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Report of the Marine Chemistry Working Group (MCWG)

15–19 March 2004
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International Council for the Exploration of the Sea

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1 OPENING OF THE MEETING

The Chair, Mr Robin Law, opened the meeting of the Marine Chemistry Working Group (MCWG) following a welcoming address by the Director of the IFREMER Centre de Nantes, Dr Robert Poggi. Dr Michel Marchand, Director of the Chemical Pollutants Division, then made a short presentation on the work of his group. At noon, a three-minute silence was observed for the victims of the Madrid bombs of 11 March, their families and friends, with the staff of IFREMER. MCWG participants introduced themselves and briefly described their main area(s) of interest. The list of participants is given in Annex 1. It transpired that the MCWG was this year somewhat depleted in membership and consequently in some areas of expertise, particularly in relation to trace metals and chemical oceanography. As a result of this, MCWG decided to conduct all work in plenary. The Chair passed on greetings from absent members, including José Biscaya who will retire during 2004. Gert Asmund presented an appreciation of Britta Pedersen, past Chair of MCWG, who died in 2003. The Group also remembered the contributions of Stig Fonselius and Karsten Palmork, past members of MCWG who had died since the last meeting. Robin Law noted that this was the 26th meeting and so the 25th anniversary of MCWG, which first met in Lisbon in 1979. Michael Haarich had compiled material from earlier meetings, which was made available to the participants.

2 ADOPTION OF THE AGENDA

The agenda, as modified and available on the Thursday prior to the meeting, was adopted.

3 REPORT OF THE 91ST ICES STATUTORY MEETING

The time set aside at the Annual Science Conference did not allow for substantive discussions concerning questions related to the work of MCWG. The membership of the parent committee for MCWG, the Marine Habitat Committee, did not include representatives from the scientific field of marine chemistry on this occasion.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR AND HELCOM

All official requests received prior to the meeting have been included in the agenda.

4.2 Intergovernmental Oceanographic Commission (IOC)

No IOC programmes of direct relevance to MCWG have been identified by study of their website.

4.3 Laboratory Performance Study QUASIMEME

David Wells provided an update on this activity.

QUASIMEME has continued its regular studies with rounds 30 to 34 being run between July 2002 and November 2003. There have been no major changes to these studies as they have fulfilled the key requirements for the OSPAR, HELCOM, and MEDPOL monitoring programmes. The details of laboratory performance are available in the QUASIMEME quarterly reports on the website and from the QUASIMEME office. Overall, performance has been maintained and was similar to that seen in previous years.

Chlorophyll *a* has been transferred from the development studies to the routine measurement scheme and is now undertaken twice annually. Trace metals in *Fucus* has been withdrawn due to limited support ($n < 8$). Rounds for PAHs in biota (shellfish) have been extended to twice yearly in line with other routine studies.

In general, QUASIMEME continues to grow with approximately 2–5% new laboratories each year. Downsizing and rationalisation of laboratories have led to fewer materials being required by some organisations.

QUASIMEME has continued with the development exercises for organotins in biota, sediments, and water. Currently there are three exercises planned for the three matrices to be held during November 2003 to April 2004, July 2004 to November 2004, and January 2005 to June 2005, with a workshop to review progress to be held in October 2005 at NERI, Roskilde, Denmark.

There have been two exercises for shellfish toxins (ASP) held during July 2003 to September 2003 and November 2003 to April 2004, which will be followed by a workshop to be held in Galway in June 2004.

Two studies concerning brominated flame retardants in biota and sediment have been held during the current QUASIMEME year, during July 2003 to November 2003 and April 2004 to July 2004. Jacob de Boer is currently assessing the data produced in conjunction with the QUASIMEME office.

QUASIMEME continues to improve the methods of data assessment using the Cofino model, developed by Wim Cofino and David Wells. The use of the bandwidth estimator to establish the level of agreement between the laboratories has allowed a more reliable estimate of the population characteristics of the data. In addition, the model now also includes the evaluation of the left censored values (*less than values*). The handbook detailing the Cofino model with numerous examples is available as a report (Wells, D.E., Cofino, W.P., and Scurfield, J.A. FRS Collaborative Report 04/04 (2004) 68pp, available from the Marine Laboratory Aberdeen and from the QUASIMEME Project Office).

The model can be applied to data other than Laboratory Performance Studies and has been used successfully to obtain information on the background reference concentrations (BRCs) for determinands in sediment and biota within OSPAR collaborative monitoring studies.

QUASIMEME is actively working with ICES to enable laboratories to accurately and more speedily report their external QA data to the ICES database during 2004 in good time for the OSPAR MON assessment. QUASIMEME will provide all laboratories that submit data to ICES with their assessed QA data on CD-ROM for checking and forwarding to ICES, after adding their ICES institute code to the CD label. All data transferred in this way will be non-attributable to the QUASIMEME laboratory coding.

QUASIMEME is currently updating the database from PARADOX to SQL/VB.net. In future, laboratories will be identified only by an identifier unique to each round rather than by their permanent laboratory identification code. This is to improve confidentiality in line with the requirements of G13:2000 and ISO 43.

The new database will also improve the use of method codes that may link more effectively to the numerical data, providing better information to participants and third parties, such as ICES/OSPAR/HELCOM/MEDPOL with regard to the improvement and the selection of methods.

During 2004, QUASIMEME will be assessed for accreditation under ILAC G13:2000 / ISO 43, the international standard for proficiency testing providers. The pre-assessment will be in May 2004 with the first assessment in September 2004. This will cover the whole QUASIMEME organisation and the LPS schemes for nutrients in sea water and estuarine water. Methods covering all other determinands in sediment and biota will be accredited in year 2, with the remaining work areas to be added in year 3 (2006).

The MCWG recognised that there is a continuing need for certified reference materials, both for new determinands and to support existing monitoring programmes.

4.4 Other activities

4.4.1 Global POPs Monitoring Network

Although unable to attend, Bo Jansson provided an update on this programme.

After the Workshop held in Geneva in March 2003, the secretariat sent out questionnaires in order to identify laboratories interested in participating in the programme. The responses will be evaluated in March 2004, and this will form the basis of the future programme. A drafting team for the guidance document for the programme met in Geneva in October, and should have delivered an initial draft by February 2004. A second draft is scheduled for March 2004, after which it will be sent to the Advisory Group for comment. In-kind donations from Canada and Germany will be used to initiate pilot projects in one or two regions (probably Africa and SE Asia) for perhaps two years. These could begin in Summer 2004. These projects will be used to test the programme and the guidance document, which will be finalised in 2005. From a report in the *New Scientist* magazine of 28 February 2004, it seems that the Stockholm Convention on POPs will come into force on 17 May 2004, France having been the 50th country to ratify the convention and so trigger the three-month countdown.

4.4.2 The work of the AMPS group in the implementation of the EU Water Framework Directive

Peter Lepom updated the group on the work of AMPS.

Peter Lepom summarised the work relevant to MCWG, which has been carried out within the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) and pollution control since 25th MCWG meeting held in Tallinn in March 2003.

Matrix for compliance monitoring of priority substances

EU Member States are primarily responsible for the provision of data to demonstrate compliance with environmental quality standards (EQSs). For organic compounds, DG ENV proposed that they should report data relating to whole water samples. For metals, the requirement is to report concentrations of dissolved metals.

Under these proposals, data referring to whole water may be generated either by analysis of the whole water sample, or by separate determinations in the liquid and solid phase and summation.

SPM can be used as a substitute for whole water samples only if it can be justified by calculations, measurements, etc.

Biota and sediment monitoring

For the time being, environmental quality standards have been derived only for water, although the Water Framework Directive included the option to derive EQSs for sediments and biota if thought appropriate.

During the AMPS-4-meeting, drafting groups on sediment and biota monitoring were established to collect, on the basis of distributed questionnaires, information on what is currently common practice in the member states. The AMPS group will compile the results and make recommendations to the Expert Advisory Forum. It was emphasised that these matrices are particularly useful for the study of temporal and spatial trends, to check for effectiveness of reduction measures and compliance with cessation targets as well as for investigative monitoring of priority substances. Reference was also made to JAMP guidelines for monitoring contaminants in biota and sediments.

Analytical methods

All methods used for priority substance monitoring should be performance based, clearly described, and so give the laboratories the flexibility to select from different options to best meet their individual requirements, as suggested by MCWG at its 2003 meeting and subsequently transmitted to the AMPS group. This implies the application of both CEN/ISO standards alongside other fully validated methods.

When comparing the proposed EQS with the lower limit of application of existing analytical methods (EAF(6)-04–02-AMPS), it becomes obvious that reliable compliance checking would not be possible for approximately 70% of the priority substances listed within the WFD. For some compounds, methods need to be revised and/or re-validated to improve sensitivity and to cover all relevant type of waters (including those with high SPM content). For short-chain chlorinated paraffins, there is no suitable method available for the time being.

A workshop on the analysis of short-chain chlorinated paraffins (SCCP) was organised by the German Federal Environmental Agency, CEN/TC230 Water Analysis, and JRC Ispra in Berlin in November 2003 to gather information on methodologies currently in use and to identify research needs. The outcome of the workshop will be made available to MCWG members as a .pdf-file by Peter Lepom.

Quality requirements for analytical methods

Irrespective of whichever method is selected and applied in monitoring of priority substances, the data quality requirements outlined in document (EAF(5)-04–02-AMPS) have to be considered. The most important issues are: combined uncertainty of measurement to be < 50%, lower limit of application to be < 1/3 of EQS; laboratories are obliged to work according to internationally accepted QA/QC schemes and to demonstrate their competence, e.g., by participation in international laboratory proficiency schemes.

Background concentration (C_{backg}) for heavy metals

The added risk approach was generally accepted (QS = C_{backg} + maximum permissible addition − MPA). DG ENV recommends the use of the following default background concentrations (ng l^{-1}):

Element	Inland waters	Transitional, coastal, and international waters
Cd	25	15
Pb	50	20
Hg	5	1
Ni	300	250

or to adopt different background concentration in accordance with a methodology to be specified in an annex to the legal act. Consensus is to be reached at a river basin scale. DG ENV requested member states to give input to this issue and organised a workshop for discussion of the issue at JRC, Ispra, on 11–12 March 2004.

Further activities

The AMPS-5 meeting will be held at JRC, Ispra, on 31 March–1 April 2004. The outcome of the survey on monitoring of priority substances in biota and sediments will be compiled by the corresponding drafting groups. Summarised results will be reported to DG ENV and discussed at the next AMPS meeting (AMPS-6). The outcome of the workshop on metal background concentrations will be reported to DG ENV and discussed at the same meeting.

Various aspects of the work of and proposals from the AMPS group were discussed. MCWG pointed to the fact that the use of whole water samples as a matrix for the determination of organic contaminants could present serious problems in the proper interpretation of the monitoring results produced. This is in particular connected to interference with suspended particulate material, SPM. There was a strong opinion expressed that water samples must be filtered prior to analysis in order to be able to distinguish between dissolved compounds and those bound to the SPM. It was also noted that sampling in oceanic waters could create additional problems, as it would sometimes require the filtration of 1,000 litres of seawater in order to collect enough SPM for further analysis.

Many of the determinands that are on the priority substances list have an extremely low solubility in seawater and so present inherent difficulties in establishing reliable values, and these compounds should, in preference, be monitored in either sediment or biota rather than in water.

The external QA required to underpin these measurements in the marine environment is available through the QUASIMEME programme, for most of the priority substances. However, if additional matrices are to be analysed, then these need to be established within the programme so as to ensure that these test materials are available in sufficient quantity and diversity to underpin the QA needs for monitoring under the WFD.

The proposal for a fixed set of background concentrations for trace metals was discussed. Members of MCWG presented examples of naturally occurring high values of various trace metals in essentially pristine oceanic areas, due to the prevailing hydrographic conditions (upwelling, for example). It was, therefore, concluded that using a fixed set of background concentrations for trace metals in marine waters might not be sensible, and could lead to false conclusions regarding the degree of anthropogenic pollution. Background values must instead be created with the knowledge of the prevailing conditions within a specific area.

5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

There were no reports under this agenda item, mainly because such items are normally considered elsewhere within the main agenda.

6 REQUESTS FROM ACE, ACME AND REGULATORY AGENCIES

All such requests have been incorporated within the agenda.

7 PLENARY PRESENTATIONS

7.1 Marie Hélène Tusseau

Concepts and applications of *in situ* diffusional techniques – DGT in environmental analytical chemistry.

This field of study began in 1994 with a paper in *Nature* by Davison and Zhang which described the use of thin-film gels, and which used a hydrogel to control the diffusion of metal cations towards a specific chelating resin at a predictable accumulation rate. This was followed by further papers on the application of the technique to pore water fluxes (1995) and the determination of dissolved phosphorus in natural waters (1998), and further development in 2000. Of the 71 citations of the original paper, 60% were in waters, but only three described studies in marine waters. Small and simple, DGT devices consist of a chelating resin and a hydrogel encased in a plastic support. Metal cations migrate through the hydrogel and are immobilised in the chelating layer. At steady-state, the flux of metals passing through the device is proportional to the labile metal concentrations at the open surface of the hydrogel. After exposure, the chelated metals are dissolved in a few ml of acid and the metal concentrations determined in a simple matrix. The major hypotheses upon which this method relies are:

- Metals are bound irreversibly in the chelating layer;
- There is no interaction of metal species with the diffusion gel;
- There is a perfect knowledge of the diffusion coefficients.

As with operationally defined measurements generally, the knowledge of what is measured (labile metal-complexes) is not well understood.

A number of questions arise as a result:

- Does the use of DGTs allow us to predict the toxicity of natural mixtures?

The coupling of biological toxicity tests (*Daphnia magna*) with DGTs has allowed the estimation of the "bioavailable" (non-complexed) fraction of, for example, copper.

- Are DGTs useful for predicting bioavailability and toxicity?
  - In natural waters with humic dissolved organic matter – yes.
  - In degrading plankton blooms – yes.

In seawater, very precise and repeatable measurements have been made. Also, in a deployment of one month in marine waters, no saturation of the binding resin was observed.

At present, DGTs are not fit for all purposes for which people would like to use them. For example, they are probably not fit for a "direct *in situ* measurement of labile inorganic species in natural waters". DGTs are, however, fit for the integrated recording of concentrations of labile metal species in very complex matrices (wastewater, for example), and for the determination of very low concentrations of trace metals (via long deployments). It may also be possible to use them as an indication of trace metal bioavailability (from the dissolved phase) in the near future. There is also a problem with the application of DGTs in studying pore water metal concentrations in sediments, as the concentrations at the DGT interface are depleted by uptake by the device, and are not easily replenished by water movement within the sediment. Overall, the precise knowledge of the diffusion coefficients of cationic and ligand-bound metals is probably the factor most limiting the application of DGTs at the present time.

Reference

Dawison, W., Zhang, H. 1994. *In situ* speciation measurements of trace components n natural waters using thin-film gels. Nature, 367: 546–548.

7.2 Michel Lebeuf

Levels and Temporal trends of Toxaphene and BDEs in beluga whales from the St Lawrence Estuary, Canada

He reported the levels and the temporal trends (1988–1999) of a suite of six environmentally relevant toxaphene congeners (P26, P40/41, P44, P50, and P62) in blubber samples of stranded beluga whales (*Delphinapterus leucas*) from the St Lawrence Estuary (SLE), Canada. P26 and P50 mean concentrations were in the same range as those reported for animals living in the Arctic environment, suggesting that the atmospheric transport represents the main input of toxaphene to the SLE. A general exponential decline of chlorobornane concentrations in belugas was observed, except for P26 and P50 in males. On average, concentrations decreased by a factor two in 8.5 years during the 1988–1999 time period. Brominated diphenyl ether congeners (BDEs) were also determined in blubber samples of adult beluga whales (*Delphinapterus leucas*). Summed concentrations of ten BDE congeners (ΣBDEs) measured in beluga samples varied between 20 ng g^{-1} and almost 1,000 ng g^{-1} wet weight. When compared to the BDE concentrations in

marine mammals reported in the scientific literature, SLE belugas appear to be relatively lightly contaminated. Only a few predominant congeners, namely BDE47, BDE99 and BDE100, account for, on average, more than 75% of ΣBDEs in SLE belugas. The accumulation of BDEs in both male and female belugas showed a significant exponential increase throughout the 1988–1999 time period. The time necessary for belugas to double their ΣBDE blubber concentration was estimated at three years or less. The temporal changes in BDE concentrations reported in this study are generally faster but in agreement with the trend observed in other organisms collected in Canada, such as lake trout (*Salvelinus namaycush*) from the Great Lakes, and ringed seal (*Phoca hispida*) and beluga whale from the Canadian Arctic. Some changes in the pattern of BDEs in belugas were also observed during the time period investigated. The recent and important increase of BDE levels in beluga whales from the SLE could explain the unexpected lack of statistical difference in BDE contamination between males and females. This suggests that to date BDEs tend to be accumulated by both male and female belugas, masking the elimination of BDEs by females through post-natal transfer to their offspring. This study confirms that the growing use of PBDEs as flame-retardants has resulted in rising contamination of Canadian aquatic environments.

Further information can be found in two recent papers:

Gouteux, B., Lebeuf, M., Muir, D.C.G. and Gagné, J.-P. 2003. Levels and temporal trends of toxaphene congeners in Beluga Whales (*Delphinapterus leucas*) from the St. Lawrence Estuary, Canada. Environmental Science and Technology, 37: 4603–4609.

Lebeuf, M., Gouteux, B., Measures, L. and Trottier, S. 2004. Levels and temporal trends (1988–1999) of polybrominated diphenyl ethers (PBDEs) in Beluga Whales (*Delphinapterus leucas*) from the St. Lawrence Estuary, Canada. Environmental Science and Technology. In press.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

8.1.1 Undertake activities relating to the implementation of the OSPAR Joint Assessment and Monitoring Programme in the light of discussions at MCWG 2003 and as required by OSPAR

Two topics arose under this agenda item:

- consideration of the feasibility of one-off surveys for six chemicals/groups as nominated by OSPAR SIME and identified through the DYNAMEC process;
- consideration of the sampling, analysis, and concentration aspects of the requirements outlined in MCWG 2004 8.1.1/4.

Six compounds/groups were identified by OSPAR as potential candidates for one-off surveys intended to establish their significance as pollutants in the marine environment. This item is not currently on the ICES work programme and emerged as an issue immediately prior to MCWG 2004. However, given the importance of the issue, MCWG has developed initial guidance, which if the task is confirmed will be followed up with the preparation of review notes for each of the compounds/groups for MCWG 2005.

Our initial thoughts were these:

Short-chain chlorinated paraffins

These are present in fish samples from the North Sea and the Baltic, at concentrations up to 300 ng g^{-1} wet weight in dab liver (North Sea), and in cod liver at up to 100 ng g^{-1} (North Sea) and 150 ng g^{-1} (Baltic). These industrial formulations are highly complex mixtures, analysis is difficult (calibration is the major problem, yielding hugely variable results), and no CRMs are available. A one-off survey is possible, but the number of laboratories which could undertake it is small. This group is also a priority group within the EU Water Framework Directive, so further method development is likely.

Endosulphan

This compound is present in North Sea water at concentrations < 0.1 ng l^{-1}, and is also frequently detected in European estuaries at low concentrations. It is a mixture of two isomers, methods are available, and full QA can be applied. A one-off survey can be undertaken.

Dicofol

This compound is not detected in water at a detection limit of 1 ng l^{-1}. Methods are not currently adequate for determination at lower concentrations. The half-life in water short (ca. one day). It is very difficult to determine due to thermal instability. More method development is needed before a one-off survey can be undertaken.

Methoxyclor

There is no information on presence. Methods are available with full QA. A one-off survey is feasible.

Musk compounds

There is a lot of information on environmental occurrence (Rimkus, 1999). Methods are available with QA, but there are no CRMs and they are not included within QUASIMEME LPS. A one-off survey is feasible.

2,4,6-tri tert butylphenol

There is no information on presence. No methods are available; due to the usage pattern, background contamination may be significant. More method development is needed before a one-off survey can be conducted.

A series of review notes on these compounds will be prepared for MCWG 2005.

SCCPs	Peter Lepom
Endosulphan and Dicofol	Norbert Theobald
Methoxyclor	Patrick Roose
Musk compounds	the Chair will approach Gerhard Rimkus
2,4,6 tri *tert* butylphenol	Robin Law

The review notes should take as their starting points the background papers on each of the compounds/groups prepared by OSPAR, which will be circulated on the MCWG 2004 CD-ROM to be prepared and circulated after the meeting.

The Group considered the paper MCWG 2004/4 regarding development of the EcoQO concerning imposex in dogwhelks. Within the document, the EAC values for TBT are cited as 0.01 to 0.1 ng l^{-1} (10 to 100 pg l^{-1}). MCWG knows of no methodology which can currently achieve detection and quantification of TBT at these concentrations. The applications group of Agilent has demonstrated detection at 0.1 ng l^{-1} using a new coupled GC-ICP/MS instrument, but such performance is unlikely to be achieved in routine operation. TBT contamination problems, possibly from the reagents used in derivatisation prior to GC analysis, currently limit limits of detection (LODs) to ca. 0.5 ng l^{-1}. The most promising route for achieving lower LODs is to transfer methodology to LC/MS or LC/MS/MS, so as to avoid the need for a derivatisation step in the analysis. The Group also noted that the summary table on page 6 of the OSPAR paper presents misleading information, and advises that the original three tables from which it has been constructed should be reinstated.

Rimkus, G.G. 1999. Polycyclic musk fragrances in the aquatic environment. Toxicology Letters, 111: 37–56.

8.1.2 Review the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website

Since the original proposal, that the ICES website should act as a host to information delivered from the producers on CRMs, this proposal seems to have travelled in a circular fashion for some years. The original proposal probably needs to be restated, in order to make the requirements of the MCWG clear. The way in which this need was met originally was that, at each annual meeting, MCWG compiled a list of available CRMs suitable for marine monitoring programmes. This process is too slow, even given the tardy rate at which CRM production proceeds under the current funding climate. Ideally, we need ICES to host, within either the main ICES website or a sub-site dedicated to MCWG, a summary page (outlining the reasons for using, and the ways in which to use, CRMs) which also includes links to producers of "suitable" CRMs. Automatic updates from the CRM producers are essential. Guidance as to which CRMs are "suitable" for particular purposes should also be given (although this can probably be lifted from earlier MCWG advice), although, of course, the ultimate responsibility remains with the end-user of the materials. As an interim position, pending the full development of the full ICES website, links to all producers of marine CRMs should be provided as a matter of urgency by the most appropriate means possible. Our aim, of course, is to facilitate access to those who do not currently have access to information on marine CRMs.

To note also a recent paper on this subject:

Bercaru, O., Gawlik, M., Bernd, F.U., and Vandecasteele, C. 2003. Reference materials for the monitoring of the aquatic environment—a review with special emphasis on organic priority pollutants. Journal of Environmental Monitoring, 5, 697–705.

8.1.3 Review how a presentation of the long-term performance of a laboratory can be represented

No new information is available, and this agenda item should be removed. Any additional information which becomes available will be included within Agenda Item 4.3

8.1.4 Review any new ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea Annexes on Quality Assurance and report the outcome. (MCWG 2004 8.1.4/1 Technical Note on the Determination of Persistent Organic Pollutants in Seawater, and MCWG 2004 8.1.4/2 a revised version of a Technical Note on Measurement Uncertainty)

With regard to the Technical Note on the Determination of Persistent Organic Pollutants in Seawater (MCWG 2004 8.1.4/1), the MCWG has the following comments:

"pollutants with log K_{ow} values > 5 are enriched" could be changed to "pollutants with log K_{ow} values > 5 are more highly enriched" because compounds with K_{ow} values between 3 and 5 might also be described as enriched.

In Section 4 pre-treatment, it should state that the pumping system used should be free of contaminants (i.e., constructed of a non-contaminating material such as Teflon where it comes into contact with the sample).

In Section 8.2, it should be mentioned that the added internal standard for volume correction in PAH and PCB analysis should be fit for purpose; that means that it can be analysed accurately and selectively with the chosen detection technique, and that the compound or another compound that interferes with its determination should not be present in the environment sampled.

In general, the MCWG considers that the extraction of "whole water" can prove troublesome. The extracted contaminants cannot be attributed to the water phase only and it is very difficult to extract the SPM-bound fraction completely. It can take a very long time (of the order of days) to extract the more hydrophobic compounds from the SPM in the whole water sample completely using liquid-liquid extraction, depending on the concentration of SPM in a particular sample. The extraction of the SPM-bound fraction using SPE will also not be exhaustive under normal conditions. Only in water samples from open sea with a very low content of SPM and dissolved organic carbon will the extracted contaminants reflect the "dissolved fraction". As the SPM and DOC content rises, the "whole water" extraction will become less efficient, initially for the most lipophilic compounds.

The name Patrick in the paper, cited in the text and reference list, should be Petrick.

MCWG has no further comments on the Technical Note on Measurement Uncertainty (MCWG 2004 8.1.4/2), which was initially considered at MCWG2003.

8.1.5 Review the revised Environmental Data Reporting Format (version 3.2) and provide comments to the ICES data centre

MCWG was pleased that the new reporting format will accept data in csv file format rather than the fully fixed-field format which has been the norm hitherto, but would eventually like the system to evolve to be able to accept data in xls format, which is the way in which the majority of analysts actually handle their own data. The MCWG was, though, appreciative of the forthcoming direct links between the various ICES databases which has sometimes limited data interpretation in the past. Members are encouraged to check www.ices.dk/datacentre/reco/ for additions to or corrections of errors in the "methods of analysis" fields.

All members are encouraged to provide further comments directly to Marilynn Sørensen [marilynn@ices.dk].

8.1.6 Develop plans for the preparation of detailed background materials to be used by the 2005 ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-sea Areas

MCWG members reported about the integration status of chemical and biological effects monitoring in their national monitoring programmes.

For the UK, Robin Law reported that both chemical and biological effects monitoring are undertaken within the UK NMMP. A range of biological effects methods have been validated and are routinely deployed, as well as chemical measurements that are made either at the same stations and sampling times or in the same tissues, but currently the two sets of measurements are not well integrated. The task of integrating these programmes has been established as a priority item and proposals should be prepared by Summer 2004. More details about the operating procedures for the UK NMMP are given in the "Green Book", which is accessible at: http://www.frs-scotland.gov.uk/FRS.Web//Delivery/display_standalone_with_ child_ menu.aspx?contentid = 1100.

Ton van der Zande reported that a number of projects involving integration of chemical and biological effects measurements have been undertaken in the Netherlands, including two combined surveys conducted in the North Sea and the Wadden Sea. In the North Sea programme, PAHs, PCBs, metals, phthalates, brominated flame retardants, PFOS, and TBT in SPM and sediments comprised the chemical component, and biological effects measurements included CALUX and Microtox for dioxin and estrogenic responses. In the Wadden Sea area, the above-mentioned parameters are also determined, but in SPM only. Additionally, investigations in sediments from the Scheldt including toxicity screening after fractionation (TIE) are conducted within the framework of another project. Within the OSPAR JAMP, the relation between TBT and intersex in *Littorina littorea* is being investigated at six locations. This species does not seem to be very sensitive to exposure to TBT.

Gert Asmund gave information that in Denmark studies have been conducted on intersex in snails, and that even in small harbours in Greenland, intersex has been observed.

Michael Haarich reported that no integrated monitoring has been set up to date as part of the German national marine monitoring programme. Since 1998, integrated sampling in open sea areas for chemical analysis in biota and biological effects measurements has been performed within the regular monitoring cruises of the Federal Fisheries Research Centre, to cover national and international monitoring requirements in the framework of HELCOM and OSPAR, in late August/September according to the relevant guidelines. Additional biological effects methods and sediment sampling have been included within certain cruises for international EU projects such as BEGPELAC and BEEP, or under the national projects STRESSTOX and ISIS (information available via website www.bfa-fisch.de). The results of these studies have been presented to WGBEC.

Marc Raemaekers from Belgium gave a presentation on the development of biological effects monitoring, starting in the early 1990s. Using the example of the measurement of EROD versus contaminant analysis in liver, he pointed out the benefits and disadvantages of the development of a biological indicator approach. This concept includes the manifestation of the effects of stress at the molecular and biochemical level, and could be the best way to assess sublethal effects and, in addition, it meets the requirements of the precautionary principle. The advantages of methods like EROD and GSH-transferase activity in liver, vitellogenin in the blood of male fish, or imposex/intersex in gastropods are that they are very sensitive techniques, working at low levels and with complex mixtures of chemicals, and providing rapid screening tests. The drawbacks of this approach that have been identified include: interpretation can be difficult as there is usually no clear causal relationship, there are complex influences of natural cofactors on the results, and there is difficulty in defining background levels.

Michel Lebeuf gave a short presentation about the monitoring of contaminants and their biological effects performed at the Maurice Lamontagne Institute in Mont-Joli, Canada. There is currently no national monitoring programme in place, so that a study combining chemical and biological effects monitoring was the subject of a research project. He demonstrated the necessity of searching for the causes of observed biological effects with an example from a Canadian paper industry plant. This facility was suspected of releasing dioxins in its wastewater due to the high EROD activity observed downstream, which was still found to be high after improved regulation of the process, and the high concentrations were eventually found to be induced by a natural wood product. Investigations of the interannual variation of EROD and PCB concentrations were performed during 1998–2001. The study reported a reduced EROD activity in large-sized, old Atlantic tomcod captured in the St. Lawrence Estuary. Most of the reduction of EROD activity was associated with emaciation, occurring in a large proportion of large-sized fish. Hepatic concentrations of PCBs increased markedly as the lipid content or the condition factor decreased. Thus, it was not possible to discriminate the effect of emaciation from the effect of contaminants on the CYP1A levels. These results demonstrate that both fish

age or size and condition factor are important variables to consider in ecotoxicological studies investigating spatial or temporal variation in EROD activity.

Further information can be found in a recent paper:

Couillard, C.M., Wirgin, I.I., Lebeuf, M. and Légaré, B. 2004. Reduction of cytochrome P450 1A with age in Atlantic tomcod from the St Lawrence Estuary: relationship with emaciation and possible effect of contamination. Aquatic Toxicology. In press.

It was concluded that biomarkers, and particularly EROD, are relatively easy to apply close to point sources, but that their usefulness becomes more questionable in remote areas, and that EROD levels observed must be carefully checked with respect to the influence of natural parameters. With the sole known exception of TBT in water and imposex, causal relationships are difficult to identify. A suite of biological effects methods provides biomarkers giving additional valuable information to that provided by chemical measurements.

8.1.7 Determine priorities for assistance from WGSAEM with statistical analyses and develop with WGSAEM a plan for the necessary collaboration.

The Chairs of MCWG and WGSAEM are in contact regarding this proposal and discussions will continue intersessionally.

8.1.8 Begin preparations to summarise the marine chemistry of the North Sea for the period 2000–2004, and any trends in chemistry and contaminants over recent decades. Where possible, the causes of any trends should be outlined; for input to REGNS in 2006.

The establishment of regional ecosystem groups was proposed by the Study Group on Ecosystem Assessment and Monitoring (SGEAM) in 2000. As a consequence of this proposal, a regional ecosystem group for the North Sea (REGNS) was established and had its first meeting in 2003. For the background for the work in REGNS, the proposal given by SGEAM 2000 is quoted below:

"SGEAM proposes that ICES establish Regional Ecosystem Groups (REGs) to provide for the preparation of integrated assessment by experts on fisheries and environmental conditions. The work in the REGs should focus on the following tasks:

1) Consider the general issue of integration of pertinent assessment information on the changing states of large marine ecosystems in the region, based on regional expertise;

2) Prepare periodic assessments of the status and trends in fish stocks and environmental conditions of the LMEs in the region with emphasis on:

   a) climatic/physical driving forces, and
   b) biological (e.g., multispecies) interactions;

3) Contribute to environmental assessments and preparation of Quality Status Reports (QSRs) in cooperation with stakeholders, academic institutions, the public, and other organizations (e.g., EEA, OSPAR, AMAP, HELCOM). The results and products of the REGs would be reviewed and translated into advice by the JASC and, as appropriate, by ACFM and ACME. The REGs would receive input to their work from thematic WGs such as status of fish stocks from stock assessment WGs, climate status from Oceanic Hydrography, pollution status from Marine Chemistry and Biological Effects, etc. The output from the REGs would in reverse be used as input to stock assessment WGs and WGs dealing with specific environmental issues such as harmful algal blooms or fish diseases. It is furthermore likely that the number of thematic WGs could be reduced as some of the tasks would be taken over by the REGs."

More background information is found in the letter to the Chair of MCWG, meeting paper MCWG 2004 8.1.8/2, and the terms of reference for the REGNS quoted in meeting paper MCWG 2004 8.1.8/1. The timetable for the process is outlined as:

WG meetings in 2004 should consider the request from REGNS and provide feedback on how sensible the request is, and should begin specifying and collecting the various data needed for the task. The WG meeting is also asked to

nominate a person to act as the chief contact point for this work. WG meetings in 2005 are required to compile relevant data and prepare a first draft assessment which then will be finalized at the WG meetings in 2006 and provide contributions to a theme session to be held at the ICES Annual Science Conference in 2006.

The MCWG discussed the request. It was pointed out that this task is relevant to tasks undertaken within other organizations, in particular OSPAR which prepares Quality Status Reports for its sea area on a regular basis. It was, however, also concluded that the MCWG is well qualified to undertake scientific assessment of the distribution and impact of contaminants and nutrients in the marine environment. Considering all the expertise which is to be found within the working groups of ICES, it was considered that working groups such as MCWG may be able to present status summaries on a yearly basis, taking consideration of new data.

As an example of an approach to ecosystem based management, Lars Føyn presented a talk outlining the Norwegian process aimed at establishing a management plan for the Barents Sea.

The request from REGNS will be included in the agenda of MCWG2005. The nominated contact point for the intersessional work is the MCWG Chair, Robin Law.

8.1.9 Review information on the age-relationship of contaminant concentrations in Baltic herring, and report the outcome.

The paper 8.1.9/1 was presented as information, in the absence of Anna-Lissa Pikkarainen. The paper summarised information for both inorganic and organic contaminants which is obtainable via the HELCOM website [http://www.helcom.fi//environment/indicators2003/contaminants_in_herring.html].

The paper is annexed to the report as Annex 3.

8.2 Trace Metal Subgroup

8.2.1 Assist the Working Group on Seabird Ecology in commencing the development of related metrics, objectives, and reference levels for ecological quality objectives relating to mercury concentrations in eggs and feathers of North Sea seabirds. [OSPAR request 2004/1]
Mercury and organochlorine contaminants in sea bird eggs and feathers

Ton van der Zande reported on information which he had received since MCWG 2003. Data had been received from Swedish, Irish, Dutch, Danish, and German monitoring programmes and surveys. Metadata comprised bird species, sampling date and location, feeding behaviour, migration behaviour, breeding age, and metabolization/excretion of contaminants. Data for ten bird species have been integrated (including gulls, terns, oystercatchers, and guillemots), and data for four regions were provided: Wadden Sea, Irish coast, Baltic Sea (Sweden), and the Western Scheldt. Prey items included herring, sprat, crustaceans, mussels, and worms. Organochlorine contaminants for which data were available included: PCBs, HCB, HCH, DDTs, PCDD/Fs, chlordane, nonachlor, and toxaphene. Problems with the overall interpretation of the collated data resulted from the different ways in which the data were expressed (on the basis of fresh weight, dry weight, or lipid weight; as the sum of different suites of CB congeners, etc.). Frequently, large standard deviations were observed for specific compounds (CVs ranged from 10% to 100%), whereas in other cases, e.g., for black guillemot eggs, very low standard deviations have been observed in individual studies for Hg and some POPs. This review focused on mercury, CB153 and HCB, as representatives of the broader contaminant groups. Profiles for these compounds in Swedish guillemot eggs have shown downward trends from the 1960s to the present day. When pooling recent monitoring data (from different locations, species), very large variations are observed. It is essential, therefore, that for monitoring purposes a limited selection of birds (non-migrating, present in a wide area, e.g., common tern) and locations should be made in the future. This is currently the case for most single studies, but a wider standardization (if possible) would facilitate broadscale comparisons. For mercury, it is known that up to 80% of the intake is deposited in the birds' feathers, and it would be interesting to know the total mass flux of contaminants in (female) birds (e.g., what proportion is transferred into the eggs?). The highest mercury contents were found in birds from the Baltic Sea area, whilst the lowest mercury contents were found in the Dollard estuary area, the Belt Sea, and Greenland.

One question which arose from the recent meeting of the OSPAR Biodiversity Committee concerned the organochlorine compounds currently included within the seabird monitoring programmes. Either in place of or in addition to the currently monitored compounds, for all of which controls are currently in place, are there other compounds (for instance, from the OSPAR list of compounds for priority action or the Stockholm Convention POPs list) which should be considered for inclusion?

MCWG considered that the following compounds should be considered:

A range of BDE congeners intended to cover the three major PBDE formulations which have been, or still are being, used in Europe (minimum of BDE47, BDE99, BDE100 (penta-mix), BDE183 (octa-mix), BDE209 (deca-mix), plus HBCD (hexabromocyclododecane) and TBBP-A (tetrabromobisphenol-A). This would allow the evolution of temporal trends for all of these flame retardant products to be studied at a high trophic level. Underpinning QA for these measurements is either in place, or could be put in place in the near future. Also, a suite of dioxins and furans should be included, particularly as it now seems that analysis of these compounds can be undertaken using GC-low resolution MS/MS, which should considerably reduce the costs of analysis (see Agenda Item 8.3.6, below). Such additions would allow us to ascertain whether management actions taken in the recent past are leading to declines in environmental concentrations.

Recent work on brominated flame retardants in bird tissues and eggs has been reviewed in two overviews:

Law, R.J., Alaee, M., Allchin, C.R., Boon, J.P., Lebeuf, M., Lepom, P. and Stern, G.A. 2003. Levels and trends of polybrominated diphenylethers (PBDEs) and other brominated flame retardants in wildlife. Environment International, 29: 757–770.

Law, R.J., Allchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S. and de Wit, C. 2004. Levels and trends of brominated flame retardants in the European environment. Proceedings of BFR2004. In press.

A reference was made to a publication on the effect on bird skins of the common method to conserve birds for museum collections (washing with detergent and treatment with Eulan U-33). It appears that, depending on the bird species and the feather type, trace metals were lost during the treatment, at least partly. The use of bird skins to obtain historical trace metal data is limited therefore.

Reference

Hogstad, O., Nygård, T., Gätzschmann, P., Lierhagen, S. and Thingstad, P.G. 2003. Bird skins in museum collections: are they suitable as indicators of environmental metal load after conservation procedures? Environmental Monitoring and Assessment, 87: 47–56.

8.2.2 Review information on arsenic speciation, and report the outcome

Evin McGovern gave a presentation of a review concerning arsenic in the marine environment, which MCWG members considered to be a timely and interesting review. The paper will be revised following comments and attached as Annex 4.

For the revision, Robin Law will provide data on arsenic and arsenic speciation in marine mammals derived from the UK strandings programme.

In Spain, the determination of arsenic in fish is a component of a current human health project, with a special focus on inorganic arsenic.

It is too early to reach any conclusion about a simplified method for the determination of arsenic species for monitoring purposes, but speciation is definitely important and the development of a simple method which can be applied widely is a priority item. Also, there are several laboratories that are interested in arsenic speciation, probably enough for it to be considered for inclusion in monitoring programmes and in proficiency testing rounds in the future.

8.2.3 Review new information on the use of membrane systems for sampling and report the outcome

No new information was available, but the plenary presentation described in Section 7.1, above, is relevant to this agenda item.

8.2.4 /(8.3.9) Background Concentrations for OSPAR-MON

Patrick Roose introduced the report on Background Reference Concentrations (BRCs) from the OSPAR workshop on BRCs, The Hague, 9–13 February 2004 [Ed. C. Moffat]. MCWG was asked to provide values for Background Concentrations (BCs) for trace metals (Cd, Hg, and Pb) and the mandatory OSPAR PAHs in biota and sediment, along with an estimate of the uncertainty for these values.

A preliminary estimate for BCs for sediments was made by WGMS at its 2004 meeting. The approach taken by that group was to collate data from (i) pristine sites remote from anthropogenic inputs and/or (ii) historic core samples. The data from each region was collated and the median established. The median of medians was then calculated and, in addition, the Cofino model (Cofino *et al.*, 2000; Wells *et al.*, 2004) was used to establish the BCs for sediment by selection of the data comprising the lowest mode. These data were also provided to MCWG for information.

Following discussion, two issues arose concerning the mechanism for establishing the BCs in biota: (i) the method for establishing the BCs, and (ii) the underlying criteria for these BCs and the associated caveats with creating such values.

(i) The method: data from contributing parties was collected prior to and (largely) during the MCWG for (1) PAHs in mussels, and (2) trace metals in mussels, and fish liver and muscle.
(ii) There was a discussion relating to the geographical and seasonal variations and the effects on the magnitude of the BCs.

Since the request from OSPAR was for a single BC for each determinand for the whole OSPAR region, all data for each determinand were taken and these factors of variability were reflected in the uncertainty of the estimate.

Due to the lateness of the request for this activity, the majority of data used were collected at the meeting. There was a maximum of 104 sites, considered to be remote from local inputs, obtained from the whole of the OSPAR area for each of the required trace elements (Cd, Hg, and Pb) in fish muscle and liver, and in mussels, and PAHs in mussels which were collated during the meeting. These were assessed using the Cofino model. The output from the model gave estimates of the BCs and their associated uncertainties, but these are not presented here as the MCWG felt that more evaluation and selection of the data to be input to the model was needed before reliable BC values could be obtained. The selection of the lowest mode given by the Cofino model was, however, felt to be a good way of deriving BCs, along with a reliable estimate of the associated uncertainty.

Within the data collected, there was a preponderance of data for Greenland and, whilst this is certainly a location remote from sources, there are natural geographical variations in, for example, Cd concentrations, which mitigate against their use across the whole OSPAR area. As a result, Cd concentrations in Greenland biota can be higher than those seen elsewhere. A similar caveat would apply, for instance, off the Atlantic coast of Spain, where upwelling occurs and the local biota are similarly high in Cd. Whilst OSPAR requires a single BC for use in the assessment, variations occur as a result of natural inputs for trace elements, and possibly for some PAHs as well. Also, the data for fish were not constrained to the species of interest to OSPAR and, although interspecies differences may not be large, it is necessary to confirm that before utilising data on other species.

For these reasons, it was not possible to finalise BCs at MCWG 2004. As OSPAR needs the values for an assessment this year, reconsideration of the topic at MCWG 2005 would not be sufficiently timely, and another way forward had to be found. It was agreed that Patrick Roose would collate a new data set, built from data supplied by MCWG members after critical evaluation of the data from their national programmes and of any data derived from the ICES database, so that only data deemed fit for the purpose of estimating BCs are used. These would be for Cd, Hg, and Pb in fish of the required species and mussels, and the OSPAR-determined PAHs in mussels only, and sampled from locations remote from sources. Members are to supply data to Patrick Roose by the end of April, in order that the statistics could be re-run during May, in time to send the final output (following external peer review of the approach and outcomes, if possible) to ACME for consideration at their meeting in June.

Cofino W.P., Wells D.E., Ariese F., van Stokkum I.H.M., Wegener J. W., and Peerboom R. 2000. A new model for the inference of population characteristics from experimental data using uncertainties. Journal of Chemometrics and Intelligent Laboratory Systems, 53: 37–55.

Wells, D.E., Cofino, W.P., and Scurfield, J.A. 2004. The Application of the Cofino Model to Evaluate Laboratory Performance Study Data using the Bandwidth Estimator, FRS Marine Laboratory, Aberdeen. Collaborative Report No 04/04.

8.3 Organics Subgroup

8.3.1 Assist the Working Group on Seabird Ecology in commencing the devlopment of related metrics, objectives, and reference levels for ecological quality objectives relating to organochlorine concentrations in eggs of North Sea seabirds. [OSPAR request 2004/1]

This agenda item was taken with Section 8.2.1 in plenary.

8.3.2 Review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish, and report the outcome

Michel Lebeuf presented new information on a study of these compounds in flatfish livers from Europe and North America. The objective was to compare concentrations and to determine whether the origin could be ascribed to DDT. Data were presented for fish from Canada (both west and east coasts), UK, the Netherlands, and Germany. The source of these compounds in the environment is not clear and it has been postulated that they are linked with DDT, as traces of these compounds have been found in DDT formulations. This study investigated the relationship between TCPM/TCPMe and DDT compounds. Higher levels of DDTs were evident in Canadian samples (Canada mean 46,700 pg g^{-1} wet weight; Europe mean 25,200 pg g^{-1} wet weight) and higher levels of TCPM/TCPMe were found in European samples (Canada mean 175 pg g^{-1} wet weight; Europe mean 2,600 pg g^{-1} wet weight). The mean ratio of the sum of DDTs/TCPM&TCPMe in Canadian fish was 318, whilst for European fish the mean ratio was 10. This does not suggest a link between the production of technical DDT and TCPM/TCPMe in flatfish.

Stefan van Leeuwen presented work by himself and Jacob de Boer on the results of the Dutch monitoring programme for these substances. Concentrations of TCPM/TCPMe were determined, along with other POPs and trace elements, in commonly consumed fish species. The highest DDT concentration was found in a herring sample from the English Channel, whilst the highest TCPM/TCPMe concentrations were found in a mackerel sample from the southwest of Ireland. A summary of the monitoring data is presented in the table below. No obvious relationship between the concentrations of DDTs and TCPM/TCPMe were observed.

			TCPM	**TCPMe**	**sum DDTs**
			ug/kg ww	ug/kg ww	ug/kg ww
Freshwater fish	n=13	Min	0,10	0,30	0,56
		Max	330,0	15,6	155,0
		Median	3,2	5,0	40,8
Marine fish	n=17	Min	0,04	<0,02	0,10
		Max	2,6	0,30	9,6
		Median	0,10		1,24
Shrimp/mussel	n=5	Min	0,30	<0,02	0,20
		Max	0,90	0,20	1,2
		Median	0,50		0,64
Farmed fish	n=3	Min	0,30	<0,03	7,0
		Max	2,2	0,30	29,4
		Median	0,90		21,6

Literature data for TCPM and TCPMe were also presented. The highest concentrations were reported in eel, *Anguilla anguilla* (TCPM 10–360 μg kg^{-1} lipid weight, TCPMe not detected to 37 μg kg^{-1} lipid weight (de Boer, 1997)).

In group discussions, it was agreed that testing at lower trophic levels was appropriate for these substances in order to assess relationships, and this is why flatfish were chosen. It was suggested that samples could be obtained from areas of the world where DDT is still used. However, it is uncertain whether TCPM/TCPMe is present in current formulations, or if they were contaminants only of technical DDT products.

Michel Lebeuf requested that members supply any further data that they have for these substances in flatfish livers, and also samples of flatfish livers from European waters for analysis. In both cases, this will provide further data for inclusion in this study. A particular request was for samples already analysed for TCPM/TCPMe to be sent to Michel Lebeuf, as laboratory analytical performance could then be compared and a real estimate of interlaboratory variability obtained.

De Boer, J. 1997. Environmental distribution and toxicity of *tris*(4-chlorophenyl)methane and *tris*(4-chlorophenyl) methanol. Reviews in Environmental Contamination and Toxicology, 150: 95–106.

Action
MCWG members to send TCPM/TCPMe data for flatfish livers and/or samples of flatfish livers to M Lebeuf. Ten fish per species and location would be ideal.

M. Lebeuf to present any further information at MCWG 2005.

8.3.3 Review new information on the use of membrane systems for sampling, and report the outcome

Ton van der Zande reported on work that his institute (RIKZ) has been conducting, testing SPSDs (semi-permeable sampling devices) deployed alongside the NIOZ mussel sampling programme. Recent studies have used 0.5 mm thick silicone rubber as the sampling matrix. In comparison with other materials, SPMDs remain in the kinetic uptake mode for about six weeks; polyethylene attains an equilibrium for compounds with a log K_{ow} of < 5; and silicone rubber remains in the kinetic uptake mode for the sampling periods studied. The use of performance reference compounds (PRCs) allows the uptake rate (equal to the release rate of the PRCs) and the sampling rate (litres per day) to be calculated. In the optimal situation, the release of PRCs during deployment equals 50% of the original concentrations. SPSDs are easy to handle and deploy, and fouling is negligible during the winter (November to February), significant during the rest of the year and reaches a peak during August. A new design has been developed which uses a "flag" design so as to increase the surface area exposed to the water column. SPSDs have been shown in recent studies to parallel the uptake in mussels for low-MW compounds, although the uptake is less than in mussels for high-MW compounds. This is probably a reflection of the fact that SPSDs represent largely or wholly uptake from the dissolved phase, whereas mussels, as filter feeders, also accumulate via the ingestion of particles. In summary:

- silicone rubber is a suitable material for SPSDs;
- the spatial patterns obtained from mussels and SPSDs are similar;
- SPSDs are well suited to the ranking of areas according to their levels of pollution.

A further presentation was given by Patrick Roose of work undertaken at RIKZ using semi-permeable samplers (SPSs) to investigate sediment and sediment pore-water contamination. Field-collected sediments were placed in jars to which SPSs were added, and shaken until equilibrated. From the uptake at different sediment:SPS ratios, it was possible to calculate both the original pore-water concentration and the water-extractable fraction of contaminants bound to sediment and available for equilibrium-partitioning. Sediments were also extracted using Soxhlet extraction and the contaminants determined. If the two concentrations were similar (as for CBs), then all of the sediment-bound contaminants can partition into the water phase; but if the Soxhlet value is higher (as for PAH), then a proportion is unavailable. This has been observed for PAHs in field studies downstream of aluminum smelters in Canada and Norway (Knutsen, 1995; Oug *et al*., 1998; Paine *et al*., 1996). The current approach using SPSs seems a promising one for estimating availability, and for identifying "hot-spots" of contamination. A lively discussion followed. MCWG thanked Foppe Smedes for supplying the presentation.

Knutsen, J. 1995. Effects on marine organisms from polycyclic aromatic hydrocarbons (PAH) and other constituents of waste water from aluminum smelters with examples from Norway. Science of the Total Environment**,** 163, 107–122.

Oug, E., Næs, K., and Rygg, B. 1998. Relationship between soft bottom macrofauna and polycyclic aromatic hydrocarbons (PAH) from smelter discharge in Norwegian fjords and coastal waters. Marine Ecology Progress Series, 173: 39–52.

Paine, M.D., Chapman, P.M., Allard, P.J., Murdoch, M.H., and Minifie, D. 1996. Limited bioavailability of sediment PAH near an aluminium smelter: contamination does not equal effects. Environmental Toxicology and Chemistry, 15: 2003–2018.

8.3.4 Review new information concerning toxaphene, and report the outcome

Michel Lebeuf presented information on the levels and trends of concentrations of toxaphene in Beluga whales from the St. Lawrence estuary as a plenary lecture (see Section 7.2 above).

Gert Asmund presented his paper (MCWG 2004 8.3.4/1) on toxaphene in the traditional Greenland diet (attached as Annex 5). Local dietary food items were classified according to their levels of contamination as very low (< 5 ng g^{-1}), low-medium (5 to 50 ng g^{-1}), high (50 to 500 ng g^{-1}), or very high (> 500 ng g^{-1}). Toxaphene concentrations in terrestrial samples were very low; whereas fish, seabirds, and marine mammals had concentrations across all four categories, including very high. The calculated mean intakes of toxaphene by those eating traditional diets significantly exceed acceptable/tolerable daily intakes (ADI/TDI) by a factor of between 2.5 and 6 times. In general, levels of toxaphene in the Greenland environment are lower than those in more densely populated and industrialised regions.

Evin McGovern will supply additional toxaphene data to Gert Asmund following the meeting.

8.3.5 Review new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants, and report the outcome

Michel Lebeuf presented information on temporal trends in concentrations of BDEs in beluga whales from the St Lawrence estuary as a plenary lecture (see Section 7.2, above).

Stefan van Leeuwen (RIVO/RIKZ) presented additional information on BDEs obtained within the overall framework of the EU project FIRE, which is aiming at an integrated risk assessment of brominated flame retardants for both humans and aquatic wildlife. After giving a general overview presentation of the project, he presented new results from Theme 5 of the project studying aquatic wildlife exposure. This exposure assessment is based on congener-specific identification, evaluation of geographical variation of exposures (i.e., reference vs. polluted sites), and temporal trends of brominated flame retardants in the aquatic food chain (water, sediment, invertebrates, fish, and top predators). Studies of the metabolic transformation of BFRs in wildlife and microorganisms, and aquatic food web modelling are also undertaken. The food chain studies include abiotic compartments (water, SPM, and sediments) and biotic components: invertebrates, and higher level predators (common tern, harbour seal, and polar bear). To further improve the comparability of analysis of BFRs, interlaboratory studies have also been organised. The sampling strategies for exposure assessment cover different regions (Western Scheldt and Wadden Sea) and, for trend studies, archive samples of harbour seal tissues and sediment cores.

Increasing concentrations of BDE47, BDE99, and HBCD from SPM to benthic invertebrates and then to predators (fish) and fish-eating top predators were demonstrated. Attention was drawn to the fact that in a few samples of tern eggs, the concentrations of BDE99 were higher than those of BDE47. Compositional differences were also seen at different trophic levels, such as the relatively low concentrations of BDE49 and BDE183 in the top predators. The geographical differences of BDE47, BDE99, and HBCD were clearly shown, with higher concentrations in the Seaftinge region of the Scheldt compared to the Terneuzen location.

The preliminary results of the interlaboratory study show that difficulties are still encountered with the analysis of HBCD, TBBP-A, BDE183, and BDE209. Samples from the Wadden Sea food web are currently being analysed and more information on the progress of the FIRE project can be found at www.RIVM.nl/FIRE

During the discussion, more information on the studies of BFRs in various European countries was presented. Robin Law added that in the UK, relatively higher concentrations of BDE99 than of BDE47 were also found in some samples of harbour porpoise blubber from Scotland.

Later in the year, the third BFR workshop will be held in Toronto, Canada in June. Robin Law will supply details of relevant papers from the proceedings to ACME 2004.

Peter Lepom observed that in both SPM and sediments, the highest concentration BFRs would often be BDE209, which could represent more that 80% of the total BDEs present. Michel Lebeuf raised the question of the importance of consideration of the biodegradation of highly polybrominated congeners within food webs, and of a better understanding of compositional differences at different trophic levels. This would be facilitated by the determination of each trophic level by means of stable ^{15}N isotope determination, as well as the determination of the dietary composition. Finally, he also drew attention to the changes in the use of PBDE technical mixtures, which are obviously reflected in the relative proportions of these compounds in the different environmental samples. However, the SPM samples may reflect these changes more rapidly, while biota samples present a more time-weighted composition.

Finally, Patrick Roose has also pointed out that the compositional similarities observed between BDEs in SPM samples and sediment filterfeeders (worms, bivalves) would suggest that depuration of the organisms may be necessary before chemical analysis, in order to purge the gut contents of particulate material. Indeed, data for BDE183 have confirmed this observation.

8.3.6 Review new information concerning the analysis of dioxins and the preparation of reference materials for these compounds (DIFFERENCE project), and report the outcome

Stefan van Leeuwen gave a presentation on the DIFFERENCE project, an EU-funded project investigating alternative and more cost-effective methods of dioxin analysis. Currently the only accepted and fully validated method is gas chromatography-high-resolution mass spectrometry (GC-HRMS), however, few labs have this instrumentation.

A number of alternative methods were investigated for the analysis of the dioxins in food samples: GC coupled to low-resolution ion-trap mass spectrometry (GC-LRMS/MS), GCxGC with electron capture detection (ECD), and the CALUX bioassay. The objectives were to:

- Optimise bio- and chemical analytical screening methods for the analysis of dioxins and dioxin-like CBs and to distinguish compliant and non-compliant samples in accordance with the requirements of EU Directive 2002/69/EC;
- Optimise extraction techniques (ASE, SPE, MASE) and clean-up methods;
- Validate and standardise methods.

EU maximum limits for dioxins in food, including fish, were set in 2001 (Commission Regulation 2375/2001/EC). Although currently legislation is only for dioxins, maximum limits for dioxin-like CBs will also be set, possibly before the end of 2004. These levels are due to be reviewed in 2006 with a view to significantly reducing the maximum levels at that time. The EU is also moving towards setting limits for non-dioxin-like CBs (ICES7 CBs).

The above alternative methods were compared to GC-HRMS as the standard reference method, with nine laboratories involved in this project. GCxGC-ECD is a relatively new technique that utilises two columns, an apolar column and a shorter more polar column. A modulator focuses eluting compounds from the first column, then releases them for analysis on the second column. Instruments using both thermal desorption and cryogenic modulators are commercially available. Using this technique, separation of all relevant (17 WHO) PCDDs/Fs and dioxin-like CBs was attained, including OCDD and OCDF.

ASE was the most promising extraction technique assessed and had the advantage that the clean-up could also be combined with the extraction step. This method gave similar results to the traditional Soxhlet extraction method when combined with GC-HRMS.

Methods were assessed against the EU requirement for dioxins and dioxin-like CBs, which are that screening methods should achieve < 30% precision and confirmatory methods < 15% precision. Methods were also assessed for their sensitivity, accuracy, and selectivity. All methods were evaluated using these criteria by the analysis of a spiked fish oil and the results assessed by comparison of z-scores. The lowest z-scores were obtained using GC-HRMS, but GC-LRMS/MS also gave acceptable z-scores. For GCxGC-ECD, there were some problems at the lowest concentrations, and, combined with upperbound reporting, this resulted in an overestimation of the actual concentration, i.e., z-scores > 2. The CALUX assay gave negative z-scores in milk samples due to a high concentration of CB118, which is believed to suppress the CALUX response. Both the GC-HRMS and GC-LRMS/MS techniques fulfilled the sensitivity, accuracy, and precision requirements. GC-LRMS/MS could therefore provide a cheap alternative confirmatory method for the analysis of dioxins. GCxGC-ECD meets the requirements for sensitivity and precision but was not as accurate as GC-HRMS. In addition, some software improvements are required. The integration of peaks is very time-consuming, as the peaks for individual compounds can be split across a number of sequential chromatograms in the second GC dimension, and must be summed. CALUX meets the precision requirement but was not as accurate or sensitive as GC-HRMS. However, this technique could be used as a screening method.

The final validation of the screening methods, in which robustness is being tested by the analysis of several matrix type materials, is currently being finalised by statistical evaluation of the data. The feasibility study on the certification of the candidate reference materials on the WHO set of dioxins, dioxin-like CBs, and the ICES7 CBs is currently ongoing.

The project is in its third and final year and will end in January 2005.

8.3.7 Review new information on the impact of alkylphenols from produced water

No new information was available as Jarle Klungsøyr was unable to attend the meeting, and this agenda item will be carried forward to MCWG 2005.

8.3.8 Review new information on the phenyl urea herbicides isoproturon and diuron

Norbert Theobald reported new data from the German monitoring programme, together with data from the Dutch monitoring programme. The monitoring area comprises the North Sea (open sea and coastal areas, such as the German Bight), the Elbe (Stade, freshwater), and the estuary of the Scheldt (Western and Eastern Scheldt, both brackish water). Apart from the phenylurea herbicides, other polar pesticides, such as metazachlor, metalochlor (low levels: 2–4 ng l^{-1}), phosphoester insecticides (mostly lower than detection limit), triazines (atrazine, simazine) and chlorinated herbicides

(2,4-D, MCPA, mecoprop), and Irgarol 1051 were determined. In general, concentrations in the open sea were 50 to 100 times lower than those found in the rivers and estuaries. Higher concentrations of atrazine, terbutylazine, and diuron were found in the Western Scheldt than elsewhere. Both in this estuary and in the Elbe, seasonal variations were observed that could probably be linked to the selective use of these pesticides in agriculture (atrazine, isoproturon, diuron, simazine). For example, in the case of isoproturon in the Western Scheldt, two concentration peaks were observed in 2003. In the coastal zones, no seasonal variations have been shown (except in the Scheldt mouth). The concentration peaks in the rivers are probably typical of these compounds, as they are polar in nature and so will run off from agricultural fields and into surface waters during rainy periods. It would be interesting to have additional data about the agricultural use (types of crops, crop areas, application period of the pesticides), in order to explain the concentration peaks. It was striking that triazine was detected in the Elbe river, although there is a ban on its use in Germany. Irgarol and diuron have been banned now in the UK from their use as booster biocides in antifouling paints, whereas their use is still allowed in France and Germany. The Baltic area was characterised by a different profile of pesticides, e.g., 2,4-D appeared dominant here (coming from the Oder). Glyphosate is not monitored currently, probably because it is very difficult to analyse, although it is a high-volume chemical in some regions.

8.3.9 Consider the request from SIME regarding the derivation of background reference concentrations for polycyclic aromatic hydrocarbons in biota

This agenda item was taken in plenary with Agenda Item 8.2.4.

8.4 Chemical Oceanography Subgroup

8.4.1 Provide guidance and assistance relating to the development of a series of data products to illustrate the eutrophication status within the ICES area

ICES has a reasonably large amount of nutrient data in its database, but there is still a lot of nutrient data that have not yet been transferred to ICES. MCWG strongly recommends that all available national data on nutrients, oxygen, primary production, chlorophyll *a*, and data on the phytoplankton composition should be transferred to the ICES data bank as soon as possible. MCWG encourages the ICES members to provide such data, as they are crucial for the ecological understanding of possible eutrophication of the area in which the data had been taken.

By compiling all available nutrient data together with data for salinity, temperature, oxygen concentration, chlorophyll *a*, and the specific phytoplankton community, it may be possible to distinguish between anthropogenic influence and the natural variations in a designated area. The use of mathematical models may provide a better picture of the various driving forces that control the biological production in this specific region. However, the remarks given in Section 8.4.2 for the use and interpretation of the data must be taken into account.

8.4.2 Consider requests from the Chairs of SGEUT for information relating to the work of the study group

MCWG discussed the request from ICES to comment on the tasks set out for the Study Group to Review Ecological Quality Objectives for Eutrophication (SGEUT), and noted that this issue has been a topic of discussion in the MCWG for many years. For the use in this Study Group meeting, scheduled to be in held the ICES Headquarters from 25–27 March 2004, it was proposed that the SGEUT should refer to the earlier MCWG reports in which eutrophication is discussed. The reports are present in ICES Headquarters and MCWG proposed that, due to the limited time available before the scheduled SGEUT meeting, the ICES Secretariat should compile the parts concerning eutrophication and nutrients from previous MCWG reports and present them to the SGEUT.

MCWG has strongly recommended that regional approaches should be taken, based on the specific environmental conditions of the particular area. It is emphasised that the selection of EcoQOs concerning eutrophication in an area must be based on a thorough knowledge of the actual conditions of the specific ecosystem.

OSPAR has defined eutrophication to be:

"The enrichment of water by nutrients causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned, and therefore refers to the undesirable effects resulting from anthropogenic enrichment by nutrients." (OSPAR, 2000)

This definition given by OSPAR has to be interpreted in that due consideration should be given to the ecosystems of the particular area of concern. This means, for example, that setting one certain common specific number for the winter concentration of nutrients for the whole OSPAR area will not be in agreement with the OSPAR definition of

eutrophication. Each area has to be considered individually so as to ensure that the definition is in agreement with the natural conditions for that specific area.

The EcoQOs selected by OSPAR are, in principle, suitable for the description and characterisation of the degree of eutrophication of the marine environment. However, to apply them for the description of eutrophication in a specific, regionally limited area, additional information and definitions are essential, e.g., a definition of "winter concentration" of nutrients, as cruises from different countries do not always occur at the same time of year.

A disadvantage of the proposed EcoQOs is that they can be used in exactly the same way to describe both natural conditions (e.g., in upwelling areas) and conditions influenced by anthropogenic activities. Therefore, additional criteria are essential to discriminate between natural and anthropogenic effects. Due to the interannual natural variability due to hydrographic, meteorological and biological conditions, this variability has to be taken into account by setting up area-specific criteria including the component of time, e.g., decreasing or increasing trends over a period of time (e.g., over several years).

Another disadvantage of the selected objectives is that they take into account measurements which have to be performed at different times of the year, e.g., nutrient concentrations have to be measured in winter (when little or no plankton growth occurs), while relevant chlorophyll *a* concentrations have to be measured in spring or summer during plankton blooms. Despite the missing clarification (whether the chlorophyll *a* concentration has to be measured at the highest density of cells—a criterion that is very difficult to control—or as an integrated value over a specified period of time), the assumption that the winter concentration of nutrients and the concentration of chlorophyll *a* during summer are directly related has to be demonstrated for each individual region. Especially in areas which have a short residence time for water, it will be very difficult to demonstrate such a linkage, particularly if no continuous records of the hydrographic processes prevailing in that area are available.

Although the proposed EcoQOs can be taken as a rough indicator of eutrophication, which may result from anthropogenic activities, additional parameters should be introduced in order to provide a more quantitative description of the situation. To avoid one of the major disadvantages described above (the measurement of parameters at different times of year), objectives should be set that allow conclusions to be drawn from measurements performed over a shorter period of time, and which are closer to the biological and chemical processes involved in the effects caused by eutrophication. It is questionable whether the selected EcoQOs are sensitive enough to describe changes in the degree of eutrophication adequately. As an excess of nutrients, once introduced into an ecosystem with restricted water exchange (i.e., with a long residence time of water), can be recycled for several years, the nutrient concentration will change only very slowly following a reduction of inputs. If targets for the reduction of eutrophication are defined, this aspect has to be taken into account, again on an area-specific basis.

The central point concerning the effects of "eutrophication" is the enhanced production of organic material, as well as its subsequent degradation and remineralisation. From this point of view, it is essential to analyse not only the chlorophyll *a* concentration and phytoplankton indicators, but also the production of organic material, e.g., carbon, nitrogen, and phosphorus fixed in organic material (TOC, TON, TOP). It is likely that these parameters will react more sensitively to changes of inputs into the ecosystem as they stem from the relevant processes which follow eutrophication, as described above. They can also be determined in the same water samples which are used for the other parameters, avoiding the misinterpretation of results from measurements performed at different times.

For practical reasons, the measurement of the partial pressure of CO_2 should also be considered as a possible parameter which could help to describe the effects of eutrophication, as the consumption of CO_2 is directly related to the production of organic material. Another advantage of using measurements of pCO_2 is that they can be performed automatically over longer periods of time, so as to provide an integrated estimate of the production of organic material.

9 PLENARY DISCUSSION OF SUBGROUP WORK

As all discussions took place in plenary this agenda item was not relevant.

10 ELECTION OF MCWG CHAIR FOR THE PERIOD 2004–2007

No nominations for the post of Chair were received. Robin Law agreed to serve for another two years, to the end of his second three-year term.

11 ANY OTHER BUSINESS

11.1 Marc Raemaekers described a Belgian research project on the risk evaluation of marine food products, entitled "Integrated evaluation of marine food products: nutritional value, safety and consumer acceptance". The project grew out of the concern raised by the Belgian "dioxin" crisis. The project will run for two years, 2004–2005, and involve the University of Ghent and the Sea Fisheries Department, Oostende. The problem is that, whilst marine foods provide a unique source of essential polyunsaturated fatty acids which have beneficial effects regarding chronic degenerative diseases such as heart disease, they also contain chemical contaminants which pose potential adverse health effects. The aim of the project is to study the Belgian population to establish:

- the position of marine foods in the diet;
- the nature and size of the potential conflict between the recommended increase in fish consumption and the potential adverse health effects;
- the attitude of and effect on consumers (information and communication).

MCWG members are asked to supply Marc Raemaekers with publications and reports on contaminant concentrations in marine fish and other marine food products. He will present a summary of the information at MCWG 2005.

A similar exercise is under way in Ireland, focused more on oily fish and their contamination by dioxins and furans, CBs, and BDEs, and there is a potential for synergy between these two projects. The key to the problem, though, is to reduce contamination levels in fish in the future. Evin McGovern will present information on this project to MCWG 2005.

11.2 Gert Asmund asked how we could demonstrate biological effects in animals such as seals and polar bears affected by pollution from diffuse sources, as in Greenland. What biological effects methods are available? We have heard earlier in the meeting of the difficulties of interpreting EROD data. In fact, EROD is a good tool when applied to hot spots and pollution incidents, but is less good when applied as a wide-scale screening tool because other confounding factors become important when induction is at a relatively low level. TIE (toxicity identification and evaluation, or bioassay-directed fractionation) can provide a means of identifying causative chemicals when biological effects are seen with no known cause. In the case of reproductive abnormalities in polar bears and other possible consequences of endocrine disruption, it is likely that the effect is triggered during the developmental stages of the animal, although effects may not be manifest until the animal reaches maturity. What are the effects of EROD induction? There is an energetic cost and metabolic stress to organisms in dealing with contaminants and detoxifying or eliminating them, as can be seen by assessing scope for growth in mussels.

Relevant references

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11.3 Stefan van Leeuwen described a new project which will involve study of PFOS and PFOA. Perfluorinated compounds (PFCs) have recently gained socio-economic and scientific interest because they have been found in biota from remote areas as well as in blood from humans. PFCs constitute a newly emanating group of environmental contaminants, with physicochemical as well as toxicological properties different from those of other halogenated compounds. Their possible sources and environmental routes are currently unknown for the most part, mainly due to a lack of physicochemical property data and reliable detection methods. The information on the prevalence of PFCs in the European environment is scattered and incomplete and does not include all environmental compartments, in contrast to more elaborate ongoing monitoring and assessment programmes in North America. The PERFORCE project has the aim of bringing the European scientific competence in this field to a level that can match current developments in North America. The major objectives of the project are to introduce and evaluate new chemical and biological techniques as tools to assess the occurrence and distribution of PFCs in the European ecosystems, to reveal the sources and routes of uptake of PFCs, and to determine experimentally their key environmental properties. In this way, a reliable exposure assessment of PFCs can be made, as a final deliverable of the project. This exposure assessment will, together with ongoing hazard assessment and toxicity testing being undertaken elsewhere, enable a proper environmental risk assessment of PFCs to be made in the near future.

11.4 The Chair raised the question of the *modus operandi* of MCWG, and asked whether in future years we should continue to aim to work in parallel subgroups or to undertake all work in plenary? Work in subgroups had been essential when the MCWG was running multiple intercomparison exercises and the data had to be assessed during the meeting, but in recent years this had not been the case. Three of the past four meetings had been held solely in plenary, due to a reduced membership in some subgroups. MCWG agreed that it was preferable to work in plenary, as many members have, in any case, interests in more than one subgroup topic, and it was agreed that this would be the future model for MCWG. Some members felt that this increased the load on the Chair to an unacceptable degree, and after discussion it was agreed that MCWG would also appoint a Co-Chair in order to provide some support. Jacek Tronczynski was proposed and accepted this role.

11.5 Another item was raised by Klaus Nagel. Now that we are able to analyse most contaminants satisfactorily, we are being asked to develop background concentrations and other data quality criteria as a means of assessing progress towards environmental targets. How can we best use monitoring data in the future? And do we have, or can we develop, suitable tools ? The input to REGNS is likely to form a significant part of the work of MCWG in the near future – how can MCWG provide a structured scientific input? Currently, there are a number of large-scale programmes running in the marine environment (IGBP, SOLAS) intended to further develop the ecosystem approach and feed discussions on biodiversity, climate change, etc. How can MCWG best contribute to this approach? This discussion will help to focus future MCWG work in a number of related areas.

12 RECOMMENDATIONS AND ACTION LIST

The action list is appended as Annex 6, and Recommendations are listed in Annex 7.

13 DATE AND VENUE OF THE NEXT MEETING

Teresa Nunes and Victoria Besada invited the Group to hold the next MCWG meeting at the Instituto Español de Oceanografia, Centro Oceanografico de Vigo, Spain, from 7–11 March 2005. MCWG gratefully accepted this invitation.

14 CLOSURE OF THE MEETING.

MCWG members thanked the secretary, Marie-Jo Thebaud, for her assistance and support during the meeting. The Chair closed the meeting at 12:20 on Friday 19 March 2004.

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Annex 2 Agenda

1 Opening of the meeting

2. Adoption of the agenda

3. Report of the 91st ICES Statutory Meeting

4. Reports on related activities

4.1 OSPARCOM and HELCOM

4.1 Any official requests from OSPARCOM or HELCOM which arose prior to the production of the agenda have been included.

4.2 Intergovernmental Oceanographic Commission (IOC)

An update on relevant IOC programmes will be given.

4.3 Laboratory Performance Study QUASIMEME

Dr Wells has been asked to provide an update on recent studies.

4.4 Other Activities
All members who wish to make a presentation under this item should prepare a note for MCWG
4.4.1 Global POPs monitoring network (Robin Law to report).
4.4.2 The work of the AMPS group in implementation of the EU Water Framework Directive (Peter Lepom to report).

5. Reports on projects and activities in Member Countries

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

6. Requests from ACE, acme and regulatory agencies

Requests from ACE and ACME which arose prior to the preparation of the agenda have been included.

7. Plenary presentations

7.1 Marie Hélène Tusseau
The use of diffusive gradients in thin film devices (DGTs) in environmental studies.

7.2 Michel Lebeuf
Temporal trends in concentrations of BDEs and toxaphene in beluga whales from the St Lawrence estuary, Canada.

8. Subgroup activities and discussions

Justification for working in subgroups:
The Marine Chemistry Working Group is a large working group organised primarily in three parallel subgroups, the Chemical Oceanography Subgroup, the Organics Subgroup, and the Trace Metals Subgroup. The work in the three subgroups is supported by plenary discussions, which add value to the work undertaken within the subgroups.

8.1 Plenary activities and those common to all subgroups.
(see also Agenda Item 9).

8.1.1 Undertake activities relating to the implementation of the OSPAR Joint Assessment and Monitoring Programme in the light of discussions at MCWG 2003 and as required by OSPAR. Consider the sampling, analysis and concentration aspects of MCWG 2004 8.1.1/4.

8.1.2 Review the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website.

8.1.3 Review how a presentation of the long-term performance of a laboratory can be standardised taking the information from the 2000 MCWG meeting into account and report the outcome.

8.1.4 Review any new ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea Annexes on Quality Assurance and report the outcome. (MCWG 2004 8.1.4/1

Technical Note on the Determination of Persistent Organic Pollutants in Seawater, & MCWG 2004 8.1.4/2 a revised version of a Technical Note on Measurement Uncertainty).

8.1.5 Review the revised Environmental Data Reporting Format (version 3.2) and provide comments to the ICES data centre.

8.1.6 Develop plans for the preparation of detailed background materials to be used by the 2005 ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-sea areas [OSPAR2004/2]. (Marc Raemaekers and Patrick Roose will present information on the integrated chemical and biological effects programme in Belgium; Michel Lebeuf on the programme at MLI in Canada; Ton van der Zande information from the Netherlands; Robin Law information from the UK).

8.1.7 Determine priorities for assistance from WGSAEM with statistical analyses and develop with WGSAEM a plan for the necessary collaboration.

8.1.8 Begin preparations to summarise the marine chemistry of the North Sea for the period 2000–2004, and any trends in chemistry and contaminants over recent decades. Where possible, the causes of any trends should be outlined; for input to REGNS in 2006.

8.1.9 Review information on the age-relationship of contaminant concentrations in Baltic herring, and report the outcome. (Anna-Liisa Pikkarainen to report).

8.1.10 Discuss matters referred to from the three subgroups, as necessary.

8.2 Trace metal subgroup

8.2.1 Assist the Working Group on Seabird Ecology in commencing the development of related metrics, objectives, and reference levels for ecological quality objectives relating to mercury concentrations in eggs and feathers of North Sea seabirds. [OSPAR request 2004/1]. (Ton van der Zande to present information).

8.2.2 Review information on arsenic speciation, and report the outcome. (Evin McGovern to present information).

8.2.3 Review new information on the use of membrane systems for sampling and report the outcome. (Ton van der Zande to present information).

8.2.4 Consider the request from SIME regarding the derivation of background reference concentrations for metals in biota, and report the outcome. (Patrick Roose to present SIME request).

8.3 Organic subgroup

8.3.1 Assist the Working Group on Seabird Ecology in commencing the development of related metrics, objectives, and reference levels for ecological quality objectives relating to organochlorine concentrations in eggs of North Sea seabirds. [OSPAR request 2004/1]. (Ton van der Zande to present information).

8.3.2 Review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish, and report the outcome.

8.3.3 Review new information on the use of membrane systems for sampling and report the outcome.

8.3.4 Review new information on the monitoring and analysis of toxaphene, and report the outcome. (Gert Asmund will present information on toxaphene concentrations in birds, whales, seals and fish from Greenland; Michel Lebeuf will present information on temporal trends of toxaphene concentrations in beluga whales from the St Lawrence estuary).

8.3.5 Review new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants, and report the outcome. (Michel Lebeuf will present information on temporal trends in concentrations of BDEs in beluga whales from the St Lawrence estuary).

8.3.6 Review new information concerning the analysis of dioxins and the preparation of reference materials for these compounds, and report the outcome.

8.3.7 Review new information on the impact of alkylphenols from produced water, and report the outcome.

8.3.8 Review new information on the herbicides isoproturon and diuron, and report the outcome.

8.3.9 Consider the request from SIME regarding the derivation of background reference concentrations for polycyclic aromatic hydrocarbons in biota, and report the outcome. (Patrick Roose to present SIME request).

8.4 Chemical Oceanography subgroup

8.4.1 Provide guidance and assistance relating to the development of a series of data products to illustrate the eutrophication status within the ICES area.

8.4.2 Consider requests from the Chairs of SGEUT for information relating to the work of the study group.

9 Plenary discussion of subgroup work

10 Election of MCWG Chair for the period 2004–2007

11 Any other business

12 Recommendations and action list

13 Date and venue of the next meeting

14 Closure of the meeting

Annex 3 The age-relationship of contaminants in Baltic herring

Inorganic and organic contaminants in different age classes of Baltic Herring

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Environmental monitoring analysis of hazardous substances is a part of the HELCOM monitoring core program (1). Since 1979, heavy metals (Cd, Hg, Pb, Cu and Zn) and polychlorinated biphenyls (CB28, CB52, CB101, CB118, CB153, CB138 and CB180), p,p'-DDT with its' two metabolites (p,p'-DDD and p,p'-DDE) have been determined in 2–3-year-old female Baltic herring (*Clupea harengus*) (2,3,4). Selected representative sampling areas are situated close to Finland (Fig. 1). In 1997–2001, different age classes of Baltic herring were studied in the frame of supporting the HELCOM monitoring program (2,5). Female herrings, age of two to twelve years, were collected each year from one defined catchment area (see Table 1). Age determinations of herrings were performed in the Finnish Game and Fisheries Research Institute (6). Sample handling and chemical analyses were conducted in the Finnish Institute of Marine Research. Heavy metals were determined with an atomic absorption spectrophotometer and organic contaminants with a gas chromatographic method of analysis (a dual-column system, ECD detection).

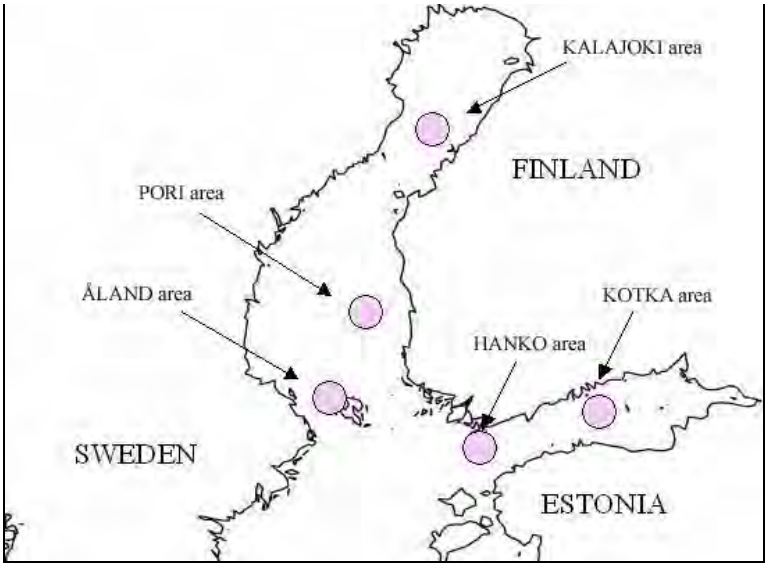

Figure 1. Location of herring sampling areas.

Table 1. Baltic herring/sample information.

Sampling year	**Area**	**Organic contaminants (Muscle)**	**Hg (Muscle)**	**Cd, Pb, Cu, Zn (Liver)**
1997/July	Bothnian Sea/Pori	Homogenate (freeze-dried)	Homogenate (freeze-dried)	-
1998/June	Gulf of Finland/Kotka	Homogenate (freeze-dried)	Homogenate (freeze-dried)	-
1999/Sep–Oct	Bothnian Bay/Kalajoki	Homogenate (freeze-dried)	Individual (fresh)	Individual (freeze-dried)
2000/May	Bothnian Sea/Åland	-	Individual (fresh)	Individual (freeze-dried)
2001/May	Gulf of Finland/Hanko	Individual (fresh)	Individual (fresh)	Individual (freeze-dried)

Results

Age-dependence was found for mercury (Fig. 2) and organic contaminants (Fig. 3) in herring muscle (5). But no common trend was found for cadmium, lead, copper or zinc in herring liver (5). In the latest age-class studies in 2001, concentration levels of organic contaminants were about five-fold (2) and the level of mercury about seven-fold in ten year-old herrings compared to two-year old herrings (on a wet weight basis). The temporal trend for sum parameters of DDTs and CBs was decreasing (Fig. 3). During 1997–2001, an average decrease in organic contaminant concentrations (on a lipid weight basis) was about 30%. The levels of contaminants were compared to findings for 1–6-year-old herrings caught from the Gulf of Finland in 1981 (see Table 2) (7). This study confirmed the decrease in concentrations of Hg, CBs, and DDTs from early 1980s until these days.

Table 2. Comparison of contaminant concentration levels.

	Age of herrings	**1981 (ref. 7)**	**1997–2001**
Hg	1–4 years	15–45 µg kg^{-1} ww	10–30 µg kg^{-1} ww
Sum of CBs	1–6 years	16–58 µg kg^{-1} ww	3.0–28 µg kg^{-1} ww
Sum of three DDTs	1–6 years	5.3–27 µg kg^{-1} ww	1.4–29 µg kg^{-1} ww

In this study, no increasing trend was found for cadmium. Cadmium concentrations in herring liver varied between 0.3–1.2 mg kg^{-1} (ww) for 2–12-year-old herrings, having the highest value in Åland 2000. Lead concentrations found in liver were mostly under the limit of determination (< 0.03 mg kg^{-1} ww), whereas copper and zinc concentrations varied 2.3–5.2 mg kg^{-1} (ww) and 21–27 mg kg^{-1} (ww), respectively.

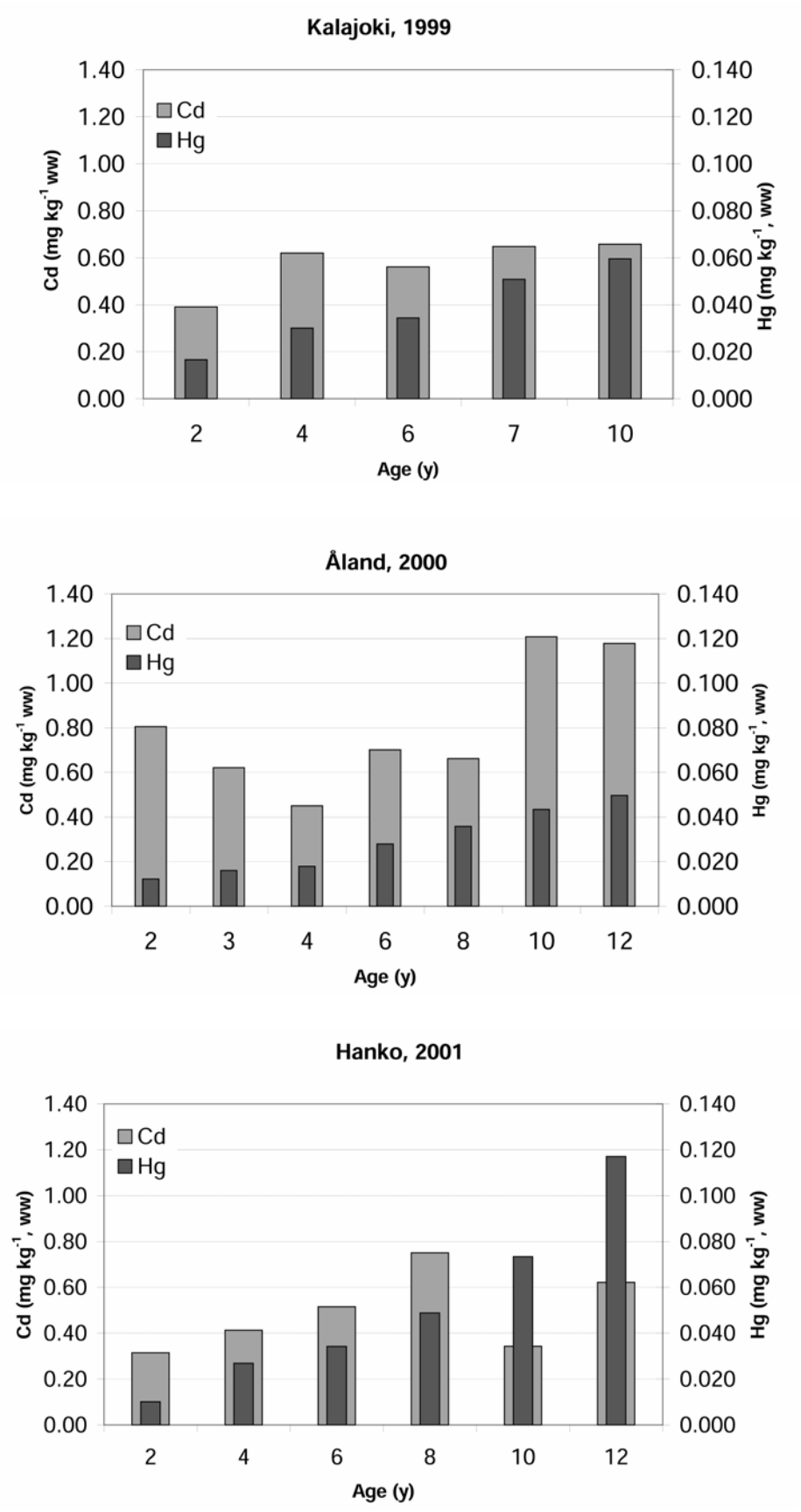

Figure 2. Inorganic contaminants in Baltic female herrings: mercury in muscle and cadmium in liver.

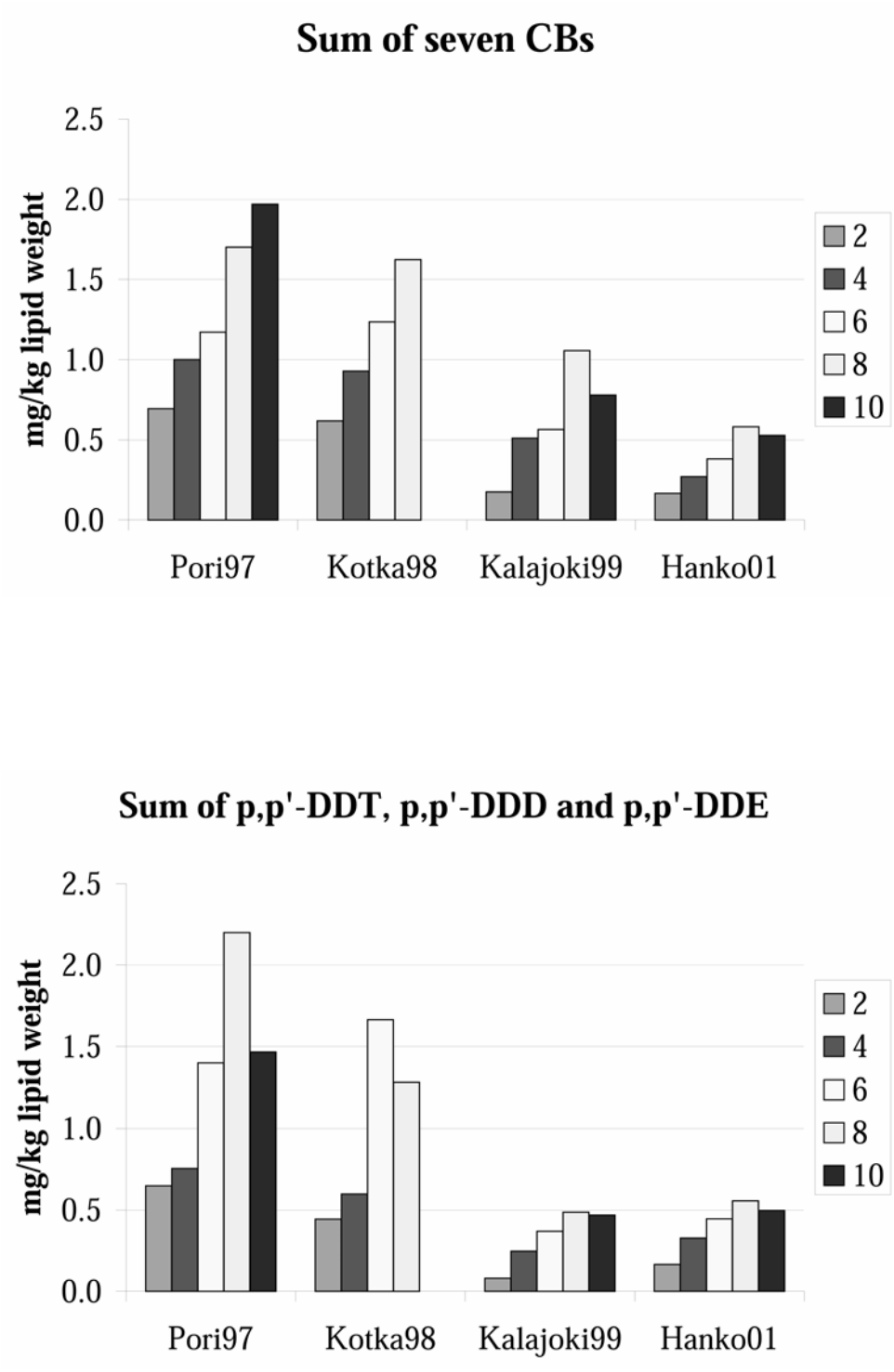

Figure 3. Organic contaminants (CBs and DDTs) in muscle of Baltic female herrings (with age of two to ten years) in 1997–2001.

Conclusions

This age class study of Baltic herring indicated that fat-soluble organic contaminants and mercury are enriched in the herring muscle and the amount of contamination is age-dependent. Temporal trends of organic contaminant concentrations were downwards from 1997 to 2001.

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Annex 4 Review of Arsenic in the Marine Environment

Introduction

Arsenic (As) is an element that raises much concern from both an environmental and a human health perspective. It is a highly abundant metalloid, occurring naturally in soils and rocks. Large quantities of arsenic compounds are released into the environment, with natural processes (e.g., weathering and volcanic activity) accounting for 60%, versus 40% from anthropogenic sources such as mining, smelting of non-ferrous metals and burning of fossil fuels (Chilvers and Peterson, 1987).

Ingestion, via food and water, is the principal source of arsenic for humans. Seafood contributes a significant percentage (50–92%) of the dietary intake of arsenic. However, the chemistry of arsenic is complex and it is well recognised that different species of arsenic produce diverse toxicological effects in organisms (including humans). The most toxic forms of arsenic found in food and water are the inorganic arsenite, As(−III) and arsenate, As(−V). In addition to their general toxicity, both of these compounds are classified as carcinogens.

A range of marine organisms have been found to accumulate arsenic from sediments and the water column, resulting in higher levels of this element in fish than in most other foods. Arsenic is the element most commonly cited in discussions of speciation and the food chain. In general, it is widely held that inorganic forms of arsenic are more toxic than organic species. However, the valency is considered a more important factor in determining the toxicity of arsenic species than the organic or inorganic nature of the compounds (Edmonds and Francesconi, 1993). Organic arsenicals generally dominate in marine animals and only a few per cent of the total arsenic in fish is present in inorganic forms. The principal arsenic species found in fish and invertebrates, arsenobetaine (AsB), is a water-soluble compound that poses little hazard to the organism or its consumer. Arsenosugars dominate in marine plants. In seaweed, arsenosugars are the quantitatively dominating arsenic species. Recent investigations into the metabolites of arsenosugars in seaweed-eating sheep have identified a thio-organoarsenate compound (Hansen *et al*., 2004). The toxicity of arsenosugars and their metabolites is not known in detail.

Despite the fact the much of the arsenic that occurs in fish, shellfish, and seaweed is non-toxic, national and international legislation and monitoring programmes continue, for the most part, to focus on total arsenic content. This is due in part to the fact that analytical methods for differentiating the various species and determining the inorganic arsenic levels are not readily available or routine.

Sources and Occurrence of Arsenic

Arsenic is the twentieth most abundant element in the earth's crust and occurs naturally in soil and in many types of rock, and is especially abundant in minerals and ores that contain copper, lead, iron, nickel, and cobalt. High levels of arsenic are also found in some coal. Elemental arsenic is ordinarily a steel grey metal-like material that is rarely found in the environment. More commonly, it bonds with various elements such as oxygen, chlorine, and sulphur; and with carbon and hydrogen to form organic arsenic compounds. Natural weathering processes release arsenic to water. Volcanic action is the most important natural source, followed by low-temperature volatilization and forest fires. Approximately one-third of the atmospheric flux of arsenic is of natural origin.

Mining and smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water, and soil. Together, these activities account for approximately 80% of anthropogenic arsenic emissions (Chilvers and Peterson, 1987). The use of arsenic in the preservation of timber (primarily as arsenic trioxide) has also led to contamination of the environment. Arsenic releases are also associated with leaching from hazardous waste disposal sites and discharges from sewage treatment facilities.

Elemental arsenic is commercially produced by reduction of inorganic arsenic trioxide (As_2O_3) with charcoal. Arsenic trioxide is the arsenic compound of chief commercial importance. It is produced commercially as a by-product of metal smelting operations. Approximately 70% of the world arsenic production is used in timber treatment as copper chrome arsenate (CCA). Metallic arsenic is used in the electronics industry as a metal alloy for use in lead-acid batteries, semiconductors, and light-emitting diodes. Other uses for arsenic include agricultural chemicals, glass, pharmaceuticals, leather pigments, and as an animal growth stimulant.

In the past, inorganic arsenic compounds were used as a pesticide, leaving large tracts of agricultural land contaminated. Organic arsenicals, namely cacodylic acid, disodium methylarsenate (DSMA), and monosodium methylarsenate (MSMA) are still used as pesticides.

Arsenic can enter the marine environment from natural diffuse sources and anthropogenic point and diffuse sources, such as those outlined above. In addition, some arsenic-containing chemical-warfare agents (e.g., Adamsite and Lewisite), used during World War II, and dumped in certain areas of the Baltic Sea, Skagerrak, and Northeast Atlantic (HELCOM, 1995 and OSPAR, 2002), may also contribute to localized inputs to the marine environment.

Occurrence of Arsenic in the Marine Environment

The marine chemistry and speciation of arsenic is complex. Its behaviour is influenced by several simultaneously occurring reactions (precipitation and dissolution of solid phases, oxidation and reduction transformations, and adsorption and desorption on particulate matter), which have important implications for its bioavailability and toxicity to marine organisms and their consumers. The arsenicals occurring in various marine compartments are outlined in Table 1 and discussed below in greater detail. Appendix I shows naturally occurring inorganic and organic arsenic species.

Table 1. Arsenic species in the various marine compartments (Francesconi and Edmonds, 1997)

Arsenic Species	Sea water	Sediments/Pore water	Marine Algae	Marine Animals
As(V)	Major	Major	Minor	Trace
As(III)	Major	Major		Trace
MMA	Minor	Minor	Trace	
DMA	Minor	Minor	Trace	Trace
Arsenosugars	ND	ND	Major	Minor
Arsenobetaine	ND	ND	ND	Major
Arsenocholine	ND	ND	ND	Trace
TMAO		Trace		Trace
TeMA	ND	ND	ND	Minor

ND – Not Detected

As(V) – Arsenate; As(III) – Arsenite; MMA – methylarsonic acid; DMA – dimethylarsinic acid; TMAO – Trimethylarsine oxide and TeMA – Tetramethylarsonium ion.

Arsenic in Sea Water

Arsenic can occur in estuarine and marine waters in four oxidation states: As(+V), As(+III), As(0), and As(−III). Arsenate, As(V) and Arsenite, As(III) are the dominant forms of inorganic arsenic in marine and estuarine waters. The dominant form of inorganic arsenic in oxygenated sea water is arsenate (Byrd, 1990). In open oceanic sea water, the ratio of arsenate to arsenite is approximately 327 (Li, 1991). In coastal waters with high primary production and freshwater runoff influence, the ratio may be much lower. Higher levels of arsenite in oxygenated waters can result from biotic and abiotic reduction of arsenate, atmospheric deposition, upwelling of anoxic waters, and input from hypoxic river basins (Cutter, 1992). Two organic forms of arsenic, methylarsonic acid (MMA) and dimethylarsinic acid (DMA), are also frequently found in sea water, but at much lower concentrations than inorganic arsenic. Their presence results from the biotransformation of arsenate by phytoplankton.

During winter the dissolved arsenic present is inorganic. Seasonal increases in concentrations of arsenite, MMA, and DMA are most likely caused by reduction followed by oxidative methylation of arsenate compounds by phytoplankton, bacteria, and yeasts. Arsenite and methylarsenic are excreted by living microbiota or released when microorganisms die. In aerobic sea water, arsenite is rapidly oxidised to arsenate by bacteria and abiotically. Thus, the proportion of arsenate, arsenite, and methylated arsenic species in sea water depends on redox conditions, temperature/season, and species composition and abundance of microorganisms. In oxygenated, biologically productive waters, arsenate is almost always the most abundant form of arsenic. The physical process most likely to limit dissolved arsenic concentrations is adsorption to particulate matter (Maher and Butler, 1988).

Concentrations of total arsenic in clean open oceans and coastal waters are typically in the order of 0.5 µg l^{-1} to 3 µg l^{-1} (WHO, 2001; Neff, 2002). Higher concentrations, up to 40 µg l^{-1}, have been recorded in some estuaries and coastal waters, and are sometimes related to the vicinity of a discharge point (Sadiq, 1992). Sadiq (1992) suggests a reference concentration for total arsenic of 2 µg l^{-1} in uncontaminated sea water. In estuarine waters, the concentration of arsenic in the water generally increases from the head to the mouth of the estuary, reflecting progressive mixing of arsenic-poor

river water with arsenic-rich sea water. For example, in the St. Lawrence estuary (Canada) arsenic concentrations increased with increasing salinity (0–31 PSU) from 0.5 µg l^{-1} to 1.4 µg l^{-1} (Tremblay and Gobeil, 1990). Methylated arsenic (MMA and DMA) accounts for between 2 and 18 percent of total dissolved arsenic (Neff, 2002). In the Tamar estuary (United Kingdom), concentrations of MMA ranged from 0.02–0.46 µg As/l and DMA from 0.02–1.27 µg As/l, typically 4% and 10% of the total soluble arsenic levels, respectively (Howard *et al*., 1988).

Arsenic in Marine Sediments

Marine sediments can act as a sink or source for arsenic, depending on the prevailing physicochemical conditions (e.g., pH and redox conditions), the presence of organic chelators, and the abundance of living organisms. As a result, they play an important role in regulating As concentrations in interstitial waters and the overlying water column.

The average total arsenic concentration in uncontaminated nearshore marine and estuarine sediments is generally in the range 3–15 µg g^{-1} (Fodor, 2001; Neff, 2002). Monitoring of surface sediments around the coast of Greenland has shown total arsenic concentrations in the range 1–59 µg g^{-1} (Data supplied by Gert Asmund, NERI). Elevated concentrations in nearshore and coastal environments are associated with natural and anthropogenic sources. For example, sediments in the southwestern North Sea contain < 0.15–135 µg g^{-1} dry wt arsenic, with the highest concentrations in the outer Thames and Humber estuaries and along the Norfolk and Yorkshire coasts (Whalley *et al*., 1999). Arsenic concentrations in deep-water sediments average 40 µg g^{-1}, with levels of up to 400 µg g^{-1} recorded from the equatorial Pacific Ocean (Bostrom and Valdes, 1969).

In oxidised marine sediments, arsenate is the most abundant form of arsenic, whilst in reduced sediment layers arsenite is the dominant dissolved and solid species (Neff, 2002). Arsenite is rapidly oxidised biotically and abiotically to arsenate in aerobic sediment layers. There have been few studies on the arsenic species present in marine sediments as extraction methods cannot fully assure the integrity of the species (Fodor, 2001). The chemical forms of arsenic in the interstitial waters of sediments have been examined (Andreae, 1979; Ebdon *et al*., 1987; Reimer and Thompson, 1988 – all cited in Francesconi and Edmonds, 1998). As with sea water, inorganic arsenic predominates in sediment pore water. Methylarsonate and dimethylarsinate can occur at levels of 1–4% (Ebdon *et al*., 1987) and trimethylarsine oxide has also been detected at trace amounts (Reimer and Thompson, 1988). These three compounds are presumably derived from microbial synthesis (Reimer and Thompson, 1988).

Concentrations of dissolved inorganic and organic arsenic are generally higher in sediment pore water than in the overlying water column. For example, total pore-water arsenic in sediments off British Columbia ranges from 3–52 µg l^{-1} (Reimer and Thompson, 1988); and in the outer Thames River estuary dissolved arsenic concentrations increased with depth in sediment to about 15 µg l^{-1} at 4 cm (Millward *et al*., 1997 – cited in Neff, 2002). Arsenic-rich pore water can be mixed up into the overlying water column via sediment resuspension and bioturbation.

Arsenic in Marine Organisms

Algae

Although the role of phytoplankton in defining the speciation of arsenic in the marine environment is well studied, relatively little has been published on the concentrations of total arsenic in phytoplankton. Benson and Summons (1981) reported 9 mg kg^{-1} total arsenic in a mixed marine phytoplankton population near Cape Ferguson (Queensland, Australia). In contrast, arsenic concentration and speciation in macroalgae has been the subject of extensive study. This work has been reviewed by Phillips (1990), Francesconi and Edmonds (1997, 1998), and Neff (1997). The consensus is that most marine macroalgae accumulate moderate to high concentrations of total arsenic (Table 2), with concentrations being generally higher in the brown algae (Phaeophyceae) than either the red or green algae (Francesconi and Edmonds, 1997). Phillips (1990) surmises that the level of arsenic present appears to be more dependent on the species concerned, rather that the degree of contamination of the ambient environment.

Table 2. Arsenic concentrations in some marine algae (Francesconi and Edmonds, 1997).

Type of Algae (No. Species)	Location	Total As Range (mg kg^{-1} dry wt)	Total As Median (mg kg^{-1} dry wt)	Ref.
Brown (8)	India	8–68	30	Dhandhukia and Seshardi, 1969
Red (5)		0–5	1.5	
Green (5)		0.1–6.3	2.2	
Brown (7)	Norway	15–109	44	Lunde, 1970
Red (2)		10–13	12	
Brown (3)	UK (inshore)	26–47	39	Leatherland and Burton, 1974
Red (2)		11–39	25	
Brown (14)	Australia	21.3–179	62	Maher and Clarke, 1984
Red (10)		12.5–31.3	19.2	
Green (9)		6.3–16.3	10.7	
Brown (14)	USA	1.06–31.6	10.3	Sanders, 1979
Red (10)		0.43–3.16	1.43	
Green (9)		0.17–23.3	1.54	

Environmental monitoring of arsenic levels in two species of seaweed (*Fucus vesiculosus* and *Fucus disticus*) around the Greenland coast was carried out during the period 1998–2002 (data supplied by Gert Asmund, NERI). Total arsenic levels in the growth tip of *F. vesiculosus* ranged from 28.2–66.6 µg g^{-1} dry wt (median = 46.4 µg g^{-1}; n = 36). In *F. disticus*, total arsenic ranged from 27.4–49.6 µg g^{-1}dry wt (median = 38.1 µg g^{-1}; n = 30). In the South Atlantic, mean total arsenic concentrations in macroalgae ranged from 5.3–70.2 µg g^{-1}, with inorganic arsenic residues ranging from 0.2–2.0 µg g^{-1} (Muse *et al*., 1989). Seasonal changes in arsenic speciation in the brown alga *Fucus gardneri* in Vancouver (Canada) have been reported by Lai *et al*. (1998). During the summer, algae contain 9 µg As g^{-1} with most (79–98%) being extractable, whereas during the winter months residues range from 16–22 µg g^{-1} with extraction efficiencies of 5.8–49%. Differences in concentration between various parts of plants have also been reported. Bohn (1979) reported total arsenic in the growing tip, main branches, and stipes of the brown alga *Fucus disthicus* of 36–37 µg g^{-1} dry weight, 13–17µg g^{-1} dry weight, and 18–22 µg g^{-1} dry weight, respectively.

Concentrations of up to 380 µg g^{-1} have been measured in the brown alga *Fucus vesiculosus* in a UK estuary heavily contaminated with arsenic from mine drainage (Langston, 1984), in comparison with levels in the range of 10.2–59 µg g^{-1} in the same species from less contaminated British estuaries, the North Sea, and the Baltic Sea (Langston, 1984; Stoeppler *et al*., 1986). Klumpp and Peterson (1979) have also reported elevated levels of arsenic in a contaminated estuary. Mean arsenic concentrations in macroalgae ranged from 83.7–141.4 µg g^{-1} dry weight (maximum 189.3 µg g^{-1}) for macroalgae in Restronguet creek, southwest England (an estuary influenced by past mining activity).

Marine macroalgae contain the greatest number of arsenic species among marine samples (Francesconi and Edmonds, 1998). Most arsenic in marine algae is bound to carbohydrate molecules and is commonly referred to as arseno-sugars. A total of fifteen arsenosugars have been found in marine algae, with just four of these (arsenosugars 1–4) dominating (Francesconi and Edmonds, 1998). Other arsenic species found in algae are arsenate and DMA, which are generally minor constituents. The organic fraction of total arsenic in marine algae is highly variable but appears to be species-dependent. Neff (1997) reviewed the available data and concluded that organic arsenic accounted for between 22% and 100% of total arsenic. Phillips (1990) reviewed arsenic data for eleven species/groups of algae and showed particularly high levels of inorganic arsenic in brown algae of the genus *Sargassum* (Whyte and Engler, 1983), *Ectocarpus* sp. (Sanders 1979), and *Hizikia fusiforme* (Shinagawa, *et al*., 1983). In the case of *H. fusiforme*, inorganic arsenic accounted for almost 60% of total arsenic (Shinagawa, *et al*., 1983). Sanders (1979) found that the absolute concentration of inorganic arsenic in marine algae was not significantly different between groups (i.e., red, green and brown algae), suggesting that the variation is due to metabolic differences between algal classes rather than to differences in the environmental concentration of arsenic.

The speciation of arsenic in marine algae is an important consideration where algae form a substantial part of daily diet. The arsenic compounds present in edible seaweeds have been studied in detail (Edmonds *et al*., 1987; Shibata *et al*., 1987, 1990; Almela *et al*., 2002). As with seaweeds in general, in virtually all edible seaweeds the majority of arsenic is in the form of arsenosugars. The only edible alga that might present a problem is Hijiki (*Hizikia fusiforme*). Edmonds *et al.* (1987) reported levels of inorganic arsenic in Hijiki at approximately the same concentration as arsenosugars, i.e., about 50% of the total arsenic burden is present as arsenate. The total and inorganic arsenic content of eighteen algae food products on sale in Spain ranged from 2.3–141 µg $g^{-1}$and 0.15–88 µg g^{-1}, respectively (Almela *et al*., 2002). At the particularly high levels of inorganic arsenic found in *Hizikia fusiforme*, a daily consumption of 1.7 g of the product would reach the Provisional Tolerable Weekly intake recommended by the WHO. The Canadian Food Inspection Agency has advised consumers to avoid consumption of Hijiki on the basis that consumption of only small amounts could result in the intake of inorganic arsenic that exceeds the tolerable daily intake for this substance (CFIA, 2001).

Invertebrates

A considerable amount of information has been published on the accumulation of arsenic in invertebrates. Unsurprisingly, much of the focus has been on molluscs and crustaceans, especially edible species. Phillips (1990) has reviewed much of the work and the findings are presented below.

Table 3. Concentrations of total arsenic in invertebrates as reported by various authors.

Species	**Location**	**Mean (Range) (mg kg^{-1})**	**Ref**
Bivalves			
Crassostrea gigas	New Zealand	10–13	Winchester and Keating, 1980
	Japan	25 (23–28)	Shiomi *et al.*, 1984
Pecten maximus	Scotland	6.0–8.4	Falconer *et al.*, 1983
Ostrea edulis	Lynher Estuary, UK	9.1 (6.9–11)	Bland *et al.*, 1982
Scrobicularia plana	UK estuaries	5.0–190	Langston, 1980
Mytilus edulis	West Greenland	14.3–16.7	Bohn, 1975
Gastropods			
Patella vulgata	Restronguet Creek, UK	37 (35–41)	Klumpp and Peterson, 1979
Nucella lapillus	Restronguet Creek, UK	48 (38–64)	Klumpp and Peterson, 1979
Littorina littorea	UK estuaries	9.0–17	Bryan *et al.*, 1983
	Scotland	13–97	Falconer *et al.*, 1983
Cephalopods			
Sepia officinalis (gills)	S. England	99	Leatherland and Burton, 1974
Loligo forbesi	Scotland	23–48	Falconer *et al.*, 1983
Crustaceans			
Carcinus maenas (whole)	Restronguet Creek, UK	22–62	Klumpp and Peterson, 1979
Pandulis borealis	Norway	30–42	Lunde, 1973
(muscle)	West Greenland	62 (52–71)	Bohn, 1975
Cancer pagurus (white meat)	Scotland	111 (40–191)	Falconer *et al.*, 1983
(brown meat)	Scotland	82 (39–127)	Falconer *et al.*, 1983
5 decapod species	South Australia	10–62 (7–91)	Maher, 1983
3 decapod species	North-east Atlantic	17–23	Leatherland *et al.*, 1973

Note: All references cited in Phillips (1990)
Data refer to whole soft parts unless otherwise stated.
Where several means are reported, these refer to different locations.

In molluscs, the concentration of total arsenic varies widely, both between species and with location in certain species. Total arsenic concentration has also been shown to vary with age (Leatherland and Burton, 1974) and seasonally (La Touche and Mix, 1982 – cited in Phillips, 1990), although the evidence to support these patterns is far from conclusive. The diet of molluscs may be an important source of arsenic for molluscs. There is some evidence to suggest higher levels of total arsenic in carnivorous gastropods than in herbivorous or planktivorous gastropods or bivalves (Shiomi *et al*., 1984). However, some pelagic crustaceans contain relatively high concentrations of arsenic.

Despite some evidence to suggest that crustaceans may have higher concentrations than other invertebrate phyla (e.g., Eisler, 1981), comparisons of total arsenic levels between organisms of different phyla have produced no consistent support for this theory (Phillips, 1990). However, the published data seem to indicate that, as with molluscs, there is significant inter-species variation. Crabs (*Cancer pagurus*) and lobsters of several genera (including *Hommarus, Nephrops, Jasus and Thenus*) may contain more than 100 mg kg^{-1} dry wt and occasionally more than 200 mg kg^{-1} of total arsenic in abdominal muscle (Falconer *et al*., 1983; Neff, 1997).

Much of the data quoted in literature relate to studies where samples were collected on a one-off basis. Monitoring data supplied by members of the ICES MCWG as part of this review are presented in Table 4.

Table 4. Total arsenic in the tissues of molluscs and crustaceans from various monitoring programmes.

Species	**Location(s)**	**Tissue**	**Wet/Dry Wt.**	**Total As Range (mg kg^{-1})**	**Total As Median (mg kg^{-1})**	**N**	**Ref.**
Molluscs							
Mytilus edulis	Greenland	Flesh	Wet	1.27–2.3	1.79	32	1
	UK	Flesh	Wet	0.9–10	2	197	2
	France	Flesh	Dry	6–33		51	3
	Belgium	Flesh	Wet	0.16–2.90	1.77	76	4
	Germany	Flesh	Wet	0.19–2.20	1.41	28	5
Crassostrea gigas	UK	Flesh	Wet	0.93–3.7	1.4	35	2
	France	Flesh	Dry	14–27		33	3
Clam	Greenland	Flesh	Wet	0.82–1.46	1.05	17	1
Serripes groenlandicum	Greenland	Flesh	Wet	2.0–2.31	2.15	10	1
Crustaceans							
Cancer pagurus	UK	Muscle	Wet	6.3–26	8.2	8	2
	UK	Hepatopancreas	Wet	5.3–31	9.2	11	2
Pink Shrimp	UK	Whole	Wet	14–22	18	21	1
Snow Crab	Greenland	Meat	Wet	13.4–28.3	27.7	18	1
	Greenland	Liver	Wet	21.5–52.6	34.8	18	1

References

1. Data supplied by Gert Asmund (NERI) for the period 1998–2002.
2. Data supplied by CEFAS for the period 1990–2002 for North Sea, Irish Sea and Celtic Sea.
3. IFREMER, 1994. Ranges quoted are of means of 4 samples taken during 1993 at each of 33 sites (oysters) and 51 sites (mussels).
4. Data supplied by Marc Raemaekers (Sea Fisheries Department, Ministry of Agriculture). Data collected during the period 1992–2002. (Data reported as individual samples but also some means). Analyses carried out by the Veterinary and Agrochemical Research Centre at Tervuren (Belgium).
5. Data for East and North Frisian coastal waters and estuaries and Helgoland (1999–2002) supplied by Michael Haarich, BSH Hamburg. Range of medians and median of medians presented in table.

Fish

Arsenic speciation in fish and invertebrates is considered together (below). As a general rule, muscle tissues of demersal fish species contain higher concentrations of total arsenic than those of pelagic species (Neff, 2002).

Table 5. Total arsenic in the tissues of fish from various monitoring programmes.

Species	**Location(s)**	**Tissue**	**Wet/Dry Wt**	**Total As Range (mg kg^{-1})**	**Total As Median (mg kg^{-1})**	**N**	**Ref.**
Spotted Wolffish (*Anarhichas minor*)	Greenland	Liver	Wet	1.42–3.11	2.59	5	1
Shorthorn Sculpin (*Myoxocephalus scorpius*)	Greenland	Liver	Wet	1.35–36.15	5.25	28	1
Cod	UK	Muscle		1.7–15	3.65	14	2
Dab	UK	Muscle		1.5–23	7.4	103	2
Flounder	UK	Muscle		0.45–19	4.2	135	2
Lesser Spotted Dogfish	UK	Liver		5.2–36	18	23	2
Plaice	UK	Muscle		4.2–64	14	40	2
Whiting	UK	Muscle		0.92–12	2.5	68	2
Flounder	Germany	Muscle	Wet	1.0 – 7.1	4.3	13	3
Dab	Germany	Muscle	Wet	1.5 – 5.3	3.1	7	3

References

1. Data supplied by Gert Asmund (NERI). Data collected during the period 1998–2002.
2. Data supplied by CEFAS for the period 1990–2002 for North Sea, Irish Sea and Celtic Sea.
3. Data for East and North Frisian coastal waters and estuaries and Heligoland (1999–2002) supplied by Michael Haarich, BSH Hamburg. Range of medians and median of medians presented in table.

The major arsenic compound in fish and invertebrates is arsenobetaine. Since it was first isolated from the western rock lobster (*Panulirus cygnus*) by Edmonds *et al.* (1977), it has been shown to be present in virtually all marine animals, and in most cases it is by far the dominant arsenic species present. It occurs at all trophic levels, although there is a tendency for it to constitute a greater percentage of total arsenic in the higher trophic-level animals. Both Francesconi and Edmonds (1997) and Phillips (1990) have reviewed the occurrence of arsenobetaine in fish, molluscs and crustaceans. Its contribution to total arsenic burden ranges from 50–90%. The tetramethylarsonium ion also commonly occurs in marine animals, particularly in bivalve molluscs where it can be the major species (Cullen and Dodd, 1989). It may occur from microbial decomposition of arsenobetaine or from microbial methylation of arsenate by the gut flora of the animals (various references cited in Francesconi and Edmonds, 1997). Although arsenobetaine in solution in seawater has not been recorded, Francesconi and Edmonds, 1990 (cited in Phillips, 1990) have shown that *Mytilus edulis* can accumulate this compound readily from seawater. Other minor arsenic species that occur in marine animals include trimethylarsine oxide and arsenocholine. A review of arsenic species in fish and invertebrates by Francesconi and Edmonds (1993) reveals that inorganic arsenic generally constitutes less than 2% of total arsenic. Flanjak (1982) found that much less than 5% of the arsenic in various species of prawn, crab and crayfish is inorganic. Furthermore, in species with higher total arsenic concentrations (> 10 mg kg^{-1}), inorganic arsenic constituted 1% or less.

In response to concerns regarding chemical weapons disposal in the Beaufort's Dyke area of the Irish Sea, fish muscle samples from around the English and Welsh coast were analysed for total and inorganic arsenic (Table 6). Total arsenic concentrations ranged from 7.9 to 26 mg kg^{-1} (wet weight), with a median value of 13 mg kg^{-1}, well within the range reported by other studies. Arsenate (As V) was not detected in any of the samples. Trace amounts of arsenite (As III) were found in some samples although the maximum amount present was 1.2% of total arsenic, which was within the range reported for fish by Francesconi and Edmonds (1993).

Table 6. Speciation analysis carried out by CEFAS (Data supplied by Bryn Jones).

Species	Arsenobetaine[1] (mg kg^{-1})	Total As (mg kg^{-1})
Cod	19.86	14
Pollack	31.93	26
Haddock	13.74	12
Whiting	2.02	2
	3.02	-
	12.45	12
Dab	10.13	9.3
Sole	5.23	6
Flounder	13.30	14
Plaice	9.42	7.4
	14.57	13

1. Arsenobetaine concentrations are indicative

Spanish data on total and inorganic arsenic data for various fish species are presented in Table 7. This summarises a survey on seafood consumed in the Basque region, reported in Munoz *et al*. (2000), and data for arsenic in fish from the Atlantic for the period 2001–2003, from a research project carried out by Instituto Español de Oceanografia, Vigo. Both surveys employed the analytical methodology described by Munoz *et al*. (2000). Results suggest low contribution of inorganic arsenic to the total arsenic determination. In the Basque survey, highest levels of inorganic arsenic were evident for bivalves, with the highest two results for the only two clam samples tested.

Table 7a. Arsenic data for fish species from the Atlantic Ocean, (IEO Vigo Spain).

Common name	Species	N	Total As Range (mg kg^{-1} wet weight)	Inorganic As Range (mg kg^{-1} wet weight)
Tuna	*Thunnus* spp.	8	0.152–1.92	0.003–0.026
Megrim	*Lepidorhombus* spp.	4	4.22–8.34	0.009–0.026
Hake	*Merluccius* spp.	8	0.353–2.49	0.006–0.019
Anglerfish	*Lophius* spp.	4	5.16–38.4	0.026–0.120
Horse mackerel	*Trachurus trachurus*	2	1.48–1.73	0.024–0.026
Sardine	*Sardina pilchardus*	2	1.55–1.85	0.028–0.033
Squid	*Loligo gahi*	2	0.136–0.218	0.006–0.008
Octopus	*Octopus vulgaris*	2	11.8–22.4	0.025–0.042
Cuttlefish	*Sepia* spp.	2	6.78–12.06	0.028–0.042

Note: Data for Atlantic fish 2001–2003 supplied by Victoria Besada (IEO-Vigo)

Table 7b. Spanish data (Basque Survey) on arsenic in fish species.

Basque Survey	N	Total As Range (mg kg^{-1} dry weight)	Inorganic As Range (mg kg^{-1} dry weight)
Megrim	12	3.08 – 53.57	0.010 – 0.116
Hake	12	3.72 – 32.04	0.008–0.054
Small Hake	12	4.05 – 24.29	0.016–0.043
Other white fish	7	9.49 – 62.97	0.029 – 0.050
Anchovy	12	2.73 – 36.87	0.042 – 0.408
Atlantic horse mackerel	12	2.20 – 14.57	0.035 – 0.198
Sardine	11	3.69 – 27.62	0.172 – 0.366
Other blue fish	17	1.02 – 74.96	0.011 – 0.142
Bivalves	12	9.15 – 24.22	0.176 – 0.877
Squid	12	0.68 – 34.27	0.022 – 0.055
Crustaceans	11	1.24 – 102.03	0.076 – 0.281

Note: Data from Basque survey from Munoz *et al.* (2000).

Higher Trophic Marine Animals

Neff (1997, 2002) reviewed studies of arsenic concentrations in marine mammal tissues and concluded that they appear to regulate arsenic at low levels in blubber, muscle, and organ tissues and are able to excrete organic arsenic ingested in food. The review showed that, with some exceptions, total arsenic concentrations rarely exceeded 1 μg g^{-1} dry wt, even in kidney and liver tissue. A review by WHO (2001) also concluded that arsenic concentrations in the liver and muscle tissue of marine mammals were generally less than 1 μg g^{-1} dry wt. Total arsenic in the liver of Greenland Ringed Seals ranged from 0.05 to 0.64 μg g^{-1} dry wt; Median = 0.29 μg g^{-1}; n = 20, (Data supplied by Gert Asmund, NERI). However, levels of up to 40 μg g^{-1} dry wt in liver and up to 20 μg g^{-1} dry wt in kidney, have been reported in dolphins (*Sousa chinesis*) and porpoises (*Neophocaena phocaenoides*) stranded along the coast of Hong Kong (Parsons, 1999a - cited in Neff, 2002). The animals may have bio-accumulated arsenic from the high concentrations in the tissue of their prey (fish), which had levels from non–detectable to 190 μg g^{-1} dry weight (whole fish), (Parsons, 1999b - cited in Neff, 2002).

A study of arsenic accumulation in the liver tissue of 16 different marine mammals by age, gender and feeding habits was conducted by Kubota *et al.* (2001). Total arsenic concentrations ranged from < 0.10 to 7.68 μg g^{-1} dry weight, and varied widely among species and individuals. No trend with age (or body length) or significant gender differences in arsenic concentration were found for most of the species. Species feeding on cephalopods and crustaceans contained higher levels of arsenic than those feeding on fishes. Finally, the study demonstrated lower arsenic concentrations in marine mammals, which are at the top of the food chain, than those of lower trophic marine organisms from other studies and concluded that the implication was that arsenic is not biomagnified in marine food chains.

In comparison to the body of work that exists in relation to marine algae and fish little is known about the chemical speciation of arsenic in higher trophic marine animals. Kubota *et al.* (2002) measured the concentrations of total arsenic and individual arsenic compounds in the livers of cetaceans (Dall's porpoise and short-finned pilot whale), seals (harp and ringed), dugong, and sea turtles (green and loggerhead), to characterize arsenic accumulation profiles. Arsenic concentrations in the livers of sea turtles were highest among the species examined. The composition of arsenic compounds was different among the species examined, possibly reflecting the differences in the metabolism of arsenic and/or the compositions of arsenic compounds in their preys. Arsenobetaine was the major arsenic compound in almost all species examined. Dimethylarsinic acid, methylarsonic acid, arsenocholine, tetramethylarsonium ion, arsenite and an unidentified arsenic compound were also detected as minor constituents. The exception, dugong, contained arsenic mainly as methylarsonic acid and dimethylarsinic acid; arsenobetaine was only a minor constituent. This difference was attributed to the diet of the dugong (marine algae).

The major arsenic compound in marine algae is arsenosugars (Francesconi and Edmonds, 1997). Arsenobetaine was a major arsenic compound in the liver of green turtle, which also feeds on marine algae. The authors (Kubota *et al*., 2002) offer two possible explanations for this inconsistency. Firstly, the green turtle is known to feed on marine animals, which contain arsenobetaine. Small quantities of arsenobetaine in their prey, which is almost completely absorbed from the gastrointestinal tract, may accumulate gradually in the liver of the green turtle. Arsenosugars, on the other hand, are

mostly excreted in the faeces of mammals (Shiomi, 1994). Secondly, arsenosugars, which are possibly precursors of arsenobetaine (Phillips, 1990), might be converted to arsenobetaine by the green turtle or by microbial flora in the intestine.

Toxicity of Arsenic to Marine Organisms

The degree of toxicity of arsenic is dependent on the form (e.g., inorganic or organic) and the oxidation state of the arsenical. Despite earlier beliefs that the organic or inorganic nature of arsenic compounds was the principal factor in determining arsenic toxicity, it is now generally considered that the valency state of arsenic is a more important factor. In general, compounds containing trivalent arsenic are much more toxic than those with a pentavalent arsenic atom. However, factors such as solubility, particle size, and rate of absorption, metabolism and excretion can also have a significant influence on toxicity of arsenic compounds. For inorganic arsenic, the pentavalent arsenate is less toxic than the trivalent arsenite (Penrose, 1974). However, reduction of arsenate to arsenite might occur in the mammalian body (Vahter and Envall, 1983) and the eventual toxicity of inorganic arsenic in either valency state should not be disregarded. Pentavalent organic arsenic compounds have very low, or no, toxic effect. Trivalent organic arsenic tends to be highly toxic (Edmonds and Francesconi, 1993). Little is known on the toxicity of arsenosugars.

The toxicity of arsenic has been determined for a range of marine organisms and reviewed by, for example, Penrose (1974), Mance *et al*. (1984), Mance (1987) and WHO (2001). Different species of marine organisms differ widely in their sensitivity to arsenic. Francesconi and Edmonds (1997) conclude that, generally, marine animals, including larval stages, are not acutely affected by arsenic levels below 200 µg l^{-1}, indicating low to moderate toxicity.

A review of toxicity data for marine invertebrates and fish from various sources (Mance *et al*., 1984; Mance, 1987; WHO, 2001) is summarised in Table 8. Although direct comparisons are difficult due to the inconsistencies in exposure time and measured effect, in general, arsenite appears to be more toxic than arsenate in acute tests. The review carried out by WHO (2001) compared the toxicity of inorganic As with that of organic As (MMA) for a small number of organisms. The 48-hr LC_{50} values for MMA ranged from 17.4 mg l^{-1} to 2361 mg l^{-1}, indicating lower toxicity than either arsenate or arsenite.

Table 8. Toxicity of arsenic to marine invertebrates and fish (Adapted from WHO, 2001 and Mance, 1987). All references quoted in WHO (2001) and Mance (1987).

Species	**Stage/Size**	**Temp (°C)**	**Salinity (g l^{-1})**	**As Species**	**Duration (hr)**	**LC_{50} (mg As/l)**	**Reference**
Polychaetes							
Nereis diversicolor	Adult	ns	Salt	Arsenite	96	> 14.5	a
Neanthes arenaceodentata	ns	ns	ns	Arsenite	ns	10.1 [m]	b
Molluscs							
Crassostrea virginica	Juvenile	15	22	As_2O_3	96	> 0.75*[n]	c
	Juvenile	13	31	Arsenate	96	> 0.4*[n]	c
Crassostrea gigas	Embryo	20	34	As_2O_3	48	0.33**[n]	d
Mytilus edulis	Embryo	17	34	As_2O_3	48	> 3.0**[n]	d
Argopecten irradians	Juvenile	20	25	Arsenite	48	4.4 [n]	e
	Juvenile	20	25	Arsenite	96	3.5 (2.1–5.8) [n]	e
Crustaceans							
Acartia clausii	Nauplius	20	35	Arsenate	96	0.011 (0.009–0.013)[n]	f
Tigriopus brevicornis	Copepodid	20	35	Arsenate	96	0.02 (0.018–0.022)[n]	f
Mysidopsis bahia	ns	ns	ns	Arsenate	96	2.3 [m]	b
Corophium insidiosum	8–12 mm	19	ns	As_2O_3	96	1.1 (0.8–1.6)[n]	g
Penaeus duorarum	Juvenile	19–24	ns	As_2O_3	48	> 30[@n]	c

Species	Stage/Size	Temp (°C)	Salinity (g l^{-1})	As Species	Duration (hr)	LC_{50} (mg As/l)	Reference
	Juvenile	19	24	Arsenate	48	< 15[@n]	c
Penaeus setiferus	Juvenile	22	25	As trisulfide	96	24 (19.1–35.2)[n]	c
Cancer magister	Zoeae	15	34	As_2O_3	96	0.23 [n]	d
Fish							
Limanda limanda	16.9 g	12	34.6	Arsenite	96	28.5 (22.7–36.0)[m]	h
Chelon labrosus	0.87 g	12	34.6	Arsenite	96	27.3(23.4–30.2)[m]	h
Onchorhynchus tshawytscha	1.99 g	12	Brackish	As_2O_3	96	21.4 (18.1–25.3)[n]	i
	1.99 g	12	Brackish	As pentoxide	96	66.5 (55.4–79.8)[n]	i
Menidia menidia	ns	ns	ns	Arsenite	ns	16 [n]	b
Morone saxatilis	1.8 g	20	22	Arsenate	96	10.3 (6.4–13.5)	j
Therapon jarbua	0.2–0.7 g	ns	36	Arsenite	96	3.38	k

n = based on nominal concentrations; m = based on measured concentrations
* = EC_{50} based on inhibition of shell disposition; ** = EC_{50} based on abnormal development; @ = EC_{50} based on abnormal development
ns = not stated
References
a - Bryan (1976); b - U.S. EPA (1985); c - Mayer (1987); d – Martin *et al.* (1981); e – Nelson *et al.* (1976); f – Forget *et al.* (1998); g – Reish (1993); h – Taylor *et al.* (1985); i – Hamilton and Buhl (1990); j – Dwyer *et al.* (1992); k – Krishnakumari *et al.* (1983).

The nauplius stages of the copepod *Tigriopus brevicornis* have the lowest acute value, with a 96-hr LC_{50} of just 10.9 µg As(V)/l (Forget *et al.*, 1998). Larvae of the echinoderm *Stronglyocentrotus purpuratus* are also particularly sensitive to arsenate, with nominal concentrations as low as 11 µg/l arsenate (approximately ten times natural concentrations of arsenate in oceanic seawater) resulting in an increased incidence of developmental abnormalities (Garman *et al.*, 1997).

Sanders (1986) showed that there was no effect on the survival of the estuarine copepod *Eurytemora affinis* during 15-day exposure tests to arsenate at concentrations of 50 µg l^{-1}. Adult copepod survival was significantly reduced at arsenate concentrations of 1 mg l^{-1} and concentrations of 100 µg l^{-1} caused a significant increase in the mortality of juveniles. Temperature has been shown to be important in determining arsenic toxicity to three estuarine invertebrates: *Corophium volutator*, *Macoma balthica* and *Tubifex costatus* (Bryant *et al.*, 1985). Survival time of the three species exposed to pentavalent arsenic for < 384 hr decreased as temperature (5, 10 and 15°C) and concentration of arsenic (1 to 128 mg $As(V)^{-1}$) increased. In the same study, salinity increases (5 to 35 g l^{-1}) had no significant effect.

Toxicity data for marine fish (Table 8) show that the 96-hr LC_{50} values are, again, generally lower for the pentavalent arsenate than for the trivalent arsenite. There are data available for the effects of variations in temperature and salinity on the toxicity of arsenic to estuarine or marine fish. However, freshwater experiments with rainbow trout (*Onchorhynchus mykiss*) found no temperature effect on arsenite toxicity (McGeachy and Dixon, 1989 – cited in WHO, 2001). The same study showed that arsenate toxicity was increased from an LC_{50} of 114.1 mg l^{-1} at 5°C to 58 mg l^{-1} at 15°C. Most of the data on the effects of arsenic on fish are based on acute toxicity tests which measure fish mortality over 96 hrs. However, some studies have also shown sub-lethal effects in freshwater fish such as growth, avoidance behaviour and fertilization/hatching.

Penrose (1974) compiled information from a range of sources of human and animal observations to rank groups of arsenical compounds in decreasing order of toxicity, as follows: arsines (trivalent inorganic or organic); arsenite (inorganic); arsenoxides (trivalent with two bonds joined to one oxygen, e.g., R-As = O where R is an alkyl group); arsenate (inorganic); pentavalent arsenicals such as arsonic acids; arsonium compounds (four organic groups with a positive charge on the arsenic – similar to arsenobetaine; metallic arsenic.

In contrast to marine animals, marine plant species (both macro– and micro–algae) and phytoplankton communities show considerable variation in their sensitivity to arsenic. Some of these impacts appear to occur at concentrations close

to those found in natural waters, particularly when ambient levels of phosphate are low (Planas and Lamarche, 1983). Growth and survival of the microalgae *Tetraselmis chui* and *Hymenomonas carterae* are not affected during exposure (6-day) to concentrations of arsenate or arsenite as high as 1 mg^{-1} (Bottino *et al*., 1978). However, growth of the diatom *Skeletonema costatum* is inhibited at concentrations of 20 μg As^{-1} arsenite and 13 µg As^{-1} arsenate, during 6–8 day exposure (Sanders, 1979). In the same study, DMA had no effect on growth at 9.8 µg As^{-1}. Arsenate and arsenite have also been shown to cause significant inhibition of ^{14}C uptake by *Skeletonema* at additions of $\geq$ 5 µg As^{-1} (Sanders, 1979). The addition of phosphate, which competes with arsenic for uptake into algal cells, eliminated the arsenate inhibition of carbon uptake.

Long-term studies with cultures of natural phytoplankton communities exposed to low levels of arsenate (1–15 µg $AS(V)^{-1}$) showed that certain species were inhibited, causing marked changes in species composition, succession and predator-prey relationships (Sanders and Vermersch, 1982; Sanders and Cibik, 1985; Sanders, 1986 – all cited in WHO, 2001). Inputs of arsenate favoured smaller diatoms and flagellates over larger diatoms. Sanders and Riedel (1987) suggest that resistant species of microalgae may have a higher affinity for phosphate and thus a lower uptake rate of arsenate, and/or some species may be able to transform arsenate intracellularly into a less toxic form, thereby making them less sensitive to arsenate and dominant in exposed communities. For marine periphyton, Blanck and Wängberg (1988) found that communities previously exposed to arsenate (concentrations from 7.5 to 22.5 µg As(V) l^{-1}) showed increased resistance to arsenate, and concluded that arsenate exerts a selection pressure on the community. This leads to the replacement of sensitive species with tolerant ones and increases the overall tolerance of the community to arsenate. Increased phosphate concentrations have also been shown to decrease toxicity of arsenate to periphyton (Wängberg and Blanck, 1990).

Growth of the macroalga *Champia parvula* is significantly reduced following exposure to arsenite at 200 µg l^{-1}, and at 300 µg l^{-1} all plants died (Thursby and Steele, 1984). At levels of 95 µg l^{-1} sexual reproduction is inhibited. The results for exposure of the same species to arsenate reveal that concentrations of 10 mg l^{-1}did not kill the plants but inhibited sexual reproduction (Thursby and Steele, 1984). Finally, as with phytoplankton, the toxicity of arsenate increases as phosphate concentration in the exposure water is decreased.

The available LD_{50} (via oral administration to mice) data for various arsenic compounds, as reported by Kaise *et al*. (1985, 1989, 1992), have been reviewed by Shiomi (1994). The acute toxicity of the trimethylated arsenic compounds present in marine organisms (arsenobetaine, arsenocholine and trimethylarsine oxide) is considerably weak compared to that for arsenic trioxide. An accurate LD_{50} cannot be determined for arsenobetaine, the most ubiquitous arsenical in marine animals, because of its extremely low toxicity (Shiomi, 1994). Arsenocholine (LD_{50} 6.5 g kg^{-1}) and trimethylarsine oxide (LD_{50} 10.6 g kg^{-1}) are 200 to 300, respectively, times less toxic than arsenic trioxide (LD_{50} 0.035 g kg^{-1}) and are judged to be virtually non-toxic (Shiomi, 1994). Experiments using rat embryos have shown that arsenobetaine and arsenocholine have no subacute or acute embryotoxicity (Irvin and Irgolic, 1988; cited in Shiomi, 1994). The tetramethylarsonium ion (TeMA), the most highly methylated arsenical, is considerably lethal (LD_{50} 0.89 g kg^{-1}) compared to the trimethylated arsenicals (above) or either methylarsonic acid (LD_{50} 1.8 g kg^{-1}) and dimethylarsinic acid (LD_{50} 1.2 g kg^{-1}) (various studies by Shiomi *et al.*, cited in Shiomi, 1994). Thus the general rule that toxicity of arsenic compounds decereases with advanced methylation is not true for TeMA. TeMA can be a major arsenic species in bivalve molluscs (Cullen and Dodd, 1989), and its nitrogenous analogue, tetramethylammonium ion (tetramine), is a known toxin. Both Shiomi (1994) and Francesconi and Edmonds (1997) conclude that further toxicological studies of TeMA are required.

Bioaccumulation and Biotransformation of Arsenic

In seawater, arsenic is usually found in the form of arsenate or arsenite. Methylated arsenic compounds (MMA and DMA) occur naturally as the result of biological activity. Organic arsenic compounds such as arsenobetaine, arsenocholine, tetramethylarsonium salts, arsenosugars and arsenic-containing lipids are mainly found in marine organisms although some of these compounds have also been found in terrestrial species. The chemical forms of arsenic play an important role in the bioaccumulation of arsenic by marine organisms and its transfer through marine food chains. Arsenate, the predominant form of inorganic arsenic, is not readily taken up by marine animals from seawater or food (Francesconi and Edmonds, 1997). However, bacteria, phytoplankton and macroalgae can take up and bioaccumulate arsenate from solution in seawater (Langston, 1984; Lindsay and Sanders, 1990) and transform it to organic forms of arsenic that are readily accumulated by marine animals (Andreae and Klumpp, 1979). In general, marine animals bioaccumulate several fold more arsenic than freshwater biota (Lunde, 1977).

Arsenic has a particularly strong affinity to sulphur and binds to a variety of sulphur-rich peptides and proteins. The principal focus to date of arsenic speciation has been on oxo-arsenicals, the most abundant in nature. Although arsenic binds to sulphur-rich proteins, As-S and As = S compounds had, until very recently, not been identified in natural samples. Recent studies of arsenic metabolism in seaweed-eating sheep from Northern Scotland (Feldmann *et al.*, 2000)

have identified a new thio-organoarsenate compound (2-dimethylarsinothioyl acetic acid) in the sheep's urine (Hansen *et al.*, 2004). The compound is a breakdown product of an arsenosugar, of which there was a high concentration in the seaweed. The authors believe that mammalian arsenic metabolism is much more complex than previously thought and that more sulphur-containing arsenic compounds will be found in biological samples. Whilst the general consensus is that arsenosugars are non-toxic, the toxicity of this metabolite remains unknown.

Human Exposure

For the general population, exposure to arsenic in the environment is primarily through the ingestion of food and water, with food being the principal contributor. The daily intake of total arsenic from food and beverages is generally between 20 and 300 µg day^{-1} (WHO, 2001). In Japan, where arsenic-rich seafood, seaweed and rice constitute a large part of the diet, the daily intake of arsenic has been estimated at 985 µg day^{-1}. By comparison, pulmonary exposure contributes up to approximately 1 µg day^{-1}in a non-smoker (10 µg day^{-1} in a smoker) and more in polluted areas. Total arsenic concentrations in foodstuffs from different countries vary widely depending on the food type, growing conditions (type of soil, water, geochemical activity, use of arsenical pesticides) and processing techniques. However, regardless of location, seafood is a major source of dietary arsenic. Monitoring studies in the USA (Yost *et al*., 1998), the United Kingdom (MAFF, 1997), Canada (Dabeka *et al*., 1993) and Australia (ANZFA, 1994) show that, of all the food groups, seafood has by far the highest concentrations of total arsenic. A recently completed EU SCOOP (Scientific Co-Operation on Questions Relating to Food) Task for the Scientific Committee for Food (SCF) assessed dietary exposure to arsenic in Member States (SCF, In Press). The results (Table 9) show high levels of arsenic in seafood compared to other foods, which is consistent with previous studies. The origin of the fish in the diet is of great importance. Marine species of fish may have As-levels more than ten times higher than that in fish from brackish water for example.

Table 9. Total As concentrations in various food groups.

Food Category	**Europe[a]**	**Canada[b]**	
	Range (µg g^{-1})	**Mean Level (µg g^{-1})**	**Range (µg g^{-1})**
Dairy products	0.0004 – 0.021	0.004	< 0.0004 – 0.026
Meat & poultry	0.0033 – 0.01	0.024	< 0.001 – 0.54
Fish & shellfish	0.15 – 18.0	1.66	0.077 – 4.8
Bakery goods & cereals	0.006 – 0.05	0.025	< 0.0001 – 0.37
Vegetables	0.0028 – 0.021	0.007	< 0.0001 – 0.084
Fruit	0.006 – 0.01	0.0045	< 0.0001 – 0.037
Fats & oils	0.003 – 0.005	0.019	< 0.001 – 0.057

a: SCF (In press) Only a few countries supplied data
b: Canada – Dabeka *et al*., 1993.

The SCOOP task estimated the total daily intake of dietary arsenic. Based on average food consumption patterns and levels of As in the major food groups, data submitted by Denmark and the UK, as part of the SCOOP task, indicate that fish and seafood provide a large portion of dietary arsenic intake. In Denmark fish contribute just over 50% to the mean daily dietary intake of arsenic (64 µg day^{-1}). In the UK, fish accounts for about 92% of the mean daily intake of arsenic, yet forms only 2%, by weight, of the average diet. Similarly high contributions by seafood to mean daily arsenic intake have been recorded in other countries (Table 10). Thus the total dietary intake of arsenic is largely determined by the amount of seafood consumed.

Table 10. Percentage contribution to mean daily dietary arsenic intake in various countries. All data quoted in Larsen and Berg, 2001).

Country	Total Arsenic Intake (µg day^{-1})	Seafood Contribution (µg day^{-1})	% Contribution by Seafood (µg day^{-1})
Canada	49	32	64
USA	56.6	51.9	92
Australia	63	39.7	63

The majority of monitoring studies quote concentration of total arsenic. However, arsenic in foods is a mixture of inorganic species and organically bound forms such as arsenobetaine and arsenosugars. These organic forms are generally considered harmless. The water-soluble Arsenate (As III) and Arsenite (As V) are the most toxic arsenic compounds. Approximately 25% of the arsenic present in food is inorganic, but this is highly dependent on food type (WHO, 2001). There are only limited data on the ratio inorganic/total As in foodstuffs and the percentage contribution of inorganic As to the total daily intake of As from food. Estimates show that inorganic arsenic accounts for a large percentage of total arsenic in meats (75%), poultry (65%), dairy products (75%), and cereals (65%) (WHO, 2001; Yost *et al*., 1998). In seafood, fruits and vegetables the organic species dominate, with inorganic arsenic accounting for just 0–10%, 10% and 5%, respectively. A review of inorganic arsenic in seafoods (excluding algae), by Edmonds and Francesconi (1993), concluded that it constituted less than 1% of total arsenic. Larsen and Berg (2001) suggest an assumption that a maximum of 5% of the arsenic ingested via seafood is inorganic. The US FDA recommends methods of analysing for total arsenic and estimating inorganic arsenic concentrations based on the assumption that 10% of the total arsenic in fish tissue is in the inorganic form (US FDA, 1993).

Dietary studies often quote only total arsenic intake and do not give speciation information. In Australia the estimated mean adult dietary intake of inorganic arsenic is 0.77 µg day^{-1}, or just 1.2% of total arsenic (Larsen and Berg, 2001). Mohri *et al.* (1990 – cited in WHO, 2001) estimated that the customary Japanese diet contained 5.7% inorganic arsenic with an intake ranging from 27 to 376 µg total arsenic day^{-1} (1.5 – 21.4 µg day^{-1} inorganic arsenic). A study in the Spanish Basque Region revealed that the mean adult dietary intake of inorganic arsenic amounted to 2.2 µg day^{-1}, accounting for 1.5% of the PTWI as recommended by WHO (Urieta *et al*., 2001)[1]. The proportion of inorganic arsenic to total arsenic in the seafood analysed was in the range 0.3–1.8%. The total adult daily dietary intake of inorganic forms of arsenic in the U.S. diet averages approximately 8–14 µg day^{-1} (New Hampshire DHSS, 2001). The Central Science Laboratory in the UK has recently started a survey to measure total and inorganic arsenic in samples of fish and shellfish. Results are not expected until end of 2005.

Exposure of populations to elevated inorganic arsenic levels in drinking water, due to geological contamination of groundwater, is of concern in a number of locations in the world, such as Taiwan and West Bengal (WHO, 2001).

Analysis

Analysis of total arsenic in marine samples

The detection and measurement of arsenic in marine samples has been carried out using a variety of techniques. Flame atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS) and atomic fluorescence spectroscopy (AFS) are widely used (WHO, 2001). These techniques are usually preceded by hydride generation (HG), which gives better sensitivity. This involves pre-reduction of arsenate to arsenite (e.g., using KI/ascorbic acid) and reduction of arsenite to arsine, often using sodium borohydride as the reductant, prior to measurement. Incomplete mineralisation of arsenic compounds may lead to poor recoveries. Many of the organoarsenicals encountered in marine biota, such as arsenobetaine, are very stable and cannot be directly reduced to form hydrides. Such compounds are sometimes referred to as 'hidden arsenic'. A strong oxidation step is required to mineralise the stable arsenical species prior to reduction (Slejkovec *et al*., 2001).

[1] WHO has set a provisional tolerable weekly intake (PTWI) for inorganic arsenic via food and water at 15 µg kg^{-1} body weight (FAO/WHO, 1989). However, the risk assessment is based on epidemiological data for inorganic arsenic in drinking water. Due to the lack of appropriate toxicological data, WHO could not establish a similar recommendation for inorganic arsenic species in food.

Inductively coupled plasma-mass spectrometry (ICP-MS) has become much more widely used for arsenic speciation and very low detection limits can be achieved. Care needs to be taken to avoid interference from $ArCl^+$ especially when analysing seawater. Nitric acid is the preferred acid for digestion of biological samples (Francesconi *et al*., 1994).

Other techniques that have been used for arsenic measurement include inductively coupled plasma optical emission spectroscopy (ICP-OES) and voltammetry.

Speciation of arsenic in marine samples

The need for more analytical speciation of trace elements in environmental and food monitoring is recognised (Cornelis *et al*., 2001). In recent years there have been many publications on the speciation of arsenic in marine samples (Jain and Ali, 2000; Richardson, 2002). One approach to food safety monitoring is to apply a method to determine inorganic arsenic only. Karsten Oygard *et al.* (1999) describes such a method for fish, crustaceans and bivalve molluscs, employing hydrochloric acid distillation as $AsCl_3$, prior to determination by flow injection HGAAS. Munoz *et al.* (1999) describes a method for determining inorganic arsenic in fish. This involves HCl solubilisation, reduction by hydrobromic acid and hydrazine sulfate and extraction of inorganic arsenic into chloroform, back extraction into HCl followed by dry ashing and quantification by HG-AAS.

The use of hyphenated techniques has been applied successfully, for example, linking chromatography coupled with element specific detection. HPLC-ICP-MS has been used successfully by many researchers to achieve arsenic speciation for marine fish, shellfish and algae samples. This combination offers the advantages of an effective separation step and sensitive detection. The interface is also relatively simple compared to other techniques. (Thomas and Sniatecki, 1995; McSheehy and Szpunar, 2000; Ackley *et al*., 1999; Goessler *et al*., 1998a). Various chromatographic approaches including ion exchange (both anion exchange and cation exchange depending on the analyte species to be measured), ion pair reverse phase and size exclusion have been employed (Larsen 1998). Wangkarn and Pergantis (2000) used narrow-bore HPLC coupled to ICP-MS.

Hydride generation techniques can also be coupled with HPLC. HPLC-HGAFS offers a sensitive method and has the advantage of being considerably less costly than HPLC-ICPMS, although the interface is more complicated. For the analysis of AsB, AsC and arsenosugars, on-line post-column thermal or photo-oxidation (UV) is required prior to HGAFS determination (Suner *et al*., 2000; Gomez-Ariza *et al.* 2000).

HPLC has also been coupled to other mass spectrometry detectors (Richardson, 2002). Most recently electrospray MS (ES-MS) has been used, especially for the analysis of arsenosugars in algae. It has the advantage of providing information on the molecular structure of the analyte (McSheehy *et al*., 2001; McSheehy and Szpurnar, 2000; Madsen *et al*., 2000).

Various extraction techniques have been applied for arsenic speciation analysis of marine biota samples, including sonication, accelerated solvent extraction (ASE), microwave and Soxhlet, often employing a methanol/water solvent (Gómez-Ariza, 2000b, 2000a; Gallagher, *et al*., 2001; McKiernan *et al*., 1999; Montperrus *et al*., 2002).

Quality assurance

There are many marine CRMs available for total arsenic in seawater, sediment and biota. DORM-2, a dogfish muscle material produced by NRC Canada, is certified for arsenobetaine (16.4 ± 1.1 mg kg^{-1} as As) and tetramethylarsonium (0.248 ± 0.054 mg kg^{-1} as As) as well as total arsenic (18.0 ± 1.1 mg kg^{-1}) (Goessler *et al*., 1998b). Many researchers have reported concentrations for various speciated arsenicals in other marine reference materials.

Relevant laboratory proficiency tests are available for total arsenic in marine matrices. QUASIMEME offers proficiency testing for total arsenic in seawater, marine biota and sediments. The Standards, Measurement and Testing Programme of the European Commission ran six interlaboratory comparisons for the determination of a number of arsenic species. A step-by-step approach was used and the laboratory performance improved throughout. This enabled the certification of a tuna-fish reference material (BCR-CRM 627) for its total arsenic, arsenobetaine and dimethylarsinic acid contents (Lagarde *et al*., 1999a,b).

Legislation

Food Safety Legislation

European Commission Regulations establish maximum levels (MLs) for certain substances in certain foodstuffs, e.g., Commission Regulation (EC) No 466/2001 and amendments. This includes MLs for cadmium, lead and mercury in certain fishery products. For arsenic no ML is yet established.

The Codex Alimentarius Commission (CAC) develops consensus on international food standards to protect consumer health and ensure fair trade practices. Its Codex Committee on Food Additives and Contaminants (CCFAC) establishes standards and maximum levels (MLs) allowed for contaminants in foodstuffs. Currently there are MLs for arsenic in some foodstuffs, e.g., fats, oils and sugar, but not seafood. The established MLs are based on total arsenic and take no account of which chemical forms are present. The CCFAC recognises the fact that analytical methods for differentiating the various species and determining the inorganic arsenic levels are not readily available or routine. A Codex position paper on arsenic as a contaminant concludes that until further knowledge on the content and toxicity of naturally occurring arsenic species in a wide range of foods (including seafood) has been established, and methodologies have been developed, there is not sufficient basis to decide whether Codex MLs are needed for these species (Larsen and Berg, 2001).

Canadian guidelines for chemical contaminants and toxins in fish and fish products set an action level of 3.5 ppm for arsenic in fish protein concentrate (Presume total arsenic).

ANZFA (Australia New Zealand Food Authority) sets a maximum permitted level of 1 μg g^{-1} of inorganic arsenic in shellfish and seaweed, and 2 μg g^{-1} in fish (ANZFA, 2003).

Animal Feed Legislation

EU Directive 2002/32/EC set out the maximum permitted levels of undesirable substances, including arsenic, in animal feed, and these are set out in Table 11. This Directive was amended in 2003 by Directive 2003/100/EC with respect to the maximum permitted content of arsenic. The amendment takes into consideration normal background concentration levels of arsenic, and acknowledges the limited toxicity of organic arsenic and its low bioavailability in marine feedstuffs. It therefore sets higher levels for feed materials from fish or marine animals (raised from 10 to 15 ppm) and recognises seaweeds as a feed material that may contain high natural levels of arsenic (i.e., raised from 2 to 40 ppm).

Table 11. Some maximum permited levels of arsenic in (in mg Kg^{-1}) feedingstuffs Dir. 2003/100/EC.

Feed materials with the exception of:	2
- phosphates and calcareous marine algae	10
- feedingstuffs obtained from the processing of fish or other marine animals	15
- seaweed meal and feed materials derived from seaweed	40
Complete feedingstuffs with the exception of:	2
- complete feedingstuffs for fish and complete feedingstuffs for fur animals	6
Complementary feedingstuffs with the exception of:	4
- mineral feedingstuffs	12

Note: Maximum content in mg kg^{-1} (ppm) relative to a feedingstuff with a moisture content of 12%

Environmental Legislation

EU: Arsenic is not included in the list of priority substances in the Water Framework Directive (Dir/ 60/2000/EC). It is a list II substance for the Dangerous Substances Directive (Directive 76/464). There are no European standards of relevance to the marine environment, although member states should have national standards. Arsenic is also one of nine metals listed in the annex of Directive 79/923/EEC on the quality required of shellfish waters, and should be monitored in designated waters.

The US EPA has set a human health criterion for total dissolved arsenic in seawater from which (Neff, 2002; ATSDR, 2000) fishery products are harvested for consumption of 0.018 µg l^{-1} (at the 10^{-6} cancer risk level).

Sediment Criteria

A comprehensive inventory of sediment quality ciriteria can be found Annex 3 of the 2003 report of the ICES Advisory Committee on the Marine Environment (ICES, 2003).

National Action Levels for Dredged Material in OSPAR Contracting Parties

OSPAR Contracting Parties generally use a system of action levels (sediment quality criteria, SQC) for dredged material (Table 12). Concentrations of contaminants in the material falling below Action Level 1 represent those of little concern. Those falling between Action Levels 1 and 2 may trigger further investigation of the material proposed for dumping. In general, dumping at sea of dredged material with a concentration of one or more contaminants above Action Level 2 is not permitted.

Table 12. Summary of Action Levels for a number of OSPAR Contracting Parties.

Country	**Sediment Fraction**	**ActionLevel 1 (mg kg^{-1} dry wt)**	**Action Level 2 (mg kg^{-1} dry wt)**
Belgium	n.s.	20	100
Germany	< 20 µm fraction	30	150
Spain	< 63 µm fraction	80	200
France	n.s.	25	50
United Kingdom	n.s.	20	50–100[1]

n.s. = not stated. 1: A revision to 70 mg kg^{-1} is currently being considered.
Source - OSPAR (2003) Contracting Parties' National Action Levels for Dredged Material. EIHA 03/2/3

North America

The Canadian system for assessing contaminated sediments employs Threshold Effects Level (TEL) and Probable Effects Level (PEL) criteria. For arsenic the TEL is 7.24 mg kg^{-1} and the PEL is 41.6 mg kg^{-1} (CCME, 1999). The US derived criteria are termed Effects Level Low (ERL) and Effects Level High (ERH). The ERL and ERM for arsenic are 8.2 and 70 mg kg^{-1}, respectively (Long *et al.*, 1995).

Conclusions

Arsenic occurs naturally in seawater and, as a result, marine biota generally have relatively high levels of arsenic. Fish consumption is most likely the main route of human exposure to total arsenic. However, this primarily occurs as arsenobetaine, which is considered non-toxic. Arsenic usually occurs as relatively non-toxic arsenosugars in marine algae, with some notable exceptions. Most monitoring focuses on total arsenic; however, food safety monitoring requires more sophisticated speciation analysis. More knowledge is required of mammalian transformation of organoarsenicals. Legislative developments need to account for the high natural levels, speciation and toxicity profiles of arsenic in the marine environment.

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Appendix I. Naturally occurring inorganic and organic As species

CAS No.	Name	Synonyms	Structure
	arsenate		[1]
	arsenite		[2]
124–58–3	methylarsonic acid	monomethylarsonic acid, MMA	[3]
75–60–5	dimethylarsinic acid	cacodylic acid, DMA	[4]
4964–14–1	trimethylarsine oxide		[5]
27742–38–7	tetramethylarsonium ion		[6]
64436–13–1	arsenobetaine		[7]
39895–81–3	arsenocholine		[8]
	dimethylarsinoylribosides		[9]–[19]
	trialkylarsonioribosides		[20], [21]
	dimethylarsinoylribitol sulfate		[22]

Note: structures [1]–[22] are presented in Figure 1.

Appendix I (continued). Naturally occurring inorganic and organic arsenic species (WHO 2001).

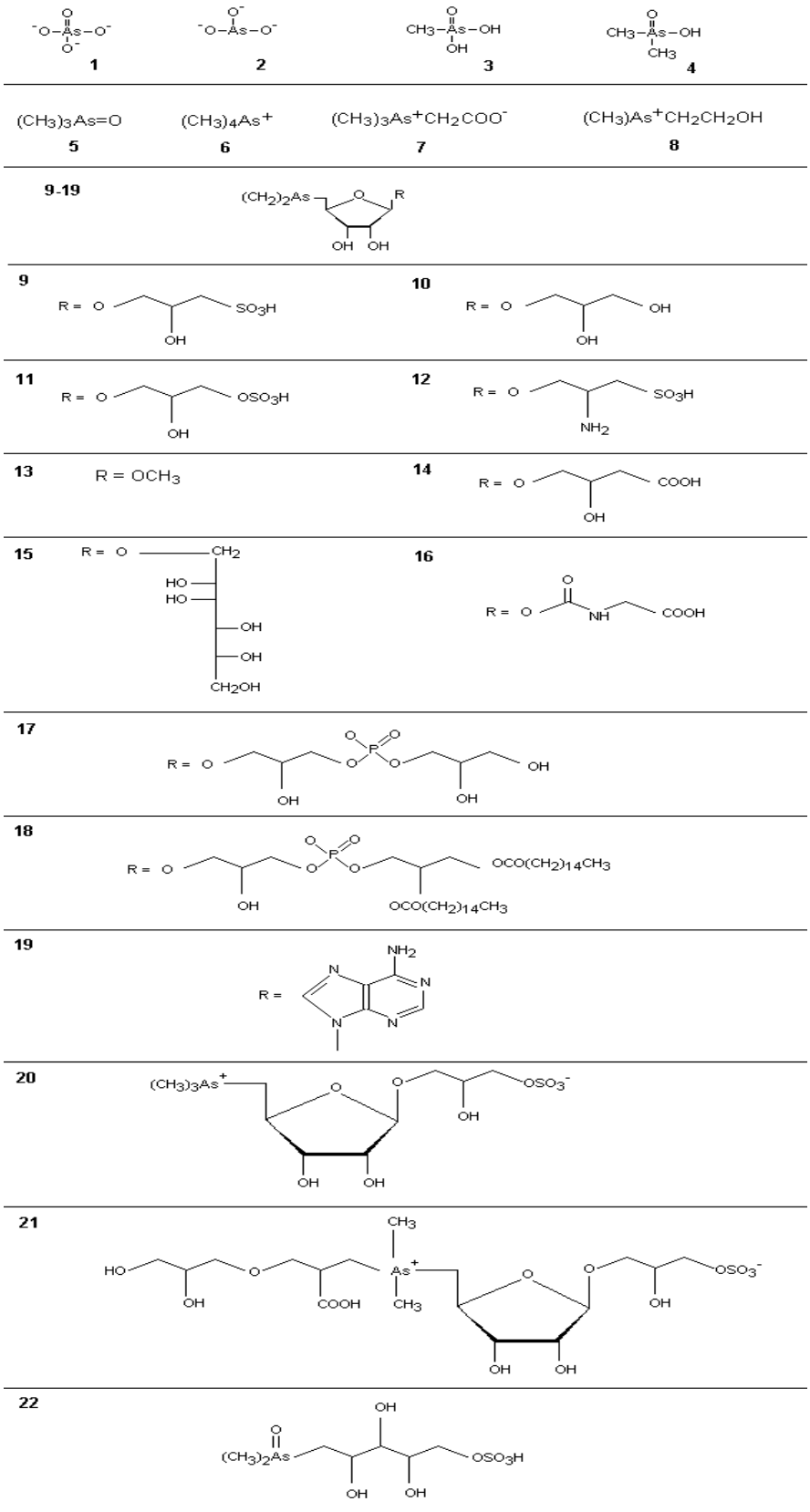

Fig. 1. Structures of naturally occurring inorganic and organic arsenic species

Annex 5 Toxaphene in the traditional Greenland diet

MCWG 2004 8.3.4/1

Toxaphene in Traditional Greenland Diet
Working document for Marine Chemistry Working Group
Meeting in Nantes March 2004

This is an extract from the report:

Contaminants in Traditional Greenland Diet

by

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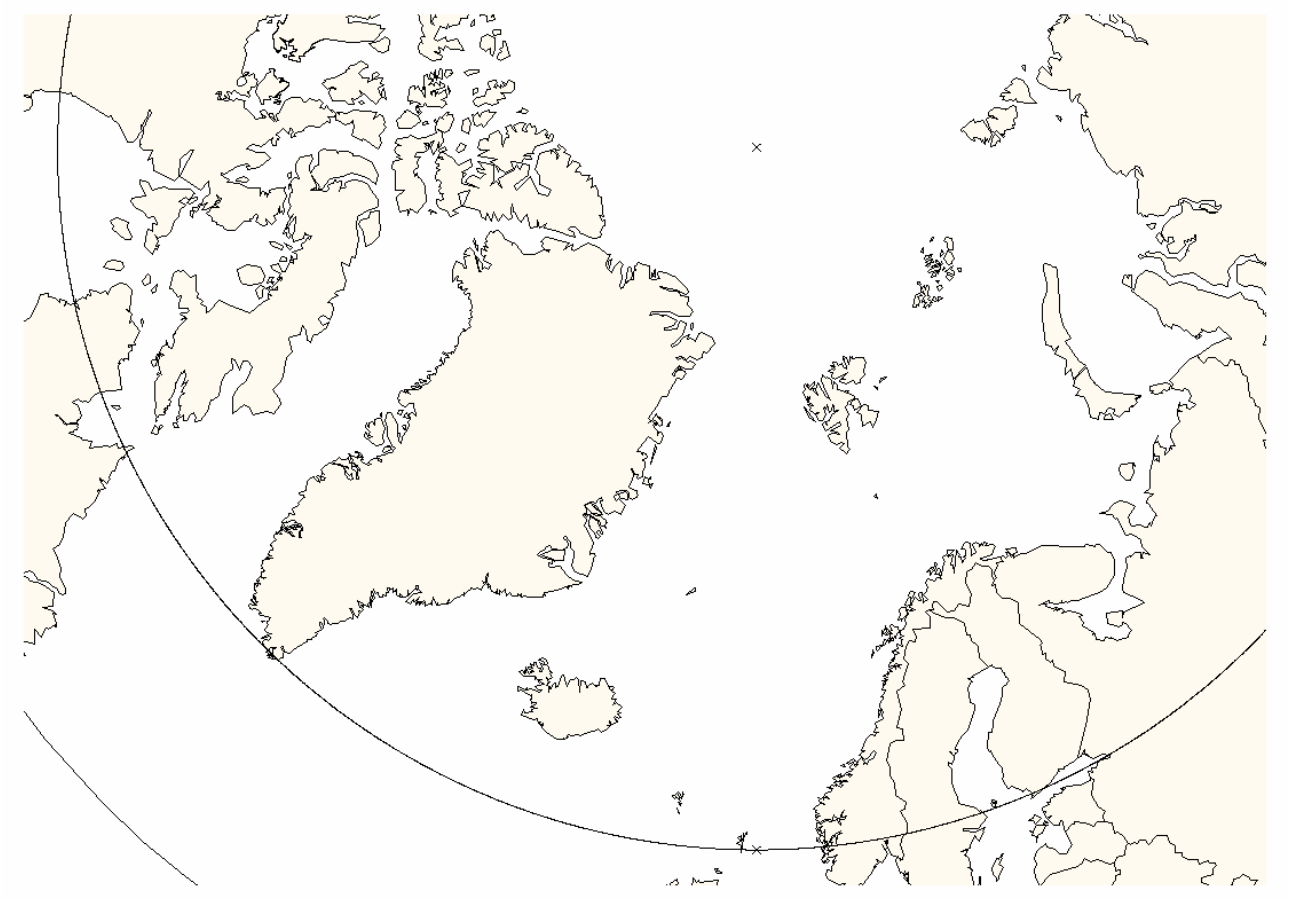

1. Introduction

People in Greenland are more exposed to contaminants from their diet than people in Europe and North America. The reason is that marine traditional food items (fish, seabirds, seals and whales) are much more important in Greenland, and because at the same time some of these food items have high levels of contaminants, i.e., metals like mercury and cadmium and organochlorines like PCBs. Within the Arctic, Greenlanders have the highest concentrations of mercury and most organochlorines (Hansen, 1998; Van Oostdam and Trembley, 2003), and estimated intakes of mercury and cadmium exceed "acceptable or tolerable intakes" (Johansen *et al.*, 2000).

Some knowledge of contaminant concentrations in the diet of Greenlanders was available before 2000, but a study to systematically survey the traditional diet was not initiated until 1999. This study was designed to cover the most important diet items, based mainly on dietary studies conducted in towns and settlements in Central West Greenland in 1995–1996 (Pars, 2000; Pars *et al.*, 2001). Appendix 1 shows the list of species and tissues identified to be significant as local diet items. The focus has been on West Greenland, which is the most densely populated part of Greenland. However, during the conduct of the study it was decided to include local diet samples from Ittoqqortormiit (Scoresbysund) in East Greenland, as this region in general, has the highest organochlorine concentrations in Greenland (Cleeman *et al.*, 2000a; Riget *et al.*, 2004). Only for toxaphene has West Greenland higher concentrations than East Greenland.

This report presents the toxaphene data of the study. An assessment of the significance to human exposure to contaminants of the different diet items has been presented by Johansen *et al.* (2004). In this report chemical groups include only toxaphene (total and selected congeners). Some of the Greenland contaminant data used in this assessment have been published by Dietz *et al.* (1996) and by Johansen *et al.* (2003). Prior to 1999 only a few analyses for organochlorines had been conducted in Greenland. We have not included these in this paper, because only few are important to human diet, and because some of the older data cannot be compared to the data obtained in the diet study initiated in 1999.

2. Methods

2.1. Study design

At first we designed a matrix of species and tissues to be included in the study (Appendix 1). This was based on the dietary survey by Pars (2000). Species, tissues and sample numbers were selected according to their importance as diet items. For example, more muscle than liver samples were included, because muscle is more important than liver, and more samples from thick-billed murre than for kittiwake, reflecting that murre is more important in the diet than kittiwake. At least five individuals, but up to 20 were analysed, depending on the importance of the species to the diet.

Since some contaminant analyses had been conducted before the diet study was initiated, we identified which contaminant data were missing, and based on this an analytical programme was designed. Most samples are from Central West Greenland, mainly between Qaqortoq (60°N–45°W) in the south to Qeqertarsuaq (69°N–54°W) in the north. Many samples were collected in important areas and seasons for hunting. For example samples from seabirds were obtained from hunting during winter in Nuuk as the most important region for hunting seabirds when they winter off Southwest Greenland. In this way samples are considered representative of the hunt and thereby of the human exposure to contaminants in the tissue and species in question.

2.2. Samples

Sampling was carried out over four years 1998–2001. Most samples were collected as part of other research programmes:

- ringed seal, hare, spotted wolffish, snow crab, blue mussel, Iceland scallop and the East Greenland samples by NERI, particularly in connection with AMAP studies;
- redfish, Atlantic cod, Greenland cod, Greenland halibut, shrimp, harp seal and minke whale by the Greenland Institute of Natural Resources in connection with several of their studies;
- Muskox, thick-billed murre, common eider, king eider, kittiwake, ptarmigan, capelin, Atlantic salmon and Arctic char by (or organized by) the Ministry of Environment and Nature of the Greenland Homerule;
- Caribou, sheep and berries by the Department of Population Ecology, University of Copenhagen in connection with a PhD study.

Sampling was by and large carried out according to the plan (Appendix 1). However, we did not succeed in getting samples from hooded seal, walrus and fin whale from West Greenland, in spite of a large effort to get these in cooperation with the Greenland Institute of Natural Resources. Appendix 2 gives an overview of the sampling carried out.

Some animals (birds and most fish) were sent frozen whole to the laboratory of NERI, where they were thawed, biological parameters (like sex and size) were recorded and tissue samples were taken for chemical analysis. In other cases (invertebrates, some fish, caribou, muskox, seals and whales) biological parameters were recorded and tissue samples collected in Greenland. These samples then were sent frozen to the laboratory of NERI, where they were thawed and tissue samples were taken for chemical analysis. These samples were cut out from the inner part of the sample so that possible contamination of the outer exposed part caused by handling and storage was avoided.

Samples for chemical analysis were either stored to be analysed later or prepared for analyses directly. Stored samples to be analysed for organochlorines were kept in glass jars rinsed with hexane and with the lid protected with aluminum foil and shipped frozen from NERI to the National Water Research Institute (NWRI) by airfreight or as personal luggage. All frozen samples were stored at –20°C in freezers at NERI or NWRI equipped with monitored alarm systems.

2.4. Analytical Methods and Quality Assurance

Table 1. A list of classes and major individual analytes in the original study. This report deals with toxaphene only.

Class	**Components**	**Number of individual analytes**	**Samples analysed**
Organochlorine pesticides and metabolites	DDT, chlordane, HCH, or dieldrin/aldrin/endrin, mirex	24	All
Miscellaneous organochlorine byproducts:	pentachloroanisole, di-, tri-, tetra-, penta- and hexachlorobenzene, hexachlorobutadiene and octachlorostyrene	13	All
Toxaphene	**total technical toxaphene + congeners including co-eluters**	**22**	**All**
PCB congeners	Congeners including co-eluters	104	All
Coplanar PCBs	PCB 77, 81, 126 and 169	4	107
Brominated diphenyl ethers	BDE congeners including co-eluters	32	44
Butyl tins	mono-, di- and tri-butyl	3	24
Short Chain Chlorinated Paraffins	Total C10, Total C11, Total C12, Total C13	4	26

Analytical methods

Procedures for analysis of PCBs, OC pesticides and toxaphene in fish and marine mammal tissue are those used by the National Laboratory for Environmental Testing (NLET). These methods are summarized here.

2.4.1. Sample preparation

Samples were homogenized prior to extraction in a small blender. Blubber samples were frozen with liquid nitrogen prior to sub-sampling.

2.4.2. Extractions

Internal recovery surrogates of 1,3,5-bromobenzene, 1,2,4,5-tetra-bromobenzene, delta-HCH, endrin ketone, PCB-30 and PCB 204 are added at the extraction step. Homogenized tissue is mixed with precleaned sodium sulfate to form a dry powder and Soxhlet extracted for 6 hrs with dichloromethane (DCM).

2.4.3. Removal of interferences

The DCM solution is reduced in volume to approximately 2 ml. The extract is applied to the top of a gel permeation column (GPC) to remove lipids using hexane: DCM (1:1) as elution solvent. Extractable lipids are determined gravimetrically on the first 150 ml of GPC eluate by evaporating off the solvent. The GPC eluate is reduced to small volume, quantitatively exchanged into hexane and chromatographed on activated Silica Gel (8 g in a 1.1 cm dia chromatographic column) to separate PCBs from other organochlorines including chlorinated bornanes (toxaphene). This latter procedure has been used successfully to separate 100% of technical toxaphene from PCBs (NLET 1997). The silica gel is activated at 350 ^{o}C for a minimum of 4 hrs; the sodium sulfate is cleaned by ashing at 450 ^{o}C for a minimum of 4 hrs. Final extracts are stored at 4^{o}C in a fridge. Prior to instrumental analysis they are reduced to an appropriate final volume under gentle nitrogen stream.

2.4.4. Brominated diphenyl ether and Toxaphene analysis

Fraction 2 from the silica gel column was analysed separately for BDPEs and toxaphene by electron capture negative ion (low resolution) MS without further cleanup. Selected samples of Fraction 1 were also run to check quantification of toxaphene congener P26. PBDEs were quantified using an external standard consisting of 32 congeners. Gas chromatographic conditions for the PBDEs were described by Luross *et al.* (2002).

2.4.5. Instrumental analysis

GC-electron capture negative ion mass spectrometry (GC-ECNIMS): Toxaphene was analysed by GC-ECNIMS using selected ion monitoring (SIM) (Swackhamer *et al*., 1987; Glassmeyer *et al*., 1999) on a Agilent 6890 gas chromatograph coupled Agilent 5973 MSD. The GC has a 30 m x 0.25 mm, 0.25 um film thickness DB-5MS column and is operated with He carrier gas at a linear flow of 40 cm/sec. A variable temperature ramp program from 40 ^{o}C to 300 C over 60 minutes is used, and may be modified to obtain maximum resolution. The same program is used consistently for samples and standards in a given day; modifications are only made if resolution deteriorates or changes. Methane is used as the reagent gas; the source is kept at 150 ^{o}C. The ion source pressure is maintained at 0.8–1.0 torr.

Quality Assurance

QA steps included method blanks, surrogate recovery spikes, and reference materials with each batch of 10 to 12 samples. In all, 39 method blanks were analysed (15 in 1999/2000, 14 in 2001 and 10 in 2002). Results were corrected using the average blank value determined each year. Method detection limits (MDL) were calculated each year using results for method (reagent) blanks. The MDL for 95% (MDL95%) confidence is defined as the mean plus two standard deviations of seven or more iterations of a procedural blank, or a standard with a very low level of analyte if none is present in the procedural blanks (Keith, 1991). Note that the multiplier of 2 results from the Student's t value for a one-sided 95% confidence level for seven degrees of freedom.

Accuracy of the work was assessed by use of laboratory spike analyses, duplicate analyses, analysis of standard reference materials (SRM) and participation in interlab studies. Spiked recovery samples consisted of reagents (e.g., sodium sulfate) spiked with representative levels of analyte and carried through analytical procedures similar to samples. The NIST (National Institute of Standards and Technology, Gaithersburg MD; http://ois.nist.gov/srmcatalog) standard reference materials cod liver oil 1588a and mussels 1974a were used along with a lake trout homogenate #EDF-2525 sold by Cambridge Isotope Laboratories, Boston MA. Criteria for acceptability were ±30% of certified values for all major PCB congeners and OC pesticides in each reference material. In the case of the lake trout only consensus values from an interlab study were available.

During this study NLET participated in 10 QUASIMEME studies as well as 1 NIST (USA) and 3 Northern Contaminants Program (Canada) interlaboratory comparisons.

2.4.6. Internal standard recoveries

Average recoveries of internal standards (surrogates) added to each samples were consistently > 80%, except for dibromobenzene, indicating very low losses of all but the most volatile analytes during extraction and isolation steps (Table 2). Based on these results no correction for recovery efficiency of standards was made on the results for the diet samples.

Table 2. Recoveries of internal standards added to each sample.

Internal standard		1999	1999	2000	2000	2001	2001	2002	2002
		N	% Recovery	N	% Recovery	N	% Recovery	N	% Recovery
1,3-Dibromo-benzene	Mean	117	60.7	135	78	127	67.4	114	72.6
	SD		14.9		19		11.1		17.9
1,3,5-Tribromo-benzene	Mean	55	84.5	135	73	127	76.3	114	76.8
	SD		32.1		35		15.4		17.0
1,2,4,5-Tetra-bromobenzene	Mean	55	94.2	135	90	127	94.2	114	94.9
	SD		32.5		29		15.9		20.1
Delta-HCH	Mean	55	102	135	83	127	84.6	114	85.6
	SD		33.2		45		25.9		21.4
Endrin Ketone	Mean	117	75.9	135	80	127	99.3	114	100.1
	SD		18.6		26		23.7		28.0
PCB30	Mean	117	87.8	135	96	127	95.9	114	95.0
	SD		14.6		31		20.8		24.3
PCB204	Mean	117	95.4	135	103	127	117	114	114.9
	SD		15.4		32		28.3		28.9

2. Reference materials

Results for the three reference materials used during the study (NIST 1588a cod liver oil, NIST 1974a mussels and the Lake trout homogenate #EDF-2525 from Cambridge Isotope Labs) showed overall good agreement with certified or consensus values.

3. Results

All contaminant levels are presented on a wet wt basis with arithmetic means and standard deviations shown. This has been chosen, because the arithmetic mean will represent the average human exposure to the contaminant in question from the diet (Johansen *et al.,* 2000), provided that the meal is selected irrespective of age, sex and region. In some cases these factors are known to affect contaminant levels, for example cadmium levels are known to increase with the age of seabirds and seals (Dietz *et al.,* 1996). However, samples are considered representative of the human exposure to contaminants in the tissue and species in question, because these samples were collected in important areas and seasons for hunting and fishing in Greenland.

Appendix 3 list levels of toxaphene in the species selected for this study. All results are from samples collected between 1999 and 2001.

Toxaphene levels are presented as “total” toxaphene quantified with a technical toxaphene standard, as the sum of 22 chlorobornane congeners (specified in Appendix 3) and as a sum of parlar 26, 50, and 62 (Appendix 3).

The mean human intake of cadmium, mercury, PCB, toxaphene, chlordane and dieldrin exceeded the ADI/TDI in the Greenland diet study (Johansen *et al.,* 2004b), while this was not the case for DDT, HCH and chlorobenzenes.

Toxaphene levels among species and tissues have been compared by grouping concentrations of toxaphene in four categories as shown in Table 4.

The result of this grouping is shown in Table 5 (toxaphene). It may be used to point to the diet items, which could be expected to be the most (or least) significant contaminant sources.

Table 4. Grouping of contaminant levels according to concentrations.

	Very low conc.	**low-medium conc.**	**high conc.**	**very high conc.**
Cadmium (µg/g)	< 0.05	0.05–0.49	0.5–5	> 5
Mercury (µg/g)	< 0.01	0.01–0.09	0.1–1	> 1
sPCB10 (ng/g)	< 5	5–49	50–500	> 500
Total toxaphene (ng/g)	**< 5**	**5–49**	**50–500**	**> 500**
Chlordane (ng/g)	< 1	1–99	10–100	> 100
Dieldrin (ng/g)	< 1	1–99	10–100	> 100

Table 5. Grouping of total toxaphene levels according to concentrations (ng g^{-1}).

Very low conc. **< 5**	**low-medium conc.** **5–49**	**high conc.** **50–500**	**very high conc.** **> 500**
Terrestrial species			
ptarmigan muscle			
ptarmigan liver			
hare muscle			
hare liver			
hare kidney			
caribou muscle			
caribou liver			
caribou kidney			
caribou fat			
muskox muscle			
muskox liver?			
muskox kidney			
muskox fat			
lamb muscle			
lamb liver			
lamb kidney			
lamb fat			
Marine invertebrates			
shrimp muscle	crab muscle		
	crab “liver”		
Iceland scallop			
Marine fish			
cod muscle	Arctic char muscle	salmon muscle	Atlantic cod liver
	Arctic char liver	halibut muscle	halibut liver
	salmon liver	Greenland cod liver	
	capelin muscle	wolffish liver	
	redfish muscle		
	wolffish muscle		
Seabirds			
	murre muscle	murre liver	
	eider muscle	kittiwake muscle	
	eider liver		
	kittiwake liver		
Seals			
ringed seal kidney	ringed seal muscle	ringed seal blubber	
harp seal kidney	ringed seal liver	harp seal blubber	
	harp seal muscle		
	harp seal liver		
Whales			
	minke whale muscle	minke whale blubber	minke whale skin
	minke whale kidney	minke whale liver	beluga blubber
	beluga muscle	beluga skin	narwhal blubber
	beluga liver	narwhal skin	
	beluga kidney	narwhal liver	
	narwhal muscle		
	narwhal kidney		

Toxaphene

Toxaphene levels are presented as "total" toxaphene quantified with a technical toxaphene standard, as the sum of 22 chlorobornane congeners (specified in Appendix 3) and as a sum of parlar 26, 50, and 62 (Appendix 3). The mean total toxaphene concentration ranges from less than 0.1 ng/g wet wt to 3103 ng/g. In the species and tissues with the highest levels, the concentration of the 22 toxaphene congeners is about half of the total toxaphene concentration, and the concentration of parlar 56, 50, and 62 is about half of the concentration of the 22 toxaphene congeners. In contrast to the other organochlorine pesticides studied and the PCBs, the highest level is not found in marine mammal blubber, but in Greenland halibut liver. In general total toxaphene concentrations appear somewhat higher than the ΣPCB10 and ΣDDT concentration, but the pattern between tissues, species and environment is similar (Table 5). It remains unexplained that the toxaphene concentration is higher in skin than in blubber from minke whale. We would have expected the highest level in blubber as is seen for beluga and narwhal.

4. Discussion

Based on the data presented in this report Johansen *et al*. (2004) conclude that the traditional diet is a significant source of contaminants to people in Greenland. In this study, the mean intakes of toxaphene significantly exceed "acceptable/tolerable intakes" (ADI/TDI) by a factor between 2.5 and 6.

The main reason that the human intake of some contaminants exceeds ADI/TDI values in this study is that a few diet items have high contaminant levels. The evaluation of contaminant intake in this study points to seal muscle, seal liver, seal kidney, seal blubber and whale blubber as the dominant contributors of contaminants in the traditional diet. Levels in liver from Greenland halibut, snow crab, king eider, kittiwake, beluga and narwhal and kidney of beluga and narwhal are also high but were, with the exception of toxaphene in Greenland halibut liver, not important sources in this study, because they were eaten in low quantities. A way to minimize contaminant intake would be to avoid or limit the consumption of diet items with high contaminant levels. If we assume a traditional diet composition in this study without fish liver, bird liver, seal liver, seal kidney, seal blubber, whale liver, whale kidney and whale blubber, the intake of all contaminants would be below the TDIs for these. This will result in a reduction of the intake of the amount of traditional food of only 24–25%, and it is not likely that this changed diet will result in deficiency of minerals, vitamins or other nutritional compounds.

Our study has mainly included cadmium, mercury, selenium, polychlorinated biphenyls (PCB), dichlorophenyltrichloroethane (DDT), chlordane, hexachlorocyclohexanes (HCH), chlorobenzenes, dieldrin and toxaphene in the major species and tissues consumed by Greenlanders. In general the levels of these are very low in terrestrial species and in muscle of many marine species. High organochlorines concentrations are typically found in blubber of marine mammals and high metal levels in liver and kidney of seals and whales.

In general, contaminant levels in the Greenland environment, including diet items, are lower than in more densely populated and industrialized regions. This is illustrated in Table 6, which compares levels in the same species and tissues in Greenland and in temperate European waters. This geographical difference is very pronounced for PCB, DDT, dieldrin, chordane and total toxaphene, while it is not as large for mercury, HCH and HCB. Cadmium is an exception to this general pattern, as cadmium concentrations are much higher in Greenland than in temperate European waters. This has been observed earlier, particularly in Arctic marine mammals (Dietz *et al.,* 1996; Wagemann *et al.,* 1997). The difference has been explained by diet, as hyperiid amphipods rich in cadmium are common in the diet of Arctic vertebrates, but also by slow growth rates in the Arctic (Fant *et al.,* 2001). It is also interesting, but remains unexplained that the sum concentration of toxaphene parlar 26, 50, and 62 in fish is significantly higher in Greenland than in the Danish waters.

Table 6. Comparison of contaminant levels (mean, ng/g wet weight) between Greenland and temperate European waters.

Contaminant	Species and tissue	West Greenland (this study)	Baltic	North Sea or Skagerrak	Ref., see below table
Total toxaphene	Ringed seal blubber	196	2300–14000		f
Toxaphene Σ# 26,50,62	Cod liver	103	28	21	g
	Salmon muscle	9.0	2.5		g

f) Andersson and Wartanian 1992

g) Fromberg *et al.,* 2000.

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This list of references is from the original study, not all references are relevant for toxaphene.

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Appendix 1. Most important traditional diet items in West Greenland.

Species marked with bold typescript were dominating in the interview survey in the Disko Bay region in 1995–1996 (Pars, 2000). Numbers refer to total number of tissue samples suggested for the analytical program, either metals or organochlorines.

	Muscle	Liver	Kidney	Blubber/fat	Skin	Whole
Marine mammals						
Ringed seal	20	5	5	10		
Harp seal	20	10	5	10		
Hooded seal	10	5	5	10		
Walrus	10	5	5	10		
Beluga	20	5	5	10	5	
Narwhal	10	5	5	10	5	
Minke whale	20	5	5	10	5	
Fin whale	10	5	5	10	5	
Seabirds						
Thick-billed murre	20	10				
Common eider	10	5				
King eider	10	5				
Kittiwake	10	5				
Fish						
Spotted wolfish	5	5				
Atlantic wolfish	5	5				
Atlantic cod	10	5				
Greenland cod	5	5				
Capelin	10					10
Greenland halibut	10	5				
Redfish	5	5				
Atlantic salmon	20	10				
Arctic char	5	5				
Invertebrates						
Deep sea shrimp	20					
Snow crab	10	5				
Blue mussel						5
Iceland scallop	10					
Terrestrial species						
Caribou	5	5	5	5		
Muskox	10	5	5	5		
Sheep	10	5	5	5		
Hare	5	5	5			
Ptarmigan	5	5				
Crowberry						5
Arctic blueberry						5

Appendix 2. Overview of sampling conducted as part of the Greenland diet study.

	Region	Municipality	Year
Marine mammals			
Ringed seal	West Greenland	Qeqertarssuaq	1999
Ringed seal	East Greenland	Ittoqqortormiit	2000–2001
Harp seal	West Greenland	Nuuk	2001
Walrus	East Greenland	Ittoqqortormiit	2001
Beluga	West Greenland	Upernavik, Ilulissat, Uummannaq	1999–2000
Narwhal	West Greenland	Ilulissat, Uummannaq	2000
Narwhal	East Greenland	Ittoqqortormiit	2001
Minke whale	West Greenland	Nuuk	1998
Seabirds			
Thick-billed murre	West Greenland	Nuuk	1999
Common eider	West Greenland	Nuuk	1999
King eider	West Greenland	Nuuk	1999
Kittiwake	West Greenland	Nuuk	1999
Fish			
Spotted wolfish	West Greenland	Nanortalik	2001
Atlantic cod	West Greenland	Nuuk	1999
Greenland cod	West Greenland	Nuuk	1999
Capelin	West Greenland	Nuuk	1999
Greenland halibut	West Greenland	Nuuk	1999
Redfish	West Greenland	Nuuk	1999
Atlantic salmon	West Greenland	Nuuk	1999
Arctic char	West Greenland	Nuuk	1999
Invertebrates			
Deep sea shrimp	West Greenland	Nuuk	1999
Snow crab	West Greenland	Qeqertarssuaq	1999
Blue mussel	West Greenland	Qeqertarssuaq	1999
Iceland scallop	West Greenland	Qeqertarssuaq	2000
Terrestrial species			
Caribou	West Greenland	Qaqortoq	2000
Muskox	West Greenland	Kangerlussuaq	1999
Sheep	West Greenland	Qaqortoq	1999
Hare	West Greenland	Qeqertarssuaq	1999
Ptarmigan	West Greenland	Nuuk	1999
Crowberry	West Greenland	Qaqortoq	2000
Arctic blueberry	West Greenland	Qaqortoq	2000

Appendix 3. Concentrations of toxaphene

(ng g^{-1} wet weight) in biota samples from West Greenland, except marine mammals from East Greenland at the end of the table. Samples collected between 1999 and 2001. Contaminant groups are explained below the Appendix.

Species	**Tissue**	**N**	**Stat**	**% Lipid**	**Total toxaphene**	**Σ-congeners**	**Σ-parlar 26,50,62**
Terrestrial							
Ptarmigan	muscle	5	Mean	3.8	0.7	0.00	0.0
			SD	0.7	0.5	0.00	0.0
	liver	5	Mean	6.8	0.7	0.00	0.0
			SD	0.5	0.5	0.00	0.0
Arctic hare	muscle	4	Mean	3.8	0.0	0.06	0.0
			SD	2.7	0.0	0.13	0.0
	liver	5	Mean	4.1	0.5	0.05	0.0
			SD	0.5	0.3	0.06	0.0
	kidney	3	Mean	32.5	1.8	0.23	0.0
			SD	18.8	1.4	0.15	0.0
Caribou	muscle	5	Mean	1.5	0.0	0.00	0.0
			SD	0.5	0.0	0.00	0.0
	liver	5	Mean	7.4	0.1	0.00	0.0
			SD	0.7	0.0	0.00	0.0
	kidney	5	Mean	3.5	0.1	0.00	0.0
			SD	0.2	0.1	0.00	0.0
	fat	5	Mean	49.9	0.0	0.01	0.0
			SD	28.7	0.0	0.02	0.0
Muskox	muscle	5	Mean	1.9	0.0	0.00	0.0
			SD	0.4	0.0	0.00	0.0
	liver	5	Mean	10.3			
			SD	1.8			
	kidney	5	Mean	3.2	0.0	0.00	0.0
			SD	0.6	0.0	0.00	0.0
	fat	5	Mean	85.5	0.0	0.00	0.0
			SD	10.7	0.0	0.00	0.0
Lamb	muscle	5	Mean	12.3	0.0	0.00	0.0
			SD	9.8	0.0	0.00	0.0
	liver	5	Mean	9.6			
			SD	2.0			
	kidney	5	Mean	4.2	0.0	0.00	0.0
			SD	0.4	0.0	0.00	0.0
	fat	5	Mean	90.2	0.0	0.01	0.0
			SD	3.1	0.0	0.01	0.0
Marine invertebrates							
Deep-sea shrimp	muscle	11	Mean	0.9	1.6	0.93	0.6
			SD	0.1	0.6	0.22	0.2
Queen crab	muscle	4	Mean	0.7	12.8	4.10	2.7
			SD	0.2	4.0	1.35	0.9
	“liver”	5	Mean	6.0	7.6	5.82	3.5

Species	Tissue	N	Stat	% Lipid	Total toxaphene	Σ-congeners	Σ-parlar 26,50,62
			SD	5.6	6.6	5.71	3.9
Iceland scallop	muscle	8	Mean	0.4	0.0	0.0	0
			SD	0.1	0.0	0.0	0
Marine fish							
Arctic char	muscle	5	Mean	3.5	5.0	2.88	1.1
			SD	2.4	3.6	2.17	1.2
	liver	5	Mean	16.7	29.3	14.52	4.2
			SD	0.7	11.1	3.64	1.2
Atlantic Salmon	muscle	10	Mean	10.9	51.7	25.67	9.0
			SD	4.8	24.0	10.41	3.5
	liver	5	Mean	8.8	33.2	14.38	2.5
			SD	1.6	8.7	2.70	0.6
Capelin	muscle	10	Mean	1.8	17.6	14.98	3.8
			SD	0.7	3.6	3.18	1.1
Atlantic cod	muscle	9	Mean	0.7	1.3	0.42	0.2
			SD	0.1	1.5	0.13	0.1
	liver	5	Mean	59.3	548.8	221.77	103.0
			SD	3.7	113.2	55.78	44.1
Greenland cod	muscle	5	Mean	0.7	0.3	0.14	0.1
			SD	0.1	0.2	0.09	0.0
	liver	5	Mean	38.3	95.9	59.26	30.5
			SD	7.1	29.3	20.13	14.9
Redfish	muscle	5	Mean	2.5	15.6	11.32	4.4
			SD	1.6	10.5	9.93	3.6
Spotted wolffish	muscle	5	Mean	1.6	22.2	7.08	2.5
			SD	0.7	11.4	5.04	1.9
	liver	5	Mean	19.2	194.7	116.18	39.5
			SD	6.3	138.2	74.57	24.6
Greenland halibut	muscle	9	Mean	9.4	279.4	125.34	49.4
			SD	5.4	517.6	206.46	80.0
	liver	5	Mean	33.9	3103.1	1427.36	683.6
			SD	10.2	5388.1	2454.48	1270.1
Seabirds							
Thick-billed murre	muscle	19	Mean	3.5	34.4	5.39	0.3
			SD	0.4	30.3	5.22	0.6
	liver	5	Mean	5.4	53.0	9.84	0.8
			SD	0.7	15.1	2.89	0.4
Common eider	muscle	10	Mean	3.9	13.5	2.82	0.6
			SD	0.8	7.5	1.44	0.3
	liver	5	Mean	5.1	12.4	4.06	0.9
			SD	0.3	4.9	1.47	0.3
King eider	muscle	10	Mean	3.9	8.7	2.43	0.4
			SD	1.2	11.2	2.39	0.5
	liver	5	Mean	5.2	13.5	4.68	0.3
			SD	0.3	10.2	2.63	0.2
Kittiwake	muscle	9	Mean	14.3	96.4	10.70	3.4

Species	Tissue	N	Stat	% Lipid	Total toxaphene	Σ-congeners	Σ-parlar 26,50,62
Kittiwake (cont.)			SD	5.4	32.7	18.54	4.3
	liver	5	Mean	6.9	47.9	0.15	0.1
			SD	2.3	23.8	0.12	0.1
Marine mammals West Greenland							
Ringed seal	muscle	18	Mean	5.4	8.6	1.88	0.1
			SD	6.4	14.5	2.87	0.2
	liver	5	Mean	5.5	39.6	14.1	0.05
			SD	0.6	12.3	4.3	0.05
	kidney	3	Mean	3.8	0.81	0.14	0.01
			SD	0.5	0.08	0.10	0.01
	blubber	20	Mean	92.2	196.5	70.9	6.77
			SD	4.9	74.2	30.9	4.49
Harp seal	muscle	20	Mean	2.5	9.2	3.33	1.3
			SD	2.4	12.7	5.74	2.3
	liver	7	Mean	6.9	21.5	5.98	1.7
			SD	1.7	7.5	2.00	1.2
	kidney	7	Mean	3.1	3.3	1.04	0.5
			SD	0.3	1.7	0.40	0.2
	blubber	12	Mean	88.9	363.7	260.87	115.3
			SD	2.3	186.3	136.62	63.1
Minke whale	muscle	19	Mean	1.8	18.8	7.90	4.0
			SD	1.3	17.3	8.53	4.1
	liver	5	Mean	6.7	57.4	21.59	8.6
			SD	1.6	23.6	12.58	5.3
	kidney	5	Mean	3.6	19.8	6.55	3.2
			SD	0.7	10.4	3.97	2.3
	blubber	17	Mean	69.6	369.1	63.37	29.7
			SD	12.2	531.2	116.07	58.4
	skin	5	Mean	45.0	1369.9	679.79	393.5
			SD	20.2	1240.1	589.79	338.6
Beluga	meat	20	Mean	2.3	31.7	15.10	10.9
			SD	1.0	34.5	15.77	10.1
	liver	5	Mean	6.8	34.3	10.66	8.0
			SD	3.0	16.0	5.37	4.1
	kidney	5	Mean	4.4	27.5	8.93	6.5
			SD	2.2	18.6	7.81	5.6
	blubber	10	Mean	87.9	778.1	531.34	311.2
			SD	2.4	477.7	309.17	175.7
	skin	5	Mean	3.6	166.2	49.81	42.9
			SD	0.8	148.5	48.70	39.5
Narwhal	muscle	7	Mean	2.3	40.9	14.92	9.1
			SD	1.2	24.7	10.04	6.7
	liver	5	Mean	5.1	87.7	28.79	17.2
			SD	0.6	16.6	7.07	4.2
	kidney	5	Mean	2.7	41.7	11.64	8.0

Species	Tissue	N	Stat	% Lipid	Total toxaphene	Σ-congeners	Σ-parlar 26,50,62
Narwhal (cont.)			SD	0.4	24.2	6.85	5.0
	blubber	7	Mean	77.1	1375.7	552.96	344.0
			SD	17.4	705.2	275.64	173.0
	skin	5	Mean	3.6	151.4	64.70	48.4
			SD	1.7	100.1	44.45	32.4
Marine mammals East Greenland							
Ringed seal	muscle	10	Mean	2.4	10.3	2.4	0.4
			SD	1.6	11.3	2.4	0.5
	liver	5	Mean	5.0	46.8	19.8	0.2
			SD	1.0	14.0	10.8	0.1
	blubber	19	Mean	101	210.6	122.2	10.1
			SD	14.6	161.6	92.3	10.6
	intestine	5	Mean	1.5	4.0	1.35	0.5
			SD	0.3	4.2	1.06	0.3
Walrus	muscle	6	Mean	1.2			
			SD	0.7			
	skin	1	Mean	13.5	495.7	143.14	98.5
Narwhal	muscle	5	Mean	0.7	44.0	22.70	15.6
			SD	0.2	23.9	24.77	17.9
	skin	1	Mean	6.5	471.1	313.09	210.6

“Total toxaphene” is quantified with a technical toxaphene standard,

“Σ-congeners”is the sum of 22 chlorobornane congeners (parlar 11–12, 15, Hex-sed, 21, Hep-sed, 25, 32, P26, 31, 38, 39, 40–41, 42, 44, 50, 51, 56, 58, 59, 62, 63),

“Σ-parlar 26,50,62” is the sum of parlar 26,50,62.

Detection limit is supposed to be 0.01 for individual congeners. “0” means less than detection limit.

Annex 6 Action list

Peter Lepom to make available the AMPS report on the workshop on the analysis of short-chain chlorinated paraffins to MCWG members when available.

Peter Lepom to prepare a review note on short-chain chlorinated paraffins for MCWG2005.

Norbert Theobald to prepare a review note on dicofol and endosulphan for MCWG2005.

Patrick Roose to prepare a review note on methoxychlor for MCWG2005.

Robin Law to prepare a review note on 2,4,6-tri *tert*-butylphenol for MCWG2005.

The Chair will approach Gerhard Rimkus and ask him whether he will be able to prepare a review note on musk compounds for MCWG2005.

All members with relevant information to supply the authors of the review notes with material for inclusion by the end of September 2004.

Robin Law to discuss the establishment of an MCWG website with Neil Fletcher of ICES, with a view to using that mechanism to make available information on CRMs suitable for marine monitoring programmes.

Robin Law to take the information from the discussion on the integration of chemical and biological effects methods forward to the ICES/IOC workshop to be held in January 2005.

Robin Law to maintain contact with the Chair of WGSAEM regarding future collaboration between the two WGs.

Robin Law to act as the intersessional contact point between MCWG and REGNS.

MCWG members to send data for DDTs and TCPM/TCPMe in flatfish and/or flatfish liver samples to Michel Lebeuf.

Michel Lebeuf to present an update on TCPM/TCPMe in flatfish to MCWG2005.

Evin McGovern to supply additional toxaphene data to Gert Asmund.

Robin Law will supply details of relevant papers from the proceedings of the third BFR workshop, Toronto June 2004, to ACME2004.

Jarle Klungsøyr to provide new information on the impact of alkylphenols from produced water to MCWG2005.

Marc Raemaekers to present information on contaminant concentrations in marine fish and other marine food products to MCWG2005.

Evin McGovern to present information on an Irish project concerning oily fish and their contamination by dioxins and furans, CBs and BDEs to MCWG2005.

Annex 7 Recommendations

The organisers of monitoring programmes concerning contaminants in seabirds and their eggs should consider the incorporation of a range of brominated flame retardants within their studies. A minimum set of determinands would comprise BDE congeners intended to cover the three major PBDE formulations which have been, or still are being, used in Europe (minimum of BDE47, BDE99, BDE 100 (penta-mix), BDE183 (octa-mix), BDE209 (deca-mix)) plus HBCD, and TBBP-A. This would allow the evolution of temporal trends for all of these flame retardant products to be studied at a high trophic level.

Annex 8 Draft resolutions

Proposed terms of references for the 2005 MCWG Meeting:

The **Working Group on Marine Chemistry** [MCWG] (Co-Chairs: R. Law, UK, and Jaceck Tronczynski*, France) will meet in Vigo, Spain, from 7–11 March 2005 to:

a) continue to provide guidance and assistance relating to the development of a series of data products to illustrate eutrophication status within the ICES area;
b) examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];
c) continue to report on new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane(TCPMe) in flatfish;
d) continue to report on new information on the use of membrane systems for sampling;
e) develop draft advice on appropriate strategies for undertaking one-off surveys to provide new information about the following chemicals identified by OSPAR for Priority Action: 2,4,6 tri-*tert* butylphenol, dicofol, endosulphan, methoxychlor (exploratory one-off surveys), and short chained chlorinated paraffins (baseline survey) according to specific OSPAR requests; taking into account sources and modes of dispersion/transport, the specific questions to be addressed for each substance (or groups of substances) under consideration are:
    i) indicate where there is any new information available on presence in the marine environment that has not already been taken into account in the relevant OSPAR background document as updated by the OSPAR lead country,
    ii) indicate whether the matrix (sediment, biota, water) proposed to be sampled is appropriate or whether an additional or more appropriate matrix should be included in the survey,
    iii) identify whether analytical techniques are available for the relevant matrices,
    iv) identify achievable detection limits, and reference materials, and
    v) determine how many stations/samples from each part of the OSPAR Convention area are necessary to address the objectives of the one-off surveys proposed, taking into account that more than one one-off survey may be required [OSPAR 2005/1];
f) continue to report on the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website;
g) report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;
h) continue to determine priorities for assistance from the Working Group on the Statistical Aspects of Environmental Monitoring (WGSAEM) with statistical analyses and develop with WGSAEM a plan for the necessary collaboration;
i) report on progress in summarising the marine chemistry of the North Sea for the period 2000–2004, and any trends in chemistry and contaminants over recent decades, for input to the Regional Ecosystem Study Group for the North Sea (REGNS) in 2006;
j) continue to report on new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants;
k) continue to report on new information concerning the analysis of dioxins and the preparation of reference materials for these compounds;
l) continue to report on new information on the monitoring and analysis of toxaphene;
m) continue to report on developments within the UNEP Global POPs Monitoring Network;
n) continue to report on new information on the impact of alkylphenols from produced water;
o) report on new information on contaminant concentrations in marine fish and other marine food products;
p) report on new information regarding perfluorinated compounds.

MCWG will report by 1 April 2005 for the attention of the Marine Habitat and Oceanography Committees and ACME.

Supporting Information

Priority:	This Group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. These activities are considered to have a high priority.
Scientific Justification and relation to Action Plan:	Action Plan Goals Nos: 1, 4, 5. a) Data available in the ICES databanks will be used to prepare illustrative data products under the OSPAR Common Procedure. b) This is in response to an OSPAR request. c) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment. d) These systems are being reviewed for application to monitoring of contaminants in the marine environment. e) This is in response to an OSPAR request. f) This is intended as an aid to laboratories participating in collaborative international marine monitoring programmes. g) This is in response to a standing request from HELCOM. h) This is in response to a request from ICES. This task will support long-term planning for WGSAEM. i) This is response to a request from the REGNS group. j) Owing to continuing concerns about the distribution and effects of polybrominated diphenylethers and other flame retardants in the marine environment, it is relevant to consider the results of recent research on this topic. k) Owing to continuing concerns about the distribution and potential health effects of dioxins and other planar compounds in the marine environment, it is relevant to consider the results of recent research on this topic. l) Owing to continuing concerns about the distribution and effects of toxaphene in the marine environment, it is relevant to consider the results of recent research on this topic. m) The development of the UNEP monitoring programme is relevant to other collaborative international monitoring programmes, and a watching brief will be maintained. n) Owing to continuing concerns about the possible endocrine-disrupting effects of alkylphenols derived from produced water in the marine environment, it is relevant to consider the results of recent research on this topic. o) Owing to continuing concerns about contaminants in marine fish and other marine food products, it is relevant to consider the results of recent research on this topic. p) These compounds are widespread contaminants in the marine environment, and it is relevant to consider the results of recent research on this topic. MCWG provides input across the field of marine chemistry which underpins the advice given by ACME, and also supports the work of national and international collaborative monitoring programmes, e.g., within OSPAR.
Resource Requirements:	The resource required to undertake activities within the framework of this group is negligible.
Participants:	The Group is normally attended by some 20–35 members.
Secretariat Facilities:	None.
Financial:	No financial implications.
Linkages to Advisory Committees:	There is a close and direct linkage with ACME.
Linkages To other Committees or Groups:	There is a close working relationship with WGMS, WGBEC, and WGSAEM.
Linkages to other Organisations:	The work of this group is closely aligned with work being undertaken within EU/AMPS on the requirements and implementation of the Water Framework Directive. This group provides the basis for some advice to OSPAR.
Secretariat Marginal Cost Share:	20% OSPAR, 80 % ICES.