in cod livers.

Figure A5.2 shows how X_f is related to the liver size, where it may be seen that a dramatic increase occurs in fat content in livers of up to about 100 g whereupon the fat levels off. The six points of 80–200 g livers that deviate from the rest, all derive from samples of 45–60 cm and 60–75 cm cod caught off NE-Iceland in 1994. Similarly, Figure A5.3. shows how the lean fraction $X_l = 1 - X_f$ decreases sharply for livers up to about 100 g where the lean fraction levels off at about 0.3.

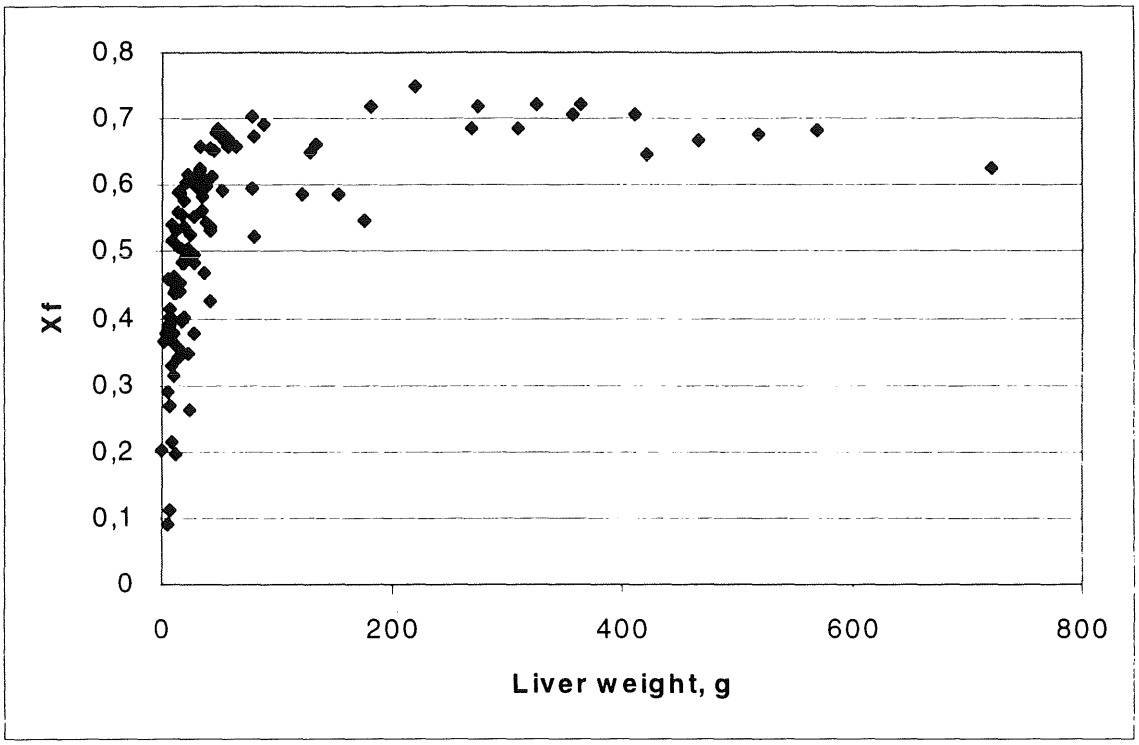

Figure A5.2. Behaviour of weight fraction of fat with increased size of cod livers.

Thus, all livers behave similarly with respect to fat content, i.e., independent of length and age of fish and independent of season or fishing ground. Liver sizes increase with length (age) of fish but the relationship between liver size and length may be quite different from one area to another and from one time to another. For example, cod samples (25 individuals each) from NW-Iceland in the years 1990–1996, one sample in March every year and of cod with average length between 35 and 40 cm, had livers with average weights ranging between 5 and 50 g. Within a year, individual livers from four samples taken from different places around Iceland vary between 2 and 100 g. Thus, the recommended sampling procedure results in liver sizes in a range where the rate of change in composition of the livers is greatest. Figures A5.2 and A5.3 imply that livers of sizes greater than about 100 g are of similar composition in macroconstituents at least. Thus, liver sizes greater than 100 g need to be sampled to ascertain samples of homogeneous composition, a sampling procedure that is not possible for practical reasons.

Weight of fat increases more slowly than the lean mass for small cod livers, Figure A5.4. However, as the liver becomes larger in size, the rate of increase in fat content increases and for 15–20 g livers, the mass of lean liver and fat are equal. For livers larger than about 20 g, both lean mass and fat weight increase linearly with liver weight where rate of increase in fat weight is about 3.5 times faster than for lean mass.

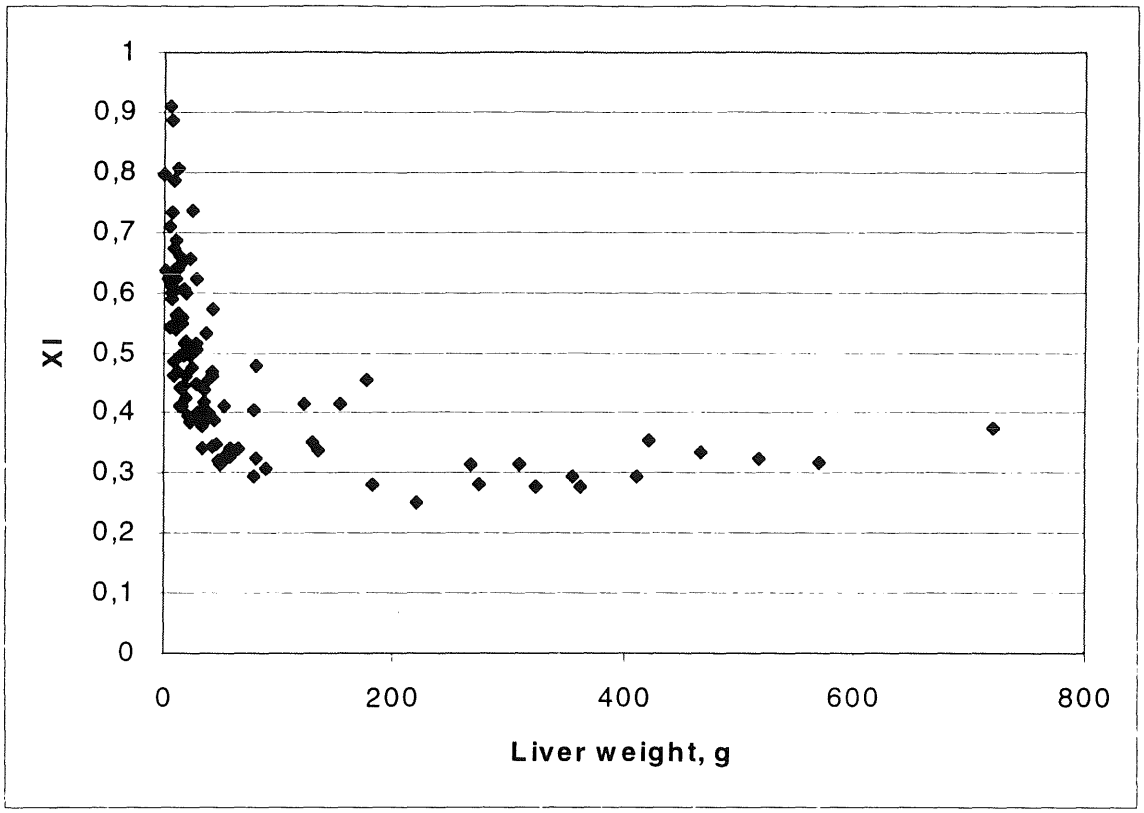

Figure A5.3. Lean weight fraction of cod livers.

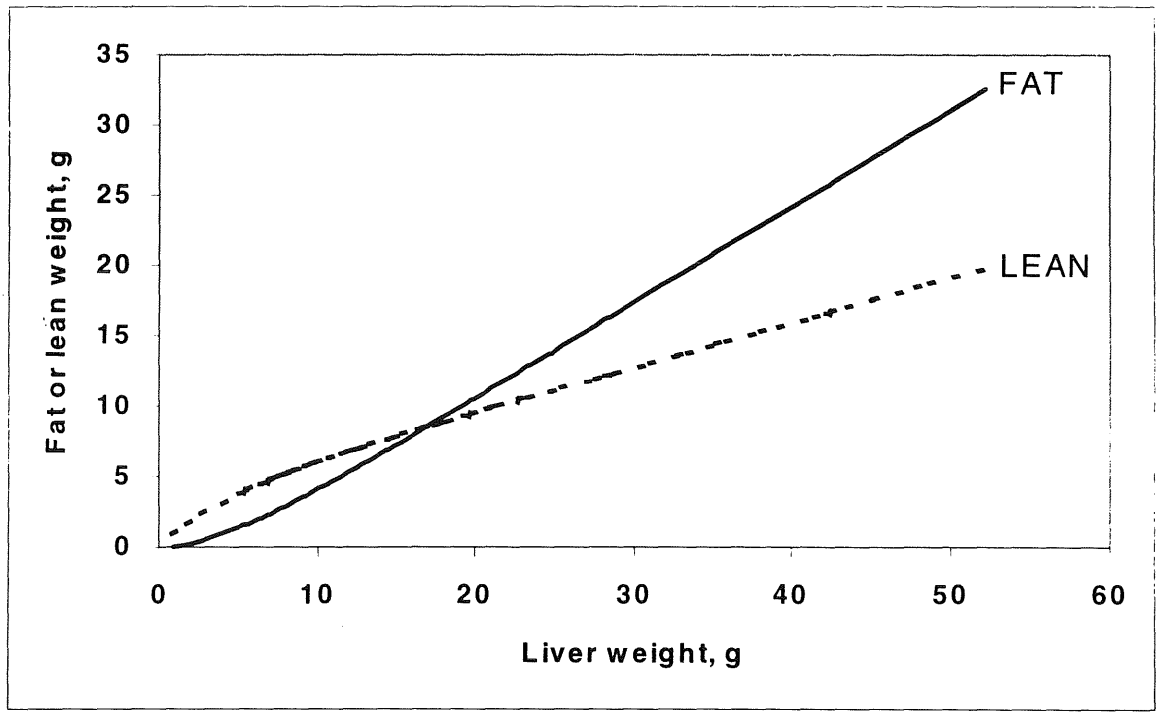

Figure A5.4. Weight of lean mass and fat in cod livers.

Microconstituents of cod livers

The behaviour of microconstituent levels with liver size in cod resembles generally that of the lean fraction, as shown for cadmium in Figure A5.5 and phosphorus in Figure A5.6. This behaviour implies that the livers not only have macroconstituents in uniform composition for liver sizes greater than 100 g but most inorganic analytes as well. The similarity in behaviour of the lean fraction and other inorganic components indicates not unexpectedly that inorganic constituents are to a large extent contained in the lean fraction and that there might exist some simple relationships between lean fraction and trace element content. In general, the liver burden of all inorganic constituents analysed in this study behaves in a linear log-log fashion with lean weight of the livers, i.e., usually a good correlation is obtained with an equation of the form

$$\mathrm{Ln}(B) = \alpha + \beta \times \mathrm{Ln}(m_l) + \delta\, \mathrm{Ln}(A)$$

where most often independence of age (A) is observed, i.e., δ is zero. (B = liver burden = $C \times M_L$, where C is wet weight concentration of analyte and M_L is the mass of liver (g); m_l is the lean weight of liver (g); A is age of fish in years; r^2 ranges from 0.83 for Fe up to 0.994 for phosphorus and nitrogen. Log-transformed data give better correlations than untransformed data since analytes and biological properties of cod-livers are log-normally distributed.

However, m_l and M_L are dependent variables since they are related by $m_l = X_l \times M_L$. Therefore it violates strict statistical methods to correlate B ($= C \times M_L$) and m_l ($= X_l \times M_L$). Using these relations, the equation

$$\mathrm{Ln}\,(B) = \alpha + \beta \times \mathrm{Ln}(m_l) + \delta\, \mathrm{Ln}(A)$$

may be rewritten as

$$\mathrm{Ln}\,(C) = \alpha + (\beta - 1) \times \mathrm{Ln}(M_L) + \beta \times \mathrm{Ln}(X_l) + \delta\, \mathrm{Ln}(A) = \alpha + \gamma \times \mathrm{Ln}(M_L) + \beta \times \mathrm{Ln}(X_l) + \delta\, \mathrm{Ln}(A)$$

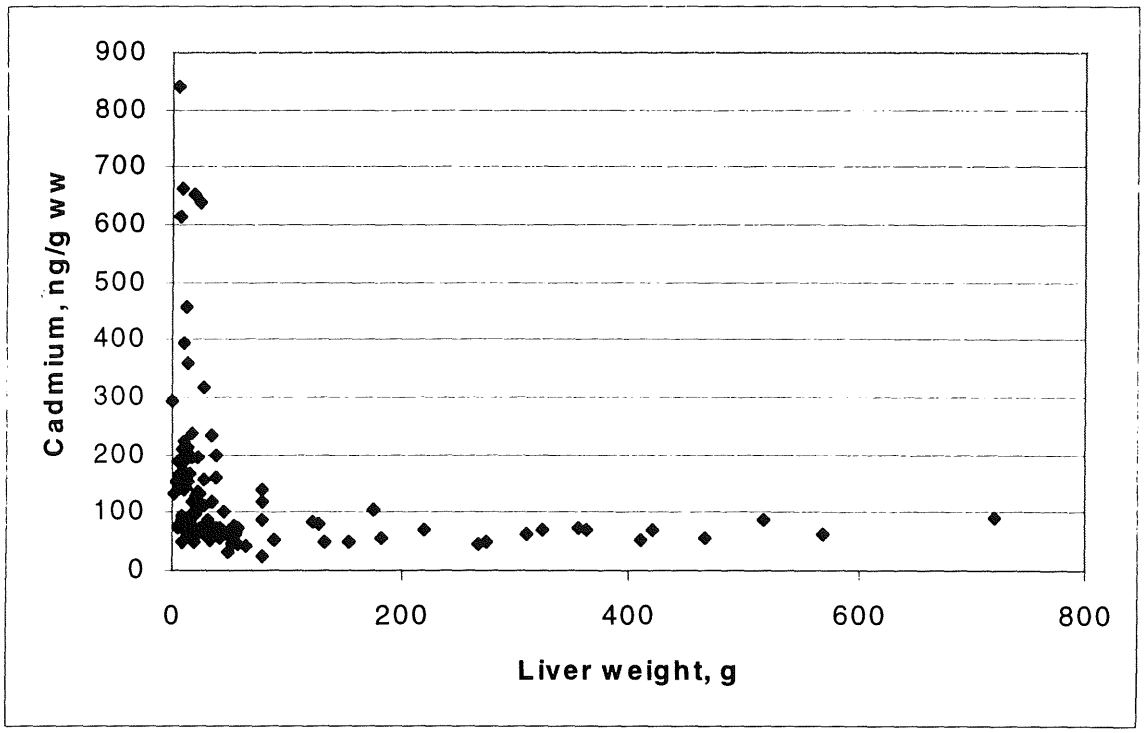

Figure A5.5. Cadmium in cod livers.

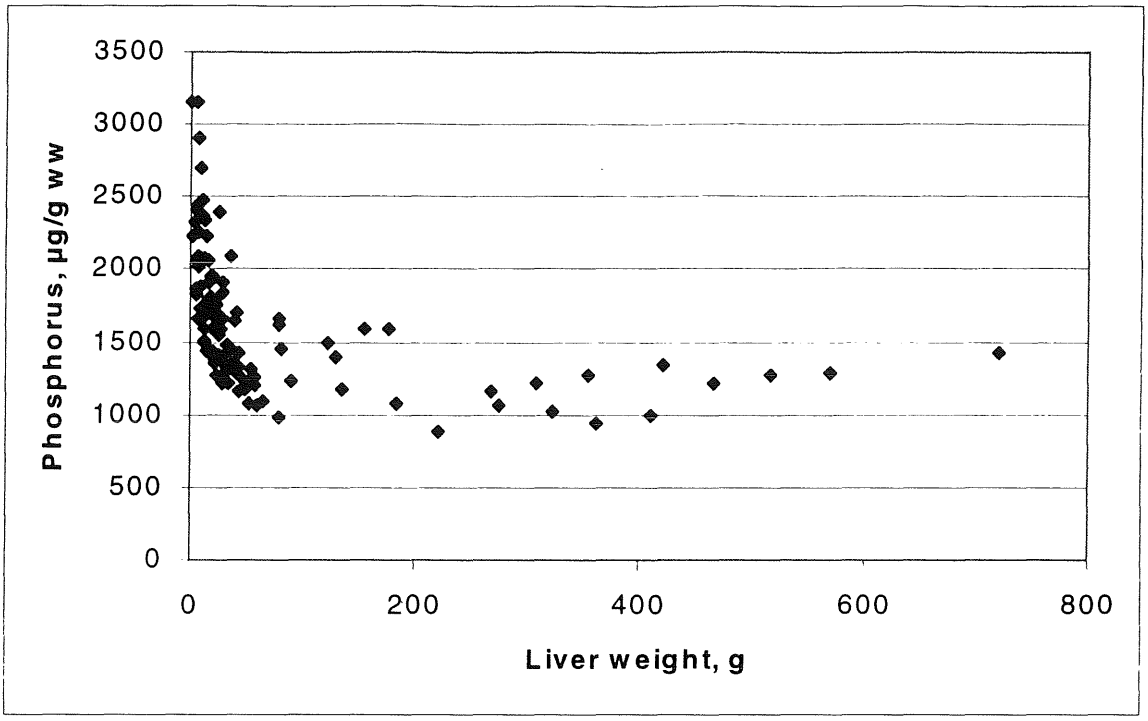

Figure A5.6. Phosphorus in cod livers.

Therefore, only if $\gamma = \beta - 1$ would it be statistically justifiable to correlate Ln(B) and Ln(m_l). Multiple regression applying this equation to the data gives the regressional parameters in Table A5.2.

Table A5.2. Estimates of α, β, γ, and δ in $\text{Ln}(C) = \alpha + \beta \times \text{Ln}(X_l) + \gamma \times \text{Ln}(M_L) + \delta \times \text{Ln}(A)$ with 95 % confidence limits and the corresponding total correlation coefficients (n = 110 except for As and Zn, n = 59).

Parameter	α	β	γ	δ	r^2
Moisture, mg g^{-1}	6.664 ± 0.013	1.022 ± 0.015	0	0	0.993
Nitrogen, mg g^{-1}	3.25 ± 0,06	0.971 ± 0,084	–0.069 ± 0.030	0.12 ± 0.08	0.95
Phosphorus, mg g^{-1}	7.96 ± 0.07	0.812 ± 0.094	–0.046 ± 0.032	0.16 ± 0.09	0.91
Total ash, mg g^{-1}	2.64 ± 0.07	0.951 ± 0.093	–0.035 ± 0.032	0.13 ± 0.09	0.93
Cd***, ng g^{-1}	4.66 ± 0.25	1.21 ± 0.34	–0.40 ± 0.11	1.78 ± 0.30	0.80
Cu, µg g^{-1}	1.65 ± 0.23	0.91 ± 0.30	–0.14 ± 0.10	0.67 ± 0.29	0.599
Mn, µg g^{-1}	1.08 ± 0.11	0.99 ± 0.21	–0.089 ± 0.048	0	0.79
Se, µg g^{-1}	1.19 ± 0.12	1.44 ± 0.22	–0.086 ± 0.050	0	0.86
Fe**, µg g^{-1}	4.63 ± 0.18	1.93 ± 0.21	0	0	0.78
As*, µg g^{-1}	2.38 ± 0.20	0.97 ± 0.23	0	0	0.56
Zn*, µg g^{-1}	3.47 ± 0.11	1.21 ± 0.12	0	0	0.877

* Only analysed for samples from 1996.

** For Fe, all the subsamples from SW-Iceland (both 1994 and 1996) were excluded in the regression as they showed significantly higher concentrations than other samples when examined for covariables (n = 98).

*** For Cd, all the subsamples taken off NW-Iceland were excluded since they showed significantly and consistently higher concentrations than other samples upon inspection for effects of covariables (n = 100); this higher concentration of cadmium off NW-Iceland has also been noted in earlier years.

The best correlation is obtained for the macroconstituents (moisture, nitrogen, phosphorus, and total ash). Of the trace elements, zinc, selenium, and cadmium show the best adherence to the equation while arsenic and copper deviate most.

On the basis of the regressional parameters shown in Table A5.2, the results may be summarised in the following way:

I. Neither age of fish nor total liver weight affects concentration ($\gamma = \delta = 0$).

Arsenic. Arsenic gives the simplest behaviour since $\beta = 1$, i.e., the concentration of arsenic is constant in the lean fraction of the liver independent of size of lean fraction, liver size or age. Thus, the equation for arsenic simplifies to $\mathrm{Ln}(C_l) = \alpha$, where C_l is the concentration based on lean weight.

Moisture, zinc, iron. For these analytes $\beta > 1$ and therefore the concentration of these, whether expressed on wet weight or lean weight, increases with increased lean fraction of the liver.

For moisture, β is only slightly but significantly (at 95 % level) higher than unity. Direct correlation of X_l and X_{aq} above gave a similar correlation ($r^2 = 0.994$) as here for the log-transformed data ($r^2 = 0.993$).

II. Total liver size influences the concentration ($\gamma \neq 0$) while age does not ($\delta = 0$).

Manganese. For manganese, γ is insignificantly different from $\beta - 1$, i.e., the use of the simplified equation for manganese is warranted: $\mathrm{Ln}(B) = \alpha + \beta \times \mathrm{Ln}(m_l)$. This equation results in better estimates of the regressional parameters due to better correlation: $\alpha = 1.057 \pm 0.102$ and $\beta = 0.896 \pm 0.036$ ($r^2 = 0.95$). From this it is seen that $\beta < 1$ and therefore the lean weight based concentration of manganese decreases with increased lean weight of the livers, also clearly seen by plotting the data [$\mathrm{Ln}(C_l)$ vs. $\mathrm{Ln}(m_l)$].

Selenium. For selenium, γ is significantly different from $\beta - 1$ and $\beta > 1$. Increased liver sizes (and concomitant decrease in lean fraction up to 100 g livers) result in decreased concentration of selenium, i.e., as for manganese both the lean fraction term [$\beta \times \ln(X_l)$] and the term with total liver mass [$\gamma \times \mathrm{Ln}(M_L)$] result in decreased concentration of selenium with increased liver size, both when the concentration is based on wet weight and when it is based on lean weight.

III. Both age and total liver size affect concentration.

The effect of older age of fish is always to increase the concentration, similarly for all the macroconstituents (total nitrogen, total phosphorus, and total ash) while copper and especially cadmium are much more affected.

Copper, nitrogen and ash. For these, $\gamma + 1$ is insignificantly different from β. Therefore, a simplified equation is justified for these, i.e.,

$$\mathrm{Ln}(B) = \alpha + \beta \times \mathrm{Ln}(m_l) + \delta \times \mathrm{Ln}(A)$$

resulting in better correlation (r^2 from 0.941 (copper) to 0.994 (nitrogen and ash)) showing that $\beta < 1$ at a 95 % confidence level. Thus, all these analytes on a lean weight basis decrease in concentration with increased lean weight of the liver. This is often counteracted by the positive effect of age since lean weight increases generally with age.

Cadmium. This element has $\gamma + 1$ significantly different from β and β is insignificantly different from unity. Thus, cadmium on a lean weight basis decreases with increased liver size but this effect is somewhat counteracted by age. For the data here under study, normalization of the cadmium concentrations with the help of the relationship obtained reduces the relative standard deviation of the whole data set from about 90 % to 25 %.

Phosphorus. This element has $\gamma + 1$ significantly different from β and $\beta < 1$. Phosphorus, on a wet weight basis, decreases with liver size, an effect strengthened by the concomitant decrease in lean fraction. However, the variability decreases somewhat when phosphorus is expressed on a lean weight basis since then the effect of lean fraction, $(\beta - 1) \times \mathrm{Ln}(X_l)$, counteracts the effect of total liver weight.

GENERAL CONCLUSIONS

It is apparent that due to the great variability of sizes and thereby composition of cod livers and the complicated effects these variations have on trace elements, cod livers are not very well suited for monitoring studies. However, they usually contain higher levels of contaminants than other tissues of cod, especially muscle tissue, and thereby the analysis of trace elements becomes more reliable. Furthermore, cod livers are believed to reflect concentrations in the marine environment. Therefore, large data sets on contaminants in cod livers have been collected, e.g., within OSPAR and AMAP. The information obtainable from these data may be substantially increased if the effects of biological covariables are taken into account. The study here presented may be of help in interpreting data from Icelandic waters but the models need not apply for other waters. The effect of biological covariables of cod livers from other areas needs to be known if meaningful spatial comparisons are to be performed and the effects of covariables must of course also be known when temporal trends in a given area are studied. A common basis for spatial and temporal comparisons might possibly be hypothetical cod livers of 1 g and 100 % lean fraction from cod of one year's age where effects of lean fraction, liver size and age cancel out, i.e., $\mathrm{Ln}(C) = \alpha$ for all elements in this study.

ANNEX 6

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

1. Participation in intercomparison exercises

1) ICES
2) QUASIMEME. Diskette from QUASIMEME enclosed: Y/N.
3) the name of the exercise
4) diskette from QUASIMEME enclosed: Y/N
5) if a diskette is not enclosed: report performance (mean, z-score, p-score)
6) other (national/international): describe in comments and provide relevant documentation

Note: It should be possible to specify more than one intercomparison exercise. All results from an intercomparison should be reported with submitted data.

2. Analyses of reference materials and/or laboratory reference materials (LRM)

1) name of material
2) mean (unit)
3) standard deviation (unit)
4) number of analyses
5) date of start of analysis
6) date of end of analysis

Notes:

a) It should be possible to specify the results of more than one reference material.
b) Reference materials and laboratory reference materials should reflect the nature of and concentrations measured in the samples being reported.
c) The same reference material should be reported more than once in order to reflect, for instance, long-term and short-term variation.
d) For internal/laboratory prepared reference material, the 'assigned'/'agreed' value should be reported as well, while this information should not be reported for publicly available reference material.

3. Other information

a) The detection limit and the method by which it was established.
b) 3 x s.d. of a procedural blank
c) derived from a procedural calibration curve
d) 3 x s.d. of a sample with low concentration
e) Non-empirical method
f) Other

The date of sampling and analysis.

Relevant cofactors.

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

- Date of sampling.
- Date of pre-treatment.

- Date of preservation.
- Date of start of storage.

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

Theme	Category	Exclusive items/pick list
Preservation	None Acidification	-Nitric acid -Hydrochloric acid -Other
	Refrigeration	(Temperature should be specified)
	Freezing	(Temperature should be specified)
	Organic solvent	Y/N. If Y, specify solvent.
	Lyophilisation	
	Other	

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

- Date of sampling.
- Date of pre-treatment.
- Date of preservation.
- Date of start of storage.

Theme	Category	Exclusive items/pick list
Sampling	Vessel	-Research vessel -Inflatable raft with engine on -Inflatable raft with engine off -Other
	Technique of collection -grab sampling	-Sampler type: (pick list) -Material in contact with sample -Cleaning of material
	Technique of collection - core sampling	-Sampler type: (pick list) -Material in contact with sample -Cleaning of material
	Subsampling facilities	-On-board clean room -On-board clean bench -Other
	Storage containers	-Material -Acid cleaned: Y/N. If Y, specify acid. -Solvent cleaned: Y/N. If Y, specify solvlent.
Packaging		Packaging materail
Storage	Prior to subsampling or preservation	Y/N. If Y, specify time and temperature. -Frozen (Temperature should be specified) -Refrigerated (Temperature should be specified) -Freeze-dried -Oven-dried (Temperature should be specified) -Other
Fractionation		-Unfractionated -Fractionated (Fraction should be specified)
Method of fractionation/grain size analysis		(To be supplied by the Marine Sediment Working Group)
Grinding		a) Agate, b) Stainless steel, c) other
Preservatives		-Y/N (If Y, specify)

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

- Date of sampling.
- Date of pre-treatment.
- Date of preservation.
- Date of storage.

Theme	Category	Exclusive items/pick list
Technique of sampling	Fish	-Sampling device: (Pick list already in the existing ICES reporting format)
		-Gutted: Alive -Gutted: Dead
	Shellfish	-Sampling device: Hand-picking -Sampling device: Dredge -Sampling device: Other -Percentage of time below sea level.
		-Depuration (Y/N, if Y specify time)
	Marine mammals	-Catching: Found dead -Catching: Shooting -Catching: Harpooning -Catching: Knocking -Catching: Other
		-Alive (Y/N, if Y: biopsy taken (Y/N))
	Birds	-Catching: Found dead -Catching: Shooting -Catching: Knocking -Catching: Strawling -Catching: Other (If shooting, specify weapon (shotgun/rifle/other) and bullet material (lead, stainless steel, other)
	Bird eggs	-Specify sequence number
	Copepods	-Catching: Type of net
	Seaweed	-Catching: Type of sampling device -Percentage of time below sea level -Whole plant sampled -New growth tips sampled
Storage	Prior to dissection/subsampling or preservation	-Y/N (If Y, specify time and temperature)
Dissection/subsampling	Organs/tissue sampled prior to preservation of whole animal	-Y/N (If Y, specify organs/tissue)
Packaging	Material	-Glass -Aluminium -Plastic (specify type: Pp/Pe/PVC/Teflon) -Other
	Cleaning of packaging material	-Y/N (If Y, specify solvent)
Equipment for dissection/subsampling, organ sampling	Material	-Stainless steel -Glass -Ceramics -Plastic (specify type: Pp/Pe/PVC/Teflon) -Other
	Cleaning of dissection/subsampling equipment	-Y/N (If Y, specify solvent)
Cleaning of subsample	Cleaning of subsample (tissue/organ) prior to homogenisation	-Y/N (If Y, specify solvent)
Homogenisation		-None -Ultra-Turrax -Blender (plastic, stainless steel, glass, other). -Grinding (ceramic, stainless steel, agate, other) -Other
Subsampling after homogenization		Y/N
Preservation prior to analysis		-Freezing (time, temperature) -Lyophilisation (time, temperature) -Drying (time, temperature) -Other -None
Lipid analysis		Method: Bligh and Dyer, Soxhlet, other

7. Analytical Methods. Overall categories (QUASIMEME system) + some additional categories not presently included in the QUASIMEME system

Note: This section will be updated with the QUASIMEME system for reporting analytical methods.

Chelating agent for aqueous extraction
Solvent for aqueous extraction
Buffer for aqueous extraction
Chromatographic separation
Standard preparation
Sample digestion (sea water)
Sample treatment procedure **
Preconcentration techniques
Sample preservation **
Standard procedure
Electrochemical detection
Detection system: AAS-FLAME
Detection system: AAS-ETA
Detection system: Other techniques
Detection system: Fluorometric (not in QUASIMEME system)
Detection system: Photometry (not in QUASIMEME system)
Analytical System: Manual (not in QUASIMEME system)
Analytical system: Automatic (not in QUASIMEME system)

** These items are covered by Sections 4, 5 and 6.

ANNEX 7

MERCURY IN THE MARINE ENVIRONMENT—A REVIEW

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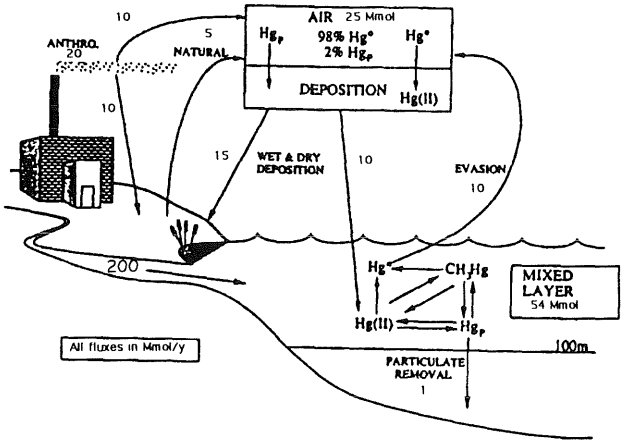
INTRODUCTION

Among the toxic trace metals, mercury (Hg) is one of the most hazardous environmental pollutants, and therefore of major concern in ecotoxicology. Monomethylmercury (MMHg) accumulation in marine fish is an important human health concern as human exposure to MMHg occurs principally through the consumption of seafood and its products. Hg exists in a large number of physical and chemical forms with a large variety of properties which determine its complex distribution, its biological enrichment and toxicity. The most important chemical forms are elemental Hg (Hg^0), inorganic Hg (Hg^{2+}), monomethylmercury (MMHg, CH_3Hg^+) and dimethylmercury (DMHg, CH_3HgCH_3). In the biogeochemical cycle of Hg, these species may all interchange in atmospheric, aquatic and terrestrial environments.

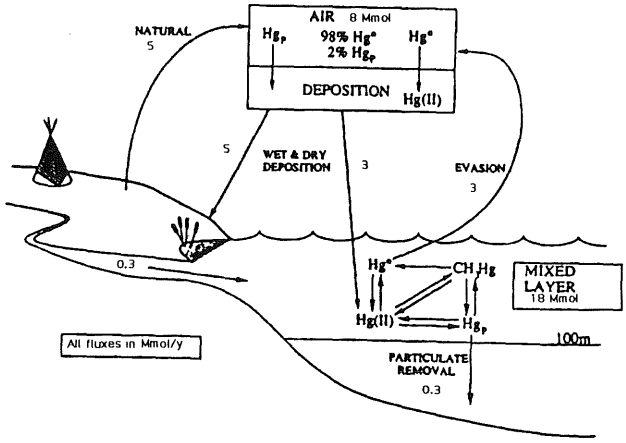
During the last decade, the introduction of contamination-free sampling and handling methodologies and sensitive and specific analytical equipment, as well as speciation and reaction oriented environmental Hg research has considerably improved the knowledge on the Hg biogeochemical cycling. However, the majority of the environmentally related research on Hg performed in the last decade has been focused on terrestrial ecosystems, whereas the marine environment has received much less attention. This is apparent from the proceedings of the last conferences on mercury (Lindqvist, 1991; Watras and Huckabee, 1995; Porcella, 1995). The database on Hg speciation in the marine environment is scarce and this results in uncertainties associated with the concentrations, stocks and fluxes of the various Hg compounds to and from the marine environment.

GLOBAL MERCURY CYCLE: ANTHROPOGENIC INFLUENCES

Mercury enters the environment through a variety of natural and anthropogenic sources. Anthropogenic emissions to the atmosphere are estimated to be about 50 % to 75 % of the current total annual input (6000–7700 t; 30–38.5 Mmol) to the global atmosphere (Nriagu and Pacyna, 1988). As anthropogenic point sources, fuel combustion, waste incineration, industrial processes (chlor-alkali plants), metal ore roasting, refining and processing are the largest point source categories on a global scale. Together, these sources account for an annual emission of 3600–4500 t (18–22.5 Mmol) (Pacyna, 1996; Fitzgerald and Clarkson, 1991). Natural sources include ocean emission, degassing of the earth's crust, weathering, emissions from volcanos, geothermal zones and Hg mineralized areas. Together, these emissions amount to approximately 3000 t (15 Mmol) per year, of which 1000 t (5 Mmol) are of terrestrial origin and 2000 t (10 Mmol) are of marine origin (Lindqvist *et al.*, 1991; Mason *et al.*, 1994). Net global emissions are probably increasing due to increased coal and gas combustion, metal mining and smelting, industrial emission processes and waste incineration (Pacyna, 1996). Recycling of mercury at the earth's surface, especially from the oceans, extends the influence and active lifetime of anthropogenic Hg releases (re-emission) (Mason *et al.*, 1994). Approximately one third of the total current Hg emissions (2000 t; 10 Mmol) are thought to cycle from the oceans to the atmosphere and back again to the ocean, but a major fraction of the emissions from the oceans consists of recycled anthropogenic Hg (Figure A7.1). Natural (pre-industrial) Hg emissions from the oceans are estimated at 600 t (3 Mmol) (Fitzgerald and Mason, 1996).



The current global Hg cycle



A premodern view of the global Hg cycle

Figure A7.1. Global mercury cycle (adapted from Mason *et al.*, 1994).

Mass balance simulations of the present and pre-industrial global Hg cycle (Figure A7.1; Mason *et al.*, 1994) provide an assessment of the extent to which anthropogenic emissions may have perturbated the Hg cycle. These estimations show that the Hg concentration in the ocean mixed layer may have increased by a factor of three over the last 100 years.

MERCURY DISTRIBUTION IN THE MARINE ENVIRONMENT

A compilation of data on Hg speciation in surface waters of rivers, estuaries, coastal and open ocean waters obtained during the last decade using ultra-clean sampling and analytical techniques is presented in Table A7.1.

Oceanic environment

Total dissolved Hg concentrations in the open ocean range from 1 to 5 pM. Significantly higher concentrations are found (up to 10 pM) in coastal areas and in the depth region of the oxygen minimum where accumulation due to particle dissolution is enhanced. Particulate Hg concentrations are usually in the range of 0.1 to 0.5 μmol kg^{-1}.

Methylated compounds have been detected in open ocean waters, with deep layers of the productive regions displaying the highest concentrations of MMHg and DMHg. The latter compound is often the major methylated species in oceanic waters. In general, the methylated species amount to 10 % of the total Hg.

Table A7. 1: Hg concentrations and speciation in rivers, coastal, and open ocean waters.

Location	Hg_T (pmol·l^{-1})	Hg_{TD} (pmol·l^{-1})	Hg_R (pmol·l^{-1})	Hg_P (pmol·l^{-1})	Hg_P (nmol·g^{-1})	$MMHg_T$ (pmol·l^{-1})	$MMHg_D$ (pmol·l^{-1})	$MMHg_P$ pmol·g^{-1}	$MMHg_P$ (pmol·l^{-1})	Hg^0 (pmol·l^{-1})	DMHg (pmol·l^{-1})	Reference
Rivers/ estuaries												
Scheldt estuary		3.5–14	1–10		1.9–8		0.065–3	10–50		0.1ñ0.65		Leermakers *et al.*, 1995
St. Lawrence (Canada)		0.4–4.5			0.2–2							Quemerais *et al.*, 1996
Pettaquamscutt (USA)		1–15	0.5–8	1–15			0.05–2		0.05–3			Mason *et al.*, 1993
Rhone (France)		1.4–16.5			0.4–7.8							Cossa *et al.*, 1996
Seine (France)		2.5–59.5			2.2–13.4							Cossa *et al.*, 1996
Loire (France)		2.1–10.1			0.45–2.45							Cossa *et al.*, 1996
Elbe (Germany)		3.8–16.4	0.8–4		1.5–7.05			11–46		0.27–0.6		Coquery and Cossa, 1995
Lena (Russia)		4.5–5.4			0.15–1.05							Coquery *et al.*, 1995
Ob (Russia)		2.4–3.2			0.2–0.3							Coquery *et al.*, 1995
Yenisei (Russia)		1.5–2.1			0.2–0.3							Coquery *et al.*, 1995
Framvaren fjord (Norway)?	10.7–30.8					0.55–11.15						Parkman e al., 1995
Coastal and open sea waters												
Alboran Sea											<dl–0.29	Cossa *et al.*, 1994a
Celtic Sea	1.8–13.7											Cossa *et al.*, 1996
North Sea	1.6–21.4	0.9–4.8	0.4–1.8	0.2–16.6	0.58–2.42		<dl	<dl–60	<dl–0.19	<dl–0.45	<dl	Coquery and Cossa, 1995
- Belgian coast	0.65–80.5	0.65–7.1			0.23–3.21		<dl–0.94	<dl–50		0.1–0.8	<dl	Leermakers, 1998
- Central North Sea	1.00									0.06	<dl	Baeyens and Leermakers,1998
- Dogger Bank		0.95–2.1	0.8–1.9		0.2–1.05							Fileman *et al.*, 1991
-Northern North Sea		1–2.5										OSPAR/ICES, 1996
English Channel	4–20.5	1.5–4.2			2.55–8.85							Cossa and Fileman, 1991
- English Channel	0.75–4.35						0.075–0.33					Leermakers, 1998
- Dover Straight		0.6–6.7		0.3–26.8								Cossa *et al.*, 1994b
Open Ocean												
North Atlantic	1.55–4.25		0.75–1.05							0.07–0.9	<0.01–0.2	Mason *et al.*, 1995a
			0.7–1.05									Dalziel, 1995
Equatorial Pacific			0.8–2							0.05–0.4	<0.01–0.3	Mason and Fitzgerald, 1996

Hg_T = total Hg HgT_D = total dissolved Hg Hg_R = reactive Hg Hg_P = particulate Hg $MMHg_T$ = total MMHg $MMHg_D$ = dissolved MMHg

Hg^0 is found in the mixed layer and in the deeper waters of the ocean with concentrations ranging from 0.01–0.5 pM. (Mason *et al.*, 1995a; Baeyens and Leermakers, 1998). In highly productive environments such as upwelling areas, concentrations as high as 1 pM are found in surface waters.

Estuarine and river systems

In unimpacted rivers and estuaries, total dissoved Hg concentrations range from 1 to 6 pM, whereas particulate Hg concentrations range from 0.2 to 0.7 μmol kg^{-1}. MMHg represents 1 to 5 % of the total Hg concentration.

In polluted estuaries, particulate Hg concentrations up to 10 μmol kg^{-1} and dissolved Hg concentrations up to 30 pM have been observed (Leermakers *et al.*, 1995; Ebinghaus and Wilken, 1996). Highest particulate Hg concentrations are found in industrialized and urbanized small rivers such as the Seine, the Scheldt, and the Elbe, whereas large industrialized rivers (Rhone, St. Lawrence) do not show the same elevated concentrations (Cossa *et al.*, 1996). Up to 50 % of the dissolved Hg concentrations could be attributed to MMHg in summer and autumn in the Scheldt, while Hg^0 constitutes between 1 % to 10 % (Leermakers *et al.*, 1995). A large fraction of dissolved estuarine and riverine Hg is bound to organic complexes and/or colloidal matter (Mantoura *et al.*, 1978; Guentzel *et al.*, 1996).

MMHg concentrations in anoxic bottom waters can exceed surface water concentrations by a factor 100. DMHg has not been detected in freshwater systems, but has been found in trace amounts (0.1 pM) in the high turbidity brackish water zone of the eutrophic Seine estuary (Cossa *et al.*, 1996). DMHg is more readily decomposed in fresh water and can easily escape from surface waters via gas evasion.

BIOGEOCHEMICAL BEHAVIOUR OF MERCURY

The present knowledge on Hg cycling in the marine environment has been summarized in a number of overview articles (Cossa *et al.*, 1996; Fitzgerald and Clarkson, 1991; Fitzgerald and Mason, 1996; Mason and Fitzgerald, 1996).

The main transformation pathways between the various Hg species in the different environmental compartments have been identified (Figure A7.2), although the reaction mechanisms and/or biological species involved in the interconversion of Hg species in the ocean remain uncertain. The *in situ* (bacterial) conversion of inorganic Hg species to MMHg is an important feature of the Hg cycle in aquatic systems as it is the first step in the bioaccumulation process. Methylation occurs both in the water column and in the sediments (its origin in the atmosphere is still unknown), and has been shown to be predominantly due to sulphate-reducing bacteria in freshwater and estuarine systems. In the ocean, DMHg is the main methylated compound in contrast to freshwater systems where DMHg is not found. MMHg in the oceans is thought to derive from the decomposition of DMHg, suggesting that probably other species are responsible for the formation of MMHg in the oceans (Mason *et al.*, 1995a). Vertical profiles of Hg species in the Atlantic and Pacific Oceans (Mason and Fitzgerald, 1991; Mason *et al.*, 1995a) as well as in the Mediterranean Sea (Cossa *et al.*, 1994a, 1997) show similar patterns: low concentrations of Hg^0, reactive Hg (Hg_R) and methylated species in the mixed layer, and increased concentrations of these species in sub-thermocline waters. Processes which govern the speciation of mercury in the oceans have been proposed (Mason and Fitzgerald, 1990, 1991, 1993; Mason *et al.*, 1995a; Cossa *et al.*, 1994a, 1997): in the surface layer, Hg(II) is reduced to Hg^0 and recycled in the atmosphere or incorporated in particulate matter and subsequently released deeper in the water column. Low concentrations of Hg^0 and DMHg in the mixed layer are the result of gas evasion to the atmosphere, and particulate scavenging removes MMHg from surface waters. Methylated species (DMHg and MMHg) show a maximum concentration below the thermocline. DMHg occurs mainly in the sub-thermocline regions where oxygen consumption is active, with the Hg(II) pool as a substrate for both methylation and reduction. Particulate dissolution in the deeper waters releases bound MMHg and Hg(II) into solution. The current available dataset suggests that there is a relationship between surface water productivity and deep water DMHg formation (Mason and Fitzgerald, 1995). Higher concentrations are found in the more productive eastern Equatorial Pacific than in the Northern Atlantic and western Equatorial Pacific. Formation of DMHg in deep water relies on the supply of Hg(II) to this zone via particle settling and remineralization, and this process is linked to surface water productivity. Deep water temperature may also influence DMHg formation. In the western Mediterranean, specific methylation rates were estimated to be six times higher than those in the Northern Atlantic (Cossa *et al.*, 1997).

The *in situ* production and air/water exchange of Hg^0 in surface waters exert a major influence on the fate of Hg in the environment. Volatilization of Hg^0 competes with MMHg formation for the available Hg(II), the substrate for both reduction and methylation. There is a relationship between primary productivity and Hg^0 in the surface mixed layer (Mason *et al.*, 1995a). The mechanisms by which Hg is reduced are still under study, but appear to be mainly biologically mediated and involve picoplankton (eukaryotic phytoplankton and bacteria) (Mason *et al.*, 1995b).

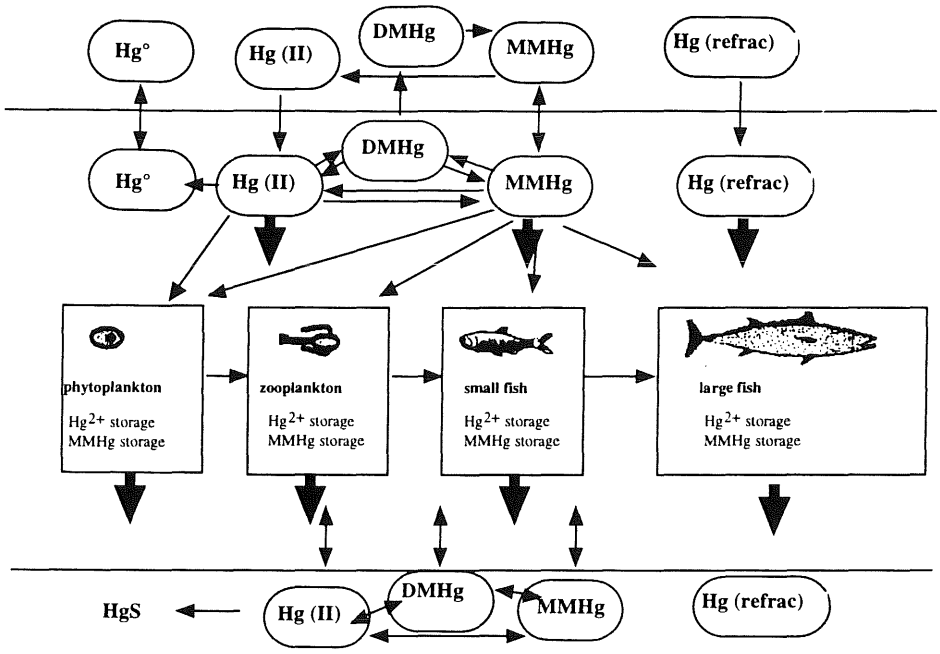


Figure A7.2. Hg transformation in the aquatic environment (adapted from Fitzgerald and Mason, 1996).

BIOACCUMULATION PATHWAYS

The factors controlling the accumulation of mercury in fish are not yet fully understood. The increasing concentrations of Hg (principally MMHg) in higher trophic levels of the food chain resemble those of hydrophobic trace pollutants. However, the lipid solubility of MMHg is an inadequate explanation because inorganic Hg complexes, which are not bioaccumulated, are as lipid soluble as their MMHg analogues, and unlike other hydrophilic compounds, MMHg in fish resides in protein rather than in fat tissue (Bloom, 1992). Mason *et al.* (1995c) have shown that the passive uptake of lipophilic neutral Hg compounds (such as $HgCl_2$ and CH_3HgCl) results in higher concentrations of both inorganic and MMHg in phytoplankton. The differences in partitioning within phytoplankton cells between inorganic Hg, which is principally membrane bound, and MMHg, which accumulates in the cytoplasma, lead to larger assimilation of MMHg during zooplankton grazing. Thus, the transfer efficiency of MMHg between plankton and plantivorous fish is approximately ten times greater than for Hg^{2+}. Most of this discrimination between inorganic Hg and MMHg thus occurs during trophic transfer, while the major enrichment factor is between water and phytoplankton (ca. $10^{5.5}$ beween water and phytoplankton and $10^{6.5}$ between water and fish). As a result, MMHg in fish is ultimately determined by water chemistry that controls MMHg speciation and uptake at the base of the food chain. In sea water, $HgCl_4^{2-}$ is the principal inorganic Hg form and the neutral $HgCl_2$ only accounts for 3 %. MMHg, if present, is nearly 100 % CH_3HgCl. Thus, despite the much lower concentration of MMHg compared to that of inorganic Hg in sea water (0.05 pM or less compared to 1 pM inorganic Hg), its overall bioaccumulation by planktivorous fish is expected to be 16 times greater. In seawater, dimethylmercury (DMHg) is often the major methylated species. As a neutral complex, passive diffusion of DMHg followed by conversion to MMHg is likely to occur. In fresh water, the relative bioaccumulation depends on the water chemistry (pH, DOC, oxygen, ellipsis) which governs the speciation and concentrations of Hg^{2+} and CH_3Hg^+. Although a larger fraction of Hg is found as $HgCl_2$, MMHg concentrations are usually considerably higher and can account for a large fraction of the total dissolved Hg (50 % or more). In addition to accumulation through the food chain, passive uptake of DMHg and CH_3HgCl (as neutral compounds) through the gills may also be an important uptake route. The relative importance of direct versus food chain accumulation has not yet been revealed.

Not all fish species follow the same bioaccumulation pattern. Three types of bioaccumulation patterns have been distinguished (Holsbeek *et al.*, 1997): Type I, which covers the majority of species, describes the normal pattern, with increasing levels of MMHg with age, combined with a low and constant inorganic level. This accumulation pattern leads to a relative increase of the organic mercury fraction with age, eventually reaching 90 % to 100 % of organic mercury in full-grown specimens. Type II is found in planktivorous fish and shows increasing levels of inorganic mercury combined with low and constant MMHg levels (leading to a relatively decreasing MMHg fraction with age). A third intermediate accumulation pattern, with increasing concentrations of both the organic and the inorganic Hg fractions with age was found in one bottom-dwelling species only.

Juvenile fish and low food chain marine organisms such as mussels, shrimps, urchins, and anemones tend to have low methylmercury to total mercury ratios that are influenced by the degree of environmental contamination, with relatively lower methylmercury to total mercury ratios in Hg-contaminated areas (Mikac *et al.*, 1985; Lasorsa and Allen-Gil, 1995).

At the higher trophic levels and more specifically in cetaceans, Hg is not only accumulated as a function of age, but this phenomenon is also linked to a change in the speciation of mercury and to a relocalization between different tissues resulting in a demethylation. Hg, present as MMHg in the food of cetaceans, is readily assimilated under its organic form, but slowly relocalized and demethylated leading to the formation of a Se-Hg compound (thiemanite). Particularly in liver tissue, thiemanite accumulates over time to extremely high but nonetheless non-toxic levels (Capelli *et al.*, 1989; Hansen *et al.*, 1990; Joiris *et al.*, 1991; Paludan-Muller *et al.*, 1993).

MERCURY IN FISH OF THE NORTH SEA AND NORTHERN ATLANTIC: CONCENTRATIONS AND TRENDS

Studies on contaminants in marine biota have mainly been conducted in the framework of joint monitoring programmes, of which the results for the time period 1987–1988 are reported in the North Sea Quality Status Report 1993 (NSTF, 1993). The main species analysed were cod (*Gadus morhua*), whiting (*Merlangius merlangus*), dab (*Limanda limanda*), flounder (*Platichthys flesus*), plaice (*Pleuronectes platessa*) and blue mussel (*Mytilus edulis*).

In these surveys, mercury concentrations in fish muscle tissue of cod, whiting, dab, place and sole ranged from 0.03 to 0.35 mg kg^{-1} wet weight (ww). Relatively higher concentrations within this range were found in the coastal zones (German Bight, Southern Bight, Norwegian coast). Most concentrations fell within the 'lower' and 'medium' JMP categories (<0.1 mg kg^{-1} and 0.1–0.3 mg kg^{-1} ww, respectively). In mussels (*Mytilus edulis*), Hg concentrations ranged from 0.002 to 0.17 mg kg^{-1}, with concentrations at the higher end in the Southern Bight, the Wadden Sea, the Ems estuary, the Western Scheldt, and at a number of locations along the English coast as well as the Danish and Norwegian coasts. This is based on present-day background concentrations in the region of the OSPAR Convention of Hg in roundfish of 0.01–0.05 mg kg^{-1} ww, in flatfish of 0.03–0.07 mg kg^{-1} ww, and in mussels of 0.005–0.01 mg kg^{-1} ww, found in areas remote from known point sources (OSPAR, 1996). Recently reported concentrations of Hg in fish from the North Sea and Northern Atantic confirm the previously reported concentration ranges, of which the lower limits confirm the estimated background concentrations (Table A7.2).

Although the inputs of Hg to the North Sea have been significantly reduced in the last decades, time trends indicating a downward trend have only been reported in a limited number of areas. In Belgian coastal waters, Hg concentrations have decreased in flounder, sole, plaice, and mussel by 50 % to 75 % between 1971 and 1993, but not in cod and shrimp (Vyncke *et al.*, 1996) and a downward trend has been observed in Hg concentrations in cod from the east coast of England between 1982 and 1988 (NSTF, 1993) and along the Dutch coast and the Wadden Sea between 1983 and 1991 (Oslo and Paris Commissions, 1994, cited in Pedersen, 1996). In all other subregions, no obvious temporal trend was found (NSTF, 1993).

The lack of clear time trends in biota is largely due to temporal fluctuations in the Hg concentrations, as have been shown for the Danish waters (Pedersen, 1996). These temporal variations may be due to biological factors, physicochemical conditions, and accumulation pathways. Important biological factors are:

1) the effect of age, length, fat content and sex on Hg accumulation (Pedersen, 1996; Riget *et al.*, 1996);
2) seasonal differences in mercury accumulation resulting from seasonal differences in metabolic activity/growth rate and bioavailability of the Hg species (Cossa, 1989);
3) migratory behaviour of the fish species: for example, fish migrating to mesopelagic environments may accumulate more Hg due to enhanced concentrations of methylated compounds at these depths (Monterio *et al.*, 1996).

Physicochemical conditions such as temperature, oxygen, organic matter concentrations and phytoplankton activity have an important influence on methylation and reduction of Hg in the water column, and this has a direct influence on the bioavailability of Hg. In addition, a better understanding of the accumulation pathways (direct versus food-chain uptake) and the methylation processes in the marine environment is required.

Table A7.2. Concentrations of Hg in finfish and shellfish of the North Sea and Northern Atlantic.

Blue mussel

Location	Period	Hg_T ($\mu g\ g^{-1}$ ww)	Reference
Bergen Harbor, Norway	1993	0.01–0.06	Andersen *et al.*, 1996
Cork Harbor, Ireland	1990	0.28–1.5	Berrow, 1991
Ems estuary, Netherlands	1985–1990	0.02–0.06 (ave. 0.035)	Stronkhorst, 1992
Western Scheldt, Netherlands	1985–1990	0.02–0.06 (ave. 0.038)	Stronkhorst, 1992
Belgian coast	1993	ave. 0.026	Vyncke *et al.*, 1996
Irish coast	1994	0.02–0.09	Nixon *et al.*, 1995
Iceland	1978	0.010–0.026	Olafsson, 1986
Iceland	1995	0.002–0.009	Audunsson, pers. comm.
Baltic Sea	1989–1993	<0.001–0.045	HELCOM, 1996
Greenland	1980–1982	0.057–0.097	Riget *et al.*, 1996
PRESENT-DAY BACKGROUND CONCENTRATION		0.005–0.010	OSPAR, 1996

Plaice

Location	Period	Hg_T ($\mu g\ g^{-1}$ ww)	Reference
Liverpool Bay, UK	1994	ave. 0.13	SIME, 1996
Morecambe Bay, UK	1994	ave. 0.09	SIME, 1996
Southern Bight (UK waters)	1994	ave. 0.05	SIME, 1996
Irish coast	1994	0.05–0.09	Nixon *et al.*, 1995
NE English coast (Tyne river)	1992	0.006–0.211	Dixon and Jones, 1994
Firth of Clyde, UK	1992	0.011–0.019	Mathieson and McLusky, 1995
St. Lawrence Gulf, Canada	1992–1995	0.049 ± 0.020	Gobeil *et al.*, 1997
North Atlantic, French coast	1988	0.028–0.15	Cossa *et al.*, 1990
English Channel	1988	0.026–0.15	Cossa *et al.*, 1990
PRESENT-DAY BACKGROUND CONCENTRATION		0.03–0.07	OSPAR, 1996

Cod

Location	Period	Hg_T (µg g^{-1} ww)	Reference
Liverpool Bay, UK	1994	ave. 0.10	SIME, 1996
Southern Bight, (UK waters)	1994	ave. 0.07	SIME, 1996
Belgian coast	1993	ave. 0.09	Vyncke *et al.*, 1996
Irish coast	1994	0.01-0.07	Nixon *et al.*, 1995
Iceland	1996	0.01-0.04	Audunsson, pers. comm.
St. Lawrence Gulf, Canada	1992–1995	0.060 ± 0.023	Gobeil *et al.*, 1997
Northern North Atlantic	1994	0.01–0.21	Stange *et al.*, 1996
Baltic Sea	1989–1996	0.002–0.365	HELCOM, 1996
PRESENT-DAY BACKGROUND CONCENTRATION		0.01–0.05	OSPAR, 1996

Whiting

Location	Period	Hg_T (µg g^{-1} ww)	Reference
Liverpool Bay, UK	1994	0.27 (n = 25)	SIME, 1996
Morecambe Bay, UK	1994	0.27 (n = 25)	SIME, 1996
NE English coast, Tyne River	1992	0.052–0.432	Dixon and Jones, 1994
Irish coast	1994	0.04–0.19	Nixon *et al.*, 1995
PRESENT-DAY BACKGROUND CONCENTRATION		0.01–0.05	OSPAR, 1996

Dab

Location	Period	Hg_T (µg g^{-1})	Reference
Liverpool Bay, UK	1994	ave. 0.20	SIME, 1996
Morecambe Bay, UK	1994	ave. 0.15	SIME, 1996
NE English coast, Tyne River	1992	0.042–0.255	Dixon and Jones, 1992
Firth of Clyde, UK	1992	0.017–0.046	Mathieson and McLusky, 1995
Iceland	1996	0.019–0.053	Audunsson, pers. comm.
Northern North Atlantic	1994	0.01–0.02	Stange *et al.*, 1996
PRESENT-DAY BACKGROUND CONCENTRATION		0.03–0.07	OSPAR, 1996

Flounder

Location	Period	Hg_T ($\mu g\ g^{-1}$ ww)	Reference
Liverpool Bay, UK	1994	ave. 0.17	SIME, 1996
Morecambe Bay, UK	1994	ave. 0.23	SIME, 1996
Ems estuary, Netherlands	1985–1990	ave. 0.107	Stronkhorst, 1992
Western Scheldt, Netherlands	1985–1990	ave. 0.106	Stronkhorst, 1992
Belgian coast	1993	ave. 0.15	Vyncke *et al.*, 1996
Denmark, the Sound	1995	ave. 0.13	Pedersen B., pers. comm.
North Atlantic, French coast	1986	0.024–0.44	Cossa *et al.*, 1990
English Channel	1986	0.3–0.27	Cossa *et al.*, 1990
PRESENT-DAY BACKGROUND CONCENTRATION		0.03–0.07	OSPAR, 1996

Sole

Location	Period	Hg_T ($\mu g\ g^{-1}$ ww)	Reference
Liverpool Bay, UK	1994	0.14 (n = 40)	SIME, 1996
Morecambe Bay, UK	1994	0.17 (n = 50)	SIME, 1996
Southern Bight	1991	ave. 0.08	De Clerck *et al.*, 1995
Irish Coast	1994	0.02–0.16	Nixon *et al.*, 1995
North Atlantic (French coast)	1988	0.03–0.27	Cossa *et al.*, 1990
English Channel	1988	0.018–0.24	Cossa *et al.*, 1990
PRESENT-DAY BACKGROUND CONCENTRATION		0.03–0.07	OSPAR, 1996

SUMMARY OF UNCERTAINTIES AND GAPS IN INFORMATION

Inputs to the Marine Environment

Rivers

The available data on the concentrations of Hg in rivers may not be truly representative of the world's rivers. For example, there is no information on Hg in tropical rivers, including such large rivers as the Amazon, and impacted rivers of South America, Europe, Asia and the former Soviet Union.

Future work should endeavour to understand the processes occurring in estuaries and coastal regions so that the flux estimates to the ocean can be further refined. Modelling the export of Hg from rivers needs to take these processes into account. Additionally, the fate of MMHg during estuarine mixing needs to be assessed.

Atmospheric deposition

The database for Hg concentrations in oceanic precipitation is limited both temporally and spatially. The flux of MMHg from the atmosphere to the ocean is unknown. Coastal rain could be an important source of MMHg and this should be a goal of future atmospheric research. Again, the database for the Southern Hemisphere, for the Russian coastline and other parts of Asia, especially the Arctic coastlines, is non-existent. Data on rain in tropical regions are also needed to assess the impacts of current activities such as biomass burning and gold extraction on the transport of Hg to the tropical oceans.

Other potential sources of mercury to the ocean

Evidence of high concentrations of Hg in terrestrial oil and gas deposits suggests that this could be a potentially important source in regions of the coastal ocean and shelf where these deposits have formed seeps into the ocean. Continental deposits have been shown to have elevated concentrations of Hg. The flux from such deposits to the ocean could be important on a regional and/or global scale. One area where this phenomenon could be studied is the North Sea as this is a region where Hg geological belts and oil deposits coincide in the sediment.

Mercury Methylation and Bioaccumulation in the Ocean

There is a need to try and assess the importance of direct uptake relative to food chain accumulation for open ocean fish, especially for long-living species, and also for marine mammals.

An investigation of the mechanisms whereby Hg is methylated in the ocean should be undertaken. It is not clear what organisms are producing DMHg and the presumption of biotic formation needs to be verified. To help assess the extent of Hg methylation in the ocean, we also need to quantify the fluxes of MMHg to and from the ocean, i.e., to produce a MMHg ocean budget.

ANALYTICAL IMPROVEMENTS

Methods for the measurement of total and methylmercury compounds in biological and some environmental samples are relatively well developed. A number of comprehensive reviews evaluate the available analytical techniques for Hg analysis and speciation as well as highlight major analytical problems and critical steps in the analytical procedures (Horvat, 1996; Puk and Weber, 1994; Baeyens, 1992; Wilken, 1992, Lindqvist *et al.*, 1991). However, systematic errors have been made, for example, the use of the widespread distillation technique for the analysis of methylmercury in sediments produces artefacts (Bloom *et al.*, 1997). Therefore, there is a need for the development of independent, accurate analytical techniques in order not to propagate systematic errors. In addition, there is a need for the development of analytical techniques for Hg speciation analysis that are applicable to ocean studies so that all speciation measurements can be performed on board research vessels, thereby alleviating problems of potential sample contamination and/or speciation change during storage.

One way to control the accuracy of analytical data is by analysing cerified reference materials (CRMs). CRMs are available for total mercury in biological, sediment, soil and water samples. However, only a few biological samples and

two sediment samples are certified for methylmercury compounds. CRMs covering various matrices and concentration ranges for total and methylmercury compounds are required. The use of CRMs can, however, only cover a limited number of environmental samples. Proficiency testing schemes such as QUASIMEME should include Hg at ambient levels in sea water as well as methylmercury. As the concentration levels of mercury in air and water are extremely low, the reliability of the results depends on the overall procedure, including sampling, storage and laboratory handling. To check the accuracy of the results, participation in field intercomparison exercises is required and comparison of the results obtained by various methodologies.

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ANNEX 8

COMMENTS OF THE TRACE METALS SUBGROUP ON THE SGQAC PAPERS

Introduction

Monomethylmercury (MM-Hg) cannot be listed under Dissolved Gaseous Mercury (DGM) species.

H.1: After the first paragraph it should be mentioned that for mercury analysis additional air cleaning in clean rooms or clean benches using activated charcoal filters is required.

H.2: (Chemicals): In mercury analysis, amalgamation and volatilization can be used as purifying methods for reductant solutions only.

H.3: (Sample and Sample Handling): In the last sentence, the words 'addition of mercury to' should be replaced by 'contamination of'.

H.7: (Instrumentation): The last sentence should be replaced by 'In the case of anoxic waters (containing sulphur compounds) see Annex J.'

H.8: (Calibration): The Trace Metals Subgroup has some doubts about using the term 'Traceability' in connection with CRMs and intercomparison exercises. The Subgroup suggests to replace that term by 'The accuracy of the standard stock solutions ....'

Furthermore, working standard solutions in trace metal analysis should be freshly (daily) prepared.

'Technical Notes on the Determination of Total Mercury in Marine Biota by CV-AAS'

The Trace Metals Subgroup recommends that

- the principle of atomic fluorescence determination of mercury traces should be mentioned in the paper,
- the Br^-/BrO_3^--digestion method should be added to the sample pretreatment section, and,
- it should be mentioned in the reducing agent section that the drawback of using the sodium tetraborate reduction system and the solution droplet formation due to its violent reaction can be overcome by a membrane or chemical drying tube between the reactor and the absorption cell.

Reference materials for organic contaminants in marine sediments

Organisation	**SRM - NIST**	**NWRI**	**NWRI**	**NWRI**	**NWRI**	**NWRI**	**BCR**	**CIL**
Country of origin	USA	Canada	Canada	Canada	Canada	Canada	European Commission	USA
Code	**SRM 1941a**	**EC-1**	**EC-3**	**EC-4**	**DX-1**	**DX-2**	**RM424**	**EDF-2513**
Matrix	Marine sediment	Harbour sediment	Niagara River Plume	Harbour sediment	Great Lakes Blend	Lakes Ontario Sediments	Harbour sediment	Fortified Soil
UNITS	µg/kg	µg/g	ng/g	µg/kg	pg/g	pg/g	µg/kg	ng/g
AS	Dry weight							Dry Weight
[±] expressed as	95% CI							
UNITS OF ISSUE	50 g.	100g	100 g	100g	50g	50g	25g	10g
FORM								Reference 1
Comment	Spiked concentrations given. Non Certified material							
PAH								
	µg/kg	**µg/g**	**ng/g**	**µg/kg**				
Acenaphthene			22 ± 9	*0.032				
Acenaphthylene			*25 ± 8	*0.048				
Anthracene	184 ± 14	1.2	*59 ± 11	*0.124				
Benz[a]anthracene	427 ± 25	8.7	312 ± 28	*0.712				
Benzo[b]chrysene	99 ± 20							
Benz[a]fluoranthene	118 ± 11							
Benz[b]fluoranthene	740 ± 110	7.8	*505 ± 88	*0.753				
Benzo[k]fluoranthene	361 ± 18	4.4	*271 ± 104	*0.560				
Benzo[a]pyrene	628 ± 52	5.3	386 ± 50	*0.675				
Benzo[e]pyrene	553 ± 59	5.3	450 ± 49	*0.747				
Benzo[ghi]perylene	501 ± 72	4.9	*348 ± 70	*0.576				
Biphenyl	*175 ± 18							
Chrysene/Triphenylene		*9.2	*458 ± 59	*1.073				
Chrysene	380 ± 24							
Dibenz[a,h]anthracene	73.9 ± 9.7	*1.3	*109 ± 17	*0.241				
Dibenz[a,c]anthracene	43.1 ± 3.7							
Dibenz[a,j]anthracene	74.3 ± 6.8							
Fluoranthene	981 ± 78	23.2	558 ± 46	*1.087				
Fluorene	97.3 ± 8.6		*42 ± 21	*0.088				
Indeno[1,2,3-cd]pyrene	525 ± 67	5.7	*359 ± 36	*0.564				
1-Methylphenanthrene	101 ± 27							
Naphthalene	1010 ±140		*35 ± 20	*0.058				
Perylene	452 ± 58	*1.1	*195 ± 21	*0.28				
Phenanthrene	489 ± 23	15.8	293 ± 33	*0.732				
Pyrene	811 ± 24	16.7	436 ± 47	*1.085				
Picene	80.0 ± 9.0							
Triphenylene	197 ± 11							
	SRM 1941a	**EC-1**	**EC-3**	**EC-4**	**DX-1**	**DX-2**	**RM424**	**EDF-2513**
Pesticides	**µg/kg**	**ng/g**	**ng/g**	**ng/g**				
Hexachlorobenzene	70 ± 25	*5.4	279 ± 33.1	*2.2				
cis - Chlordane	2.33 ± 0.56							
trans-Nonachlor	1.26 ± 0.13							
Dieldrin	*1.26							
cis - Nonachlor	*2.59							
2,4'-DDE	0.73 ± 0.11							
4,4'-DDE	6.59 ± 0.56							
2,4'-DDD	*20							
4,4'-DDD	5.06 ± 0.58							
4,4'-DDT	*1.25							
	SRM 1941a	**EC-1**	**EC-3**	**EC-4**	**DX-1**	**DX-2**	**RM424**	**EDF-2513**

* non certified values

PCBs	µg/kg	ng/g		ng/g
PCB18	*1.15	*47.4		*3.7
PCB28	*9.8	*48.7		*6.8
PCB 31	*6.2			
PCB 44	4.80 ± 062	*64.7		*7.5
PCB 49	9.5 ± 2.1			
PCB 52	6.89 ± 0.56	*99.4		*12.5
PCB 66	6.8 ± 1.4			
PCB 87		*44.9		*8.3
PCB 95	7.5 ± 1.1			
PCB 99	4.17 ± 0.51			
PCB 101	11.0 ± 1.6	*109.4		*22.4
PCB 105	3.65 ± 0.7	*34.2		*8.1
PCB110	9.47 ± 0.85	*120.1		*29.1
PCB118	10.0 ± 1.1	*79.8		*17.8
PCB128	1.87 ± 0.32	*14.5		*4.6
PCB 137		*3.8		*1.7
PCB 138	13.38 ±0.97	*72.0		*28.7
PCB 141		*19.4		*8.3
PCB 149	9.2 ± 1.1			
PCB 151	*2.62	*16.6		*9.4
PCB 153	17.6 ± 1.9	*68.2		*27.3
PCB 156	0.93 ± 0.14			
PCB 170	3.00 ± 0.46	*16.8		*11.8
PCB 180	5.83 ± 0.58	*44.9		*26.1
PCB 183		*15.2		*8.4
PCB 187	*7.0			
PCB 194	1.78 ± 0.23	*13.1		*6.9
PCB 196				
PCB 199				
PCB 201		*7.3		*8.1
PCB 206	3.67 ± 0.87	*7.0		*3.2
PCB 209	8.34 ± 0.49	*1.4		*1.6
Total PCBs		**µg/g**	**ng/g**	**µg/g**
Total		2.00	*660 ± 54	*0.577

Other Chlorinated Compounds	ng/g	ng/g	ng/g
1,4-dichlorobenzene	*30.9	*108.2 ± 11.8	
1,3-dichlorobenzene	*5.9	105.4 ± 17.5	*6.8
1,2-dichlorobenzene	*4.9	20.7 ± 3.1	*6.8
1,3,5-trichlorobenzene	*2.7	113.6 ± 9.6	*4.4
1,2,4-trichlorobenzene	*3.4	*141.2 ± 13.7	*6.7
1,2,3-trichlorobenzene	*2.3	8.9 ± 1.2	*1.9
1,2,4,5-tetrachlorobenzene	*3.4	*155.6 ± 17.4	*2.4
1,2,3,4-tetrachlorobenzene	*1.5	44.3 ± 5.1	*1.6
1,2,3,5-tetrachlorobenzene	*0.76	*13.6 ± 1.3	*0.34
Pentachlorobenzene	*1.7	65.4 ± 8.2	*1.9
Hexachlorobutadiene	*0.66	61.3 ± 6.9	*0.55
octachlorostyrene	*6.0	*41.0 ± 6.2	*1.04

Antifouling	µg/kg
Tributyltin (TBT)	20

	DX-1	DX-2	EDF-2513

* non certified values

Dioxins and Furans	pg/g	pg/g	ng/g
2,3,7,8 - TCDF	*89 ± 44	*134 ± 61	0.45 ± 0.03
1,2,3,7,8 - PCDF	39 ± 14	46 ± 10	0.87 ± 0.04
2,3,4,7,8 - PCDF	62 ± 32	88 ± 28	0.86 ± 0.06
1,2,3,4,7,8, - HxCDF	714 ± 276	825 ± 348	0.88 ± 0.05
1,2,3,6,7,8, - HxCDF	116 ± 37	153 ± 61	0.95 ± 0.09
1,2,3,7,8,9 - HxCDF	*28 ± 42	*36 ± 45	0.82 ± 0.06
2,3,4,6,7,8 - HxCDF	*57 ± 36	*70 ± 47	0.91 ± 0.06
1,2,3,4,6,7,8 - HpCDF	2397 ± 796	3064 ± 745	1.27 ± 0.11
1,2,3,4,7,8,9 - HpCDF	137 ± 62	152 ± 84	1.12 ± 0.12
OCDF	7122 ± 2406	7830 ± 3087	2.25 ± 0.15
1,2,7 - TCDD			
1,2,3,4 - TeCDD			
2,3,7,8 - TCDD	263 ± 53	262 ± 51	0.46 ± 0.03
1,2,3,7,8 - PCDD	22 ± 8	28 ± 14	0.96 ± 0.06
1,2,3,4,7,8, - HxCDD	23 ± 7	25 ± 8	0.90 ± 0.06
1,2,3,6,7,8, - HxCDD	77 ± 27	85 ± 33	0.87 ± 0.05
1,2,3,7,8,9 - HxCDD	53 ± 24	58 ± 19	0.90 ± 0.06
1,2,3,4,6,7,8 - HpCDD	634 ± 182	757 ± 320	1.39 ± 0.10
OCDD	3932 ± 933	4402 ± 1257	3.51 ± 0.22

* non certified values

ANNEX 10

Chlorinated Paraffins, CPs

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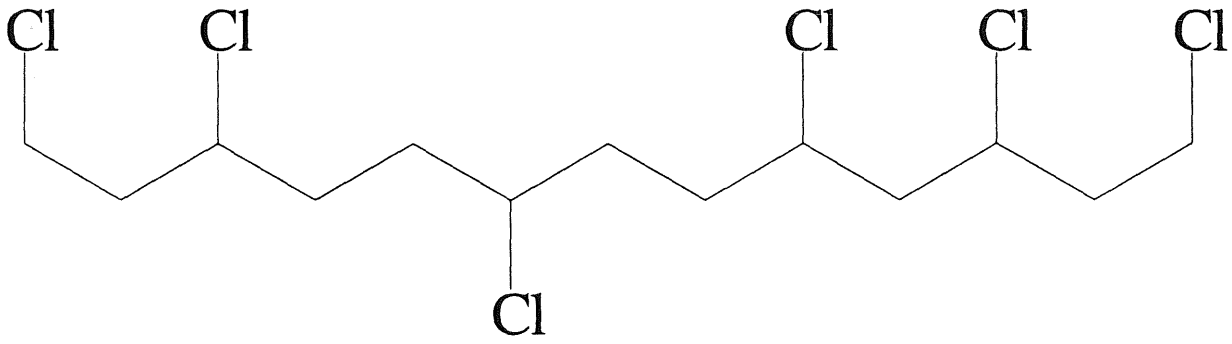
What are CPs?

- Mainly polychlorinated n-alkanes
- Chain lengths between 10 and 30 carbon
- Chlorination degrees between 30 % and 70 %
- Extremely complex mixtures
- Used as plasticisers, flame retardants, cutting oil additives

Classification of CPs

% Cl	Chain length		
	C_{10}–C_{13} (short)	C_{14}–C_{17} (medium)	C_{18}–C_{30} (long)
30 – 50 (low)	CP-SL	CP-ML	CP-LL
50 – 70 (high)	CP-SH	CP-MH	CP-LH

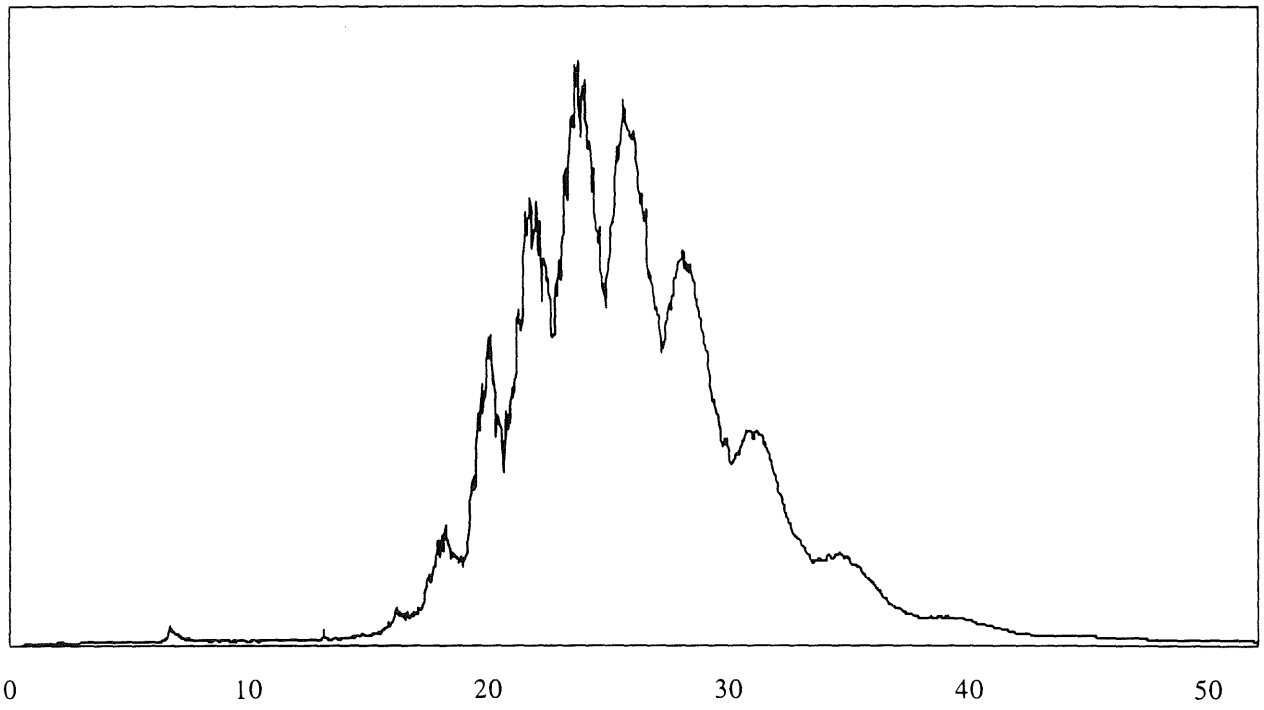
One of 868 possible $C_{13}Cl_6$ congeners



Analysis of CPs

- LC, TLC/argentation
- DIP, MS(NCI)
- LC, GC/MS(NCI)
- GPC, GC/MS(NCI)
- GPC, reduction GC/FID
- HPLC, GC/HRMS(NCI)
- GPC, GC/ECD

Gas chromatography
CP-SH



CP levels in marine sediment

Location	Conc (µg/kg)
Irish Sea	100
Barmouth Harbour	500
North Sea	50

CPs in marine biota

Species	Country	CP conc (µg/kg)
Mussels	UK	3250
Pouting	UK	100
Herring	SE	66
Plaice	UK	30
Heron eggs	UK	1500
Grey seal	UK	75
	SE	210
Ringed seal	NO	110
	CD	530
Beluga	CD	790
Walrus	CD	430

CPs in aquatic and terrestrial environments

Species	CB153	CP
Rabbit	45	2900
Moose	58	4400
Reindeer	17	140
White fish	200	1000
Arctic char	1200	570
Herring	360	1500
Ringed seal	500	130
Grey seal	92000	280
Osprey	36000	530

CP activities

- IPCS EHC No 181,1996
- EU assessment for CP-SH agreed
- Voluntary reductions discussed for CP-SH
- Swedish consumption has decreased dramatically over the last decade
- Examined for inclusion in the UN-ECE LRTAP POP protocol to be signed soon

Conclusions

- CPs are difficult to analyse in environmental samples
- There are limited estimates of CP levels in several compartments
- CPs do not seem to have the same environmental distribution as, e.g., PCBs
- CPs may pose a larger risk for the terrestrial environment than for the aquatic

Some references

- Campell and McConnell, 1980, Environ. Sci. Technol, 14: 1209-1214.
- Jansson et al., 1993, Env. Tox. Chem., 12: 1163-1174.
- IPCS Env. Health Crit., 181, 1996, 181 pp.
- Tomy et al., 1997, Anal. Chem., 69: 2762-2771.

ANNEX 11

ACTION LIST

All members of MCWG	Try to seek information about IOC and report back at the next MCWG meeting.
ICES, M. Haarich, M. Lebeuf and Organics Subgroup members	All subgroup members to send additional data on CBs in marine mammals to ICES, by 1 April 1998, and M. Haarich to conduct a literature search of the ASFA database and M. Lebeuf to contact colleagues in North America for additional information on the same topic. ICES data manager to compile all data submitted and to pass the information to Norway as the lead country within OSPAR.
ICES data manager	Update the ICES data collection system covering not only analytical information but also sampling, sample handling and storage information including all recommendations given by the different subgroups.
R. Law, E. Evers and all MCWG members	All MCWG members to forward relevant information on butyltin in the marine environment to R. Law before 1 June 1998, and R. Law assisted by E. Evers to prepare a review note for MCWG 1999 summarizing the current knowledge about butyltins. R. Law to contact the MWGBE (J. Boone) for information.
M. Krysell	Make the comments on the annexes and technical notes of the ICES/HELCOM paper on Quality Assurance of Chemical Measurement in the Baltic Sea available for the ICES/HELCOM Steering Group.
Chairman MCWG	Send comments on draft guidelines on the determination of PAHs in sediments to the Chairman of WGMS before their meeting within 2 weeks, with the recommendation that the present guidelines should be revised.
E. Evers	Approach J.M. Suijlen (NL) with a view to requesting that he considers presenting a lecture at MCWG 1999 on the use of organic compounds in riverine waters as tracers.
E. McGovern, J. de Boer and J. Klungsøyr	Prepare a note for information for the MCWG meeting 1999 concerning the MATT project under the EU-FAIR programme.
M. Leermakers	Complete the speciation paper on mercury and send a copy to ICES for submission to ACME as soon as possible.
G. Asmund	Act intersessionally as chairman of Trace Metal Subgroup and for MCWG 1998.
J. de Boer	Act as chairman of the Organic Subgroup for MCWG 1998 and in the intersessional period.
S. Carlberg	Act as chairman of the Chemical Oceanographic Subgroup for MCWG 1998 and in the intersessional period.
D. Wells, J. de Boer, M. Haarich, J. Klungsøyr, M. Lebeuf, P. Roose and R. Law.	Analyze different species for TCPM and TCPMe and seek additional information on the toxicology of these compounds. Organise and participate in an interlaboratory study (Who?)
B. Janson, P. Roose, J. Klungsøyr and all MCWG members	All members to send information on national priorities regarding hazardous and toxic compounds to B. Janson, who will prepare a proposal for MCWG 1999 on how to identify topics under 'New Contaminants and their relevance to the Marine Environment'.
E. Andrulewicz and D. Schulz-Bull	Contact relevant colleagues for a presentation concerning the status of research and monitoring activities relating to Atmospheric Inputs of Contaminants to the Marine Environment and inform the Organics Subgroup Chairman of their response.

J. de Boer	Prepare un update of his earlier paper on PBDEs and PBBs for MCWG 1999.
Gert Amund	Contact ICES Environmental Data Centre and ask for cod liver data, to complement the study of Icelandic cods and report back on the progress at MCWG 1999.
Trace Metals Subgroup, G. Asmund, G. Audunson	Work by e-mail in March on the Icelandic cod liver study until 1 April 1998. (GA to ask Shier Berman, Uwe Harms, and Victoria Besada if they want to join the intersessional work about cod liver). G. Audunson to update the paper including all relevant recommendations given by the different subgroup members and send the updated version to the chairman and Trace Metals Subgroup Chairman before 15 April 1998, in order to make it possible to include the updated version as an annex to the 1998 MCWG report.
J. F. Chiffoleau and K. Parmentier	Prepare a working paper on estuarine transport of trace metals for the next meeting (1999).
J. de Boer	Contact G. Rimkus concerning the preparation of a review note on synthetic musk compounds and A. Abarnou concerning a presentation of modeling PCB accumulation in the Seine Estuary for/at the MCWG meeting in 1999.
J. Klungsøyr and R. Law	To complete guidelines for the determination of PAHs in biota by 15 April 1998 and send them to ICES for submission to ACME 1998 to be included as an annex to the 1998 ACME report.
M. Bloxham and P. Woitke	Prepare a working paper for the next meeting, based on available literature on how well biological media reflect the state of the environment in relation to contaminants.
P. Woitke	Prepare a working paper for the next meeting about the QA system of a German laboratory involved in marine monitoring.
P. Woitke	Collect information on German seabird egg studies (trace metals) to MCWG 1999.
E. McGovern	Update the list of relevant certified reference materials for organic compounds for use in marine monitoring in advance of MCWG 1999.
D. Wells (who will act as the coordinator), G. Asmund, E. McGovern, A. Aminot, and M. Lebeuf.	Update the list of contaminants which can be monitored routinely in advance of the MCWG 1999 meeting including available information from relevant proficiency testing shemes, e.g. information from QUASIMEME 2 and NOAA. D. Wells to contact NOAA.
K. Nagel, members of the Chemical Oceanographic Subgroup (CO-SG).	Members of CO-SG to send relevant sea water samples to K. Nagel for the analysis of TN/TDN by a HTO/HTCO method. K. Nagel to prepare a report for the 1999 MCWG meting.
L. Føyn	Prepare a working paper on information on experience in the use of automated *in situ* chemical oceanographic systems for observations of chemical variables.
A. Aminot, all members of the CO-SG.	A. Aminot to act as coordinator for the intersessional work on developing a strategy for monitoring inputs of nutrients to the coastal zone. All CO-SG members to send relevant information to A. Aminot.
K. Krysell, all members of MCWG	All members to send information to M. Krysell about the quality assessment for nutrient and oxygen data used in their institutes. M. Krysell to act as coordinator, to contact WGMDM to get their view. and present preliminary guidelines on the topic at the next MCWG meeting.
Chairman of MCWG	To contact WGSSO and WGOH to seek their view on their demands for chemical data in relation to what is available from data centres and what is currently being produced.

Chairman of CO-SG	A. Aminot's paper regarding routine determination of chlorophyll *a* as a biomass marker to be sent to the chairman of WGPE to seek the view of that working group at its meeting in late March.
M. Krysell and K. Nagel	Scrutinize existing data on POC in anoxic waters with a view to producing a report for the 1999 MCWG meeting.
D. Wells	D. Wells to contact the members of the original study group on PCBs in fish-eating mammals and other members of MCWG with relevant data with a view to arranging a workshop and taking the work forward.

ANNEX 12

RECOMMENDATIONS

Recommendation 1

MCWG recommends that the final version of the guidelines for monitoring PAHs in biota, by J. Klungsøyr and R. Law, incorporating all comments, should be forwarded to ACME for information and appended to their report,

Recommendation 2

MCWG recommends that the paper on mercury speciation by M. Leermaker, after minor technical revisions, should be forwarded to ACME for information and appended to their report.

Recommendation 3

MCWG recommends that both the OSPAR Joint Assessment and Monitoring Programme (JAMP) and the HELCOM Baltic Monitoring Programme (BMP) use the same OSPAR guidelines for the determination of PAHs in biota, which have been accepted in Recommendation 1.

Recommendation 4

MCWG recommends that the task concerning guidelines for the determination of PAHs in sea water should be forwarded by the Chairman of SGQAC, M. Krysell, to persons involved in the BMP, taking into account the advice given in Section 8.1.11 of the MCWG 1998 report.

Recommendation 5

MCWG recommends that comments on the present guidelines for measuring PAHs in sediment should be forwarded to the Chairman of WGMS with the recommendation that the guidelines should be revised .

Recommendation 6

MCWG (Chairman, B. Pedersen) should accept the offer made by the Marine Institute Fisheries Research Centre to host the next meeting in Dublin, Ireland. This meeting should be held from 8–12 March 1999 to carry out the following tasks:

a) review a note on tributyltin in the marine environment;
b) review the updated list of contaminants which can be monitored on a routine basis;
c) review the progress in the joint study on PCBs in fish-eating mammals;
d) review the progress in the collaborative work on TCPM and TCPMe;
e) review the note on synthetic musk compounds in the marine environment;
f) review information on modeling PCB bioaccumulation in the Seine estuary;
g) review a note on progress in the application of high temperature techniques for the determination of total nitrogen in sea water;
h) review information on strategies for monitoring inputs of nutrients to the coastal zone;
i) review information on experience in the use of automated *in situ* chemical oceanographic systems for observation of chemical variables;
j) review an updated paper on PBDEs and PBBs;
k) review a note on how to identify topics under 'New contaminants and their relevance to the marine environment';
l) review the progress on the supplementary work to the Icelandic cod liver study;
m) review information on estuarine transport of trace metals;

n) review information on contaminant concentrations in biological media (including seabird eggs) as environmental indicators;

o) review information on QA systems used in a laboratory involved in marine monitoring;

p) review preliminary guidelines concerning QA of nutrient and oxygen data;

q) review the report on POC in oxidizing waters.