Marine Habitat Committee **ICES CM 2003/E:02**
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REPORT OF THE

Marine Chemistry Working Group

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

Palægade 2–4 DK–1261 Copenhagen K Denmark

Contents

15 Annexes

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 Research Director of the Estonian Marine Institute and ICES Delegate, Dr Evald Oyaveer, presented at 10.00 hrs on 3 March 2003. The 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 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.

2 Adoption of the agenda

The Terms of Reference for this meeting of the Marine Chemistry Working Group (C. Res. 2002/2E01) are:

A. Chemical Oceanography Subgroup

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

B. Organics Subgroup

a) provide information on the availability of suitable analytical methods to allow the determination of environmental concentrations of organic substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome [OSPAR 2003/1];

b) 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 2003/3.2];

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

d) review new information on the analysis of PAH metabolites in bile, critically review the robustness of the methods, and report the outcome;

e) review new information on the use of membrane systems for sampling and report the outcome;

f) review new information on the monitoring and analysis of toxaphene and report the outcome;

g) review new information concerning polybrominated diphenylethers (PBDEs) and report the outcome;

h) consider a review note on phenylurea herbicides (diuron and isoproturon) and report the outcome;

C. Trace Metals Subgroup

a) provide information on the availability of suitable analytical methods to allow the determination of environmental concentrations of inorganic substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome [OSPAR 2003/1];

b) 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 2003/3.2];

c) review information on trace metal speciation and its effects on behaviour and toxicity, and report the outcome;

d) review new information on the use of membrane systems for sampling and report the outcome;

D. Plenum

a) review the relevant aspects of the implementation table of the OSPAR Joint Assessment and Monitoring Programme and indicate activities that could be proposed to be carried out by MCWG;
b) 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;
c) 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;
d) review any new SGQAC Annexes on Quality Assurance and report the outcome;
e) review the revised ICES Environmental Data Reporting Format (Version 3.2) and provide comments to the ICES Marine Data Centre;
f) consider and finalise draft guidelines for integrated chemical and biological effects monitoring (with WGBEC and WGMS);
g) discuss matters referred from the three subgroups, as necessary.

MCWG will report by 24 March 2003 for the attention of the Marine Habitat and Oceanography Committees and ACME.

All of these items had been incorporated into the agenda. The annotated agenda, circulated prior to the meeting, and subsequently updated at the meeting, is provided in Annex 2.

3 Report of the 90th ICES Statutory Meeting

The Chair informed the group that all tasks referred to the MCWG at the 2002 ICES Annual Science Conference had been incorporated into the agenda. Lars Føyn advised the group that, from a personal view, the main message to take from the ASC was the high importance of the developing ecosystem approach.

4 Reports on related activities

4.1 OSPAR and HELCOM

All official requests from the OSPAR Commission or the Helsinki Commission which arose prior to the production of the agenda have been included.

4.2 Intergovernmental Oceanographic Commission (IOC)

No information on relevant IOC programmes was available at the meeting.

4.3 Laboratory Performance Study (LPS) QUASIMEME

David Wells presented information on recent developments within QUASIMEME. A report which was submitted to OSPAR SIME summarises these, and it is attached to this report as Annex 3. In discussion, two points arose: firstly, a workshop on imposex and intersex will be held during 2003; secondly, Gert Asmund enquired whether it would be possible for determinations of methylmercury (MeHg) to be included within the QUASIMEME Laboratory Proficiency Scheme. Dr Wells said that he would need to be able to work with at least one laboratory that is able to undertake these analyses in advance in order that the assigned values can be set. Jacek Tronczynski will investigate the possibility of a collaboration between QUASIMEME and IFREMER for MeHg as the latter institute has considerable expertise in this area built up over many years. The discussion under Section 8.1.3, below, is also relevant to the discussions of the QUASIMEME LPS programme.

4.4 Other activities

4.4.1 POPs Global Monitoring Network

Robin Law informed the MCWG that UNEP will hold a meeting in Geneva from 23–27 March 2003, at which a global POPs monitoring programme intended to allow the effectiveness of the Stockholm Convention to be assessed will be developed. Topics to be discussed at the meeting, and on which reports and recommendations will be prepared, are:

1. The choice of substances and analytical techniques.
2. Site selection, matrices and sampling techniques.
3. QA/QC and data treatment.
4. Data communication.
5. Capacity building.

Robin Law and Jacob de Boer will both be attending this meeting, and probably Bo Jansson as well. Feedback will be provided to MCWG2004.

5 Reports on projects and activities in Member Countries

5.1 Endocrine disruption in the Scheldt estuary: distribution, exposure and effects

ENDIS-RISKS is a four-year project conducted by a consortium of one Dutch and five Belgian partners. The project is financed within the framework of the “Second Plan for Scientific Support for a Policy of Sustainable Development” (SPSD-II) as a strategic scientific research. The project aims to assess the distribution and possible effects of endocrine-disrupting substances in the Scheldt estuary. Priority substances, their physico-chemical distribution (speciation within the different compartments: sediment, water, suspended particulate material), their concentration in biota (mysid shrimp and gobies) and their geographic distribution will be assessed.

The results of the ENDIS-RISKS project will yield a thorough, integrated and multidisciplinary description of the current status of the Scheldt estuary in relation to endocrine disruption. This study will allow a fundamental, ecotoxicological risk assessment of endocrine-disrupting substances in the Scheldt estuary to be produced.

More information can also be found on the ENDIS-RISKS website
http://www.vliz.be/En/Activ/Projects/endis.htm.

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 Peter Lepom

The work of the AMPS group.

Peter Lepom presented an overview on the work of the Working Group on Analysis and Monitoring of Priority Substances and Pollution Control (AMPS), which was established in 2002 to give support to decision makers on all aspects of analysis and monitoring of priority substances during the process of implementation of the European Water Framework Directive. All member states, Norway and the ten accession countries are represented in the group, which is chaired by the Institute of the Environment and Sustainability of JRC. The major tasks are to give recommendations on:

- analytical methods for the analysis of priority substances which might be suitable for compliance checking of EQS;
- preferred matrix for monitoring of priority substances;
- sampling of suspended particulate matter and sediment;
- the use of SPM/sediment and biota for monitoring purposes;
- methods for determination of background concentrations of naturally occurring metals;
- data quality requirements;
- the analysis and monitoring of substances not on the priority substance list (river basin specific compounds, substances mentioned in EEC 76/464 dangerous substance directive list, emerging chemicals that might be considered for inclusion in the priority substance list when under revision);
- reporting to the expert advisory forum on priority substances.

In addition, research needs on analysis and monitoring of priority substances should be identified.

To date there have been two meetings of the AMPS group, and three major documents have been produced: a table of existing standard methods for the analysis of priority substances, a background document on analytical determination of substance groups (PBDEs, SCCPs, Alkylphenols): Proposal for indicator substances, analytical methods and need for actions, and a table of available certified reference materials for priority substances. These documents have been finalised and are open for discussion. These documents were made available to the group members, and will be included on the MCWG2003 CD-ROM to be circulated to members and ICES.

Details on the table of existing standard methods for the analysis of priority substances were given and the following conclusions were drawn:

- for about two-thirds of the priority substances, compliance with the proposed EQS can be checked using available standard methods;
- for some fields of application there are no standards available for the time being, e.g., for the analysis of priority substances in transitional and coastal waters, solid particulate matter, sediments and biota;
- for some of the priority substances, e.g., SCCPs (short-chain chlorinated paraffins), there are no standard methods available;
- other validated procedures for the analysis of priority substances shall be taken into consideration as well as standard methods;
- data quality requirements have to be identified;
- there is no information on the costs of the monitoring of priority substances including the costs of sampling;
- there is only limited information to show whether the listed standard methods have been widely applied in routine laboratories or not;
- there is an urgent need for more certified standards and reference materials for QA/QC;
- there is a need to establish a European laboratory proficiency testing scheme for inland water monitoring;
- there is a need for further method development and validation studies for several priority substances.

Due to the high log K_{ow} value of many of the priority substances, monitoring in the water phase is not appropriate. Hence, other matrices must be taken into account for compliance monitoring, particularly SPM. At the moment SPM sampling is not established in most of the member states and accession countries and SPM cannot be collected in all water body types to be monitored, e.g., in clear-water lakes, or fast-flowing mountain rivers. Therefore the identification of proper monitoring approaches for different water body types is under discussion.

A further issue of discussion is how to establish background concentrations for naturally occurring metals and what geographic scale might be appropriate.

The next meeting of the AMPS group will be held at the JRC, Ispra in April 2003. Drafting groups on metal background concentrations and data quality requirements will be established and a background document on SPM, sediment and biota monitoring will be provided.

Further discussion on this topic and on how the MCWG could interface with AMPS is presented under Agenda Item 11.5.

7.2 Ott Roots

POPs monitoring in the Baltic Sea ecosystem: Estonian data.

Ott Roots, from the Estonian Environmental Research Centre, described the results of a large-scale environmental monitoring of the hazardous substances (persistent organic pollutants and heavy metals) in Estonian coastal water ecosystems. Results for toxic substances in the Baltic Sea have been published since the end of the 1970s. In the first period (1974–1988), the aim of the research project was to investigate the mechanisms that determine how organochlorines and heavy metals spread and move around in the environment. Findings on deposition and the concentrations in air and precipitation will be combined with studies of atmospheric transport, seawater processes and cycling between water, plankton, fish, algae, molluscs, seals, etc. The data have shown that many organochlorine substances which have never been used in Estonia have been carried to the Estonian coast by air or surface currents.

For this period the monitoring results were published in two parts:

Roots, O. 1996. Toxic chlororganic compounds in the ecosystem of the Baltic Sea. Ministry of the Environment, Tallinn, 144p (ISBN 9985–9072-0-5).
Jankovski, H., Simm, M., and Roots, O. 1996. Harmful Substances in the Ecosystem of the Gulf of Finland. Part I. Trace Metals, EMI Report series, No.4, Tallinn, 158p (ISBN 9985-9058-3-0).

After Estonia became independent, the Estonian National Environmental Monitoring Program started in 1994 with state funding. Currently, the programme is based upon the Manual for Marine Monitoring within the COMBINE Programme of HELCOM. Marine monitoring undertaken after 1994 seems to confirm the earlier conclusions, that the concentrations of organochlorines and heavy metals in fish, seals and bottom fauna have decreased steadily, and even the maximum concentrations of organochlorine compounds in fish (herring, perch, etc.) caught in Estonian coastal waters are considerably lower than the standards set by the World Health Organization.
(see http://www.envir.ee/ministeerium/trykised/keskkond21_inglise.pdf).

The decrease in seawater salinity in the Baltic has had a noticeable effect on the ecosystem of the sea and, for example, has altered the diet of the grey seal. The fatty fishes formerly consumed have been largely replaced by roach and perch, the PCB content of which is one of the lowest in fish in the Baltic Sea area. The integration of chemical and biological monitoring provides more comprehensive information for quality assessment and on the ecological functioning of aquatic ecosystems. The profile of CB congeners, and the sum of their concentrations in grey seals from the Baltic, eastern and northeastern England, and the St. Lawrence Estuary were examined using principal components analysis (PCA). The patterns observed differed between juvenile and adult animals, but the gender of adults and geography do not appear to play a role.

7.3 Jarle Klungsøyr

Reproductive effects of C_4 – C_7 alkylphenols in cod.

Jarle Klungsøyr presented the results of work carried out during 1997–2001 at the Institute of Marine Research, with the aim of studying the biological effects on hormones and reproduction in cod (*Gadus morhua*) of selected C_4–C_7 alkylphenols found in produced water. Produced water is a by-product of the production of offshore oil and gas, and arises from the underground formation where the oil and gas are located. It contains a wide range of dissolved organic and inorganic compounds and, after treatment to reduce the oil content, is often discharged to sea. The study was carried out under controlled laboratory conditions. Model compounds tested included 4-*tert*-butylphenol, 4-*n*-pentylphenol, 4-*n*-hexylphenol and 4-*n*-heptylphenol. Variations in hormone (17 β -oestradiol, testosterone and 11-ketotestosterone) levels in blood plasma and gonadal development in control groups of fish were compared with groups of cod exposed to these alkylphenols.

During a four-week period, five groups of cod were administered a single oral dose each week of 5 ppb, 500 ppb, 5 ppm, 10 ppm and 20 ppm total body dose of each of the four C_4–C_7 alkylphenols. A control group (which was not dosed) and a positive control group (dosed with 5 ppb 17β-oestradiol, a potent natural steroid hormone) were also included in the experiment. Each group consisted of 40 fish. A total body burden in cod of 20 ppb (four compounds) is theoretically equivalent to a 0.032 ppb concentration in seawater, using a bioconcentration factor of 600 for each of the the four selected alkylphenols.

Levels of 17β -oestradiol in blood plasma were reduced in female cod given the lowest dose of C_4–C_7 alkylphenols. The gonads of exposed female cod displayed a lower gonadosomatic index (GSI) compared to controls, and their gonads also developed more slowly. It was calculated that, in cod given the lowest dose, spawning would begin approximately 21 days later than in controls. If this was to occur in wild populations of cod, it might reduce their reproductive potential.

Testosterone levels also fell in male fish given the lowest dose. The male fish started to produce vitellogenin, which is a yolk protein normally only found in females. There were significant changes in the maturation status of the testis. At the lowest exposure to alkylphenols, the quantity of spermatozoa was reduced, whilst there were increases in spermatogonia and spermatocytes. This may influence the ability of these males to fertilize eggs. Additional work is now under way, and will be reported to MCWG at a future meeting.

8 Subgroup activities and discussions

Whilst MCWG usually works in three subgroups relating to Chemical Oceanography, Trace Metals, and Organic Contaminants, the reduced attendance at the meeting (and the lack of representation within the first two topics) made this impractical, and the MCWG met in plenary throughout the meeting.

8.1 Plenary activities and those common to all subgroups

8.1.1 Review the relevant aspects of the implementation table of the OSPAR Joint Assessment and Monitoring Programme and indicate activities that could be proposed to be carried out by MCWG

MCWG discussed the implementation framework outlined in MCWG2003 8.1.1/1. It was suggested that the following JAMP products could receive input from MCWG if required.

JAMP product	Suggested MCWG input
EM-3	Advice regarding nutrient concentrations.
HT-1 a-c	Advice on the feasibility of monitoring specific compounds.
HT-2	Develop initial guidelines for integrated chemical and biological effects monitoring, and review later JAMP guidelines (with WGBEC).
HT-5	Review draft guidelines
HT-7	Review draft guidelines
HM-3	Inform OSPAR of novel contaminants.
HA-2	Advise on long-term quality of chemical data

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

MCWG has previously made a recommendation to ICES regarding making information on reference materials available to laboratories via the ICES website (MCWG2001; agenda item 8.1.1). Examination of the ICES website suggests that this information is not currently available in a form which is useful to laboratories seeking suitable reference materials with which to underpin their AQC procedures. Searching the site for “reference materials” yields information solely for materials used in QUASIMEME LPS studies, and for which data have been reported under Convention requirements. What we need is information relating to currently available CRMs in a list which can easily be browsed (MCWG2001; agenda item 8.1.1) so as to allow suitable CRMs to be identified to meet the needs of specific monitoring programmes. This list was originally prepared by MCWG at its 2001 meeting. For the future, the ideal would be for producers to be able to maintain this as an up-to-date list, as otherwise (a) new materials would not be listed until some time after the next MCWG meeting, and (b) materials which are no longer available would continue to be listed until some time after the next MCWG meeting. MCWG recommends that ICES work to develop the producer/website link as a matter of priority, including a list of available CRMs and SRMs, with links to the appropriate producer websites. If that is not possible, then we suggest that ICES simply list producer organisations, and their website links and contact details, as this would assist laboratories to make direct contact.

MCWG reminds ICES of the paramount importance of CRMs to international collaborative marine monitoring programmes, and asks that ICES contact the director of IRMM, Geel (Hendrik Emons) to express its concern that the closure of the EU Measurement and Testing Programme could result in delays to the production of these invaluable materials. It is also important that this remains a rolling programme, so as to ensure that new materials become available as stocks of others become exhausted. In monitoring studies following recent oil spills, from the *Sea Empress* to the *Erika* and *Prestige*, the poor supply of biological tissue CRMs certified for a wide range of PAH compounds has proved to be an issue.

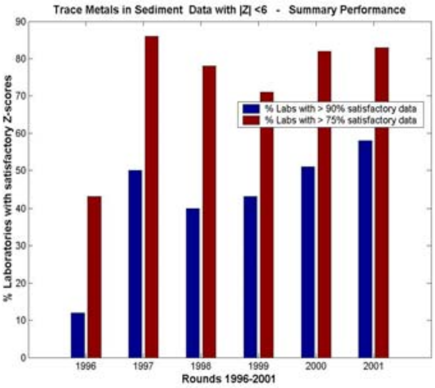
8.1.3 Review how a presentation of the long-term performance of a laboratory can be standardised taking the information from the 2000 MCWG meeting into account and report the outcome

David Wells presented information from a paper presented at the QUASIMEME Conference held in Barcelona in 2002. This provided an overview of progress within the QUASIMEME project 1996–2002. A series of Quality Performance Indicators were used to indicate year-by-year progress.

On a laboratory basis, two categories are defined within any specified group, e.g., nutrients in seawater, or trace metals in biota:

- % of laboratories that have > 90 % satisfactory performance (| Z | < 2) for a specified group of determinands;
- % of laboratories that have > 75 % satisfactory performance (| Z | < 2) for a specified group of determinands.

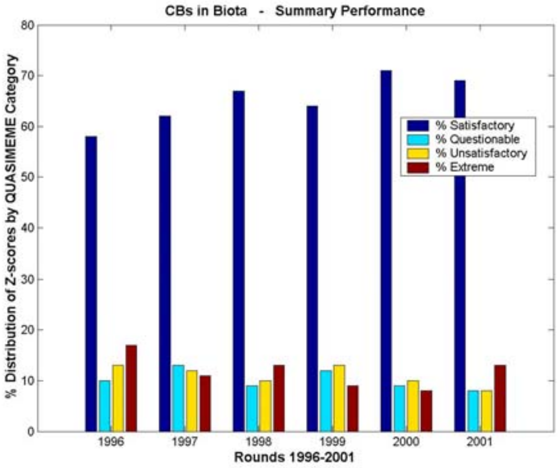
An example is given below for trace metals in sediment:



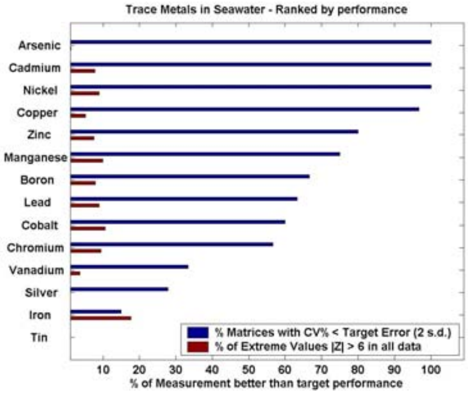
A second classification used the standard approach used by ISO 43 in grouping laboratory performance:

- % of laboratories with satisfactory performance (| Z | < 2);
- % of laboratories with questionable performance (2 < | Z |< 3);
- % of laboratories with unsatisfactory performance (3 < | Z | < 6);
- % of laboratories with extreme values (| Z | > 6).

An example is given below for CBs in biota:



On a determinand basis, a comparison has been made on the actual between-laboratory performance and the target performance for each determinand group. An example is given below for trace metals in seawater:



The long-term precision and bias can be determined on the basis of a re-scaled sum of Z scores over a prescribed time period, to map the long-term performance. This approach is now part of the ISO 43 guidelines for laboratory performance.

Of the 20 groups of determinands studied in the QUASIMEME Project 1996–2002 most show an overall improvement in the between-laboratory agreement. In some cases the improvement was modest and still requires further attention. However, the value of long-term participation in an external QA programme has clearly been demonstrated.

Total Groups = 20	**Performance by Laboratory**	**Overall performance by determinand group**
Improved	11	13
Consistently high	5	3
Poor, erratic or declined	4	4

Each of these approaches has been completed by the QUASIMEME project for the period 1996–2002 and is currently being complied for participants in the LPS scheme or the Conference on CD-ROM. This is available to others on request. A detailed overview is also being prepared for publication.

Asmund, G., Scurfield, J., and Wells, D. (In press). Treatment of Laboratory performance study data. Proceedings of the QUASIMEME conference Measurement in the Marine Environment: Challenges and Achievements. Barcelona, 23–26 October 2002.

8.1.4 Review any new ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC) annexes on Quality Assurance and report the outcome

Three draft annexes were referred to MCWG by ICES during the meeting, but due to e-mail/server problems only Annex 11 was able to be printed and considered by the group. MCWG agreed that the Chair would approach the appropriate subgroup Chairs regarding the other two annexes following the meeting and solicit some comments for SGQAC from MCWG members as a minimum response this year.

Annex 11: ICES/HELCOM SGQAC 2003 Annex B-4: Technical note on the determination of measurement uncertainty.

The expertise available within MCWG is limited and MCWG was not able to fully evaluate the document, including statistical aspects, definitions, etc. However, this is a subject that has been given much consideration through many international fora, such as ISO, EURACHEM, IUPAC, etc. Nevertheless, MCWG felt that it was very positive that the SGQAC recognises the importance of taking into account uncertainty when evaluating monitoring data.

It is noted that the estimation of uncertainty is a useful tool for the analyst; a pragmatic approach to its estimation is recommended. In this regard, MCWG considered the document to be too theoretical, and recommends that it be elaborated by providing practical examples that could be used in the laboratory. It was also considered that inclusion of definitions in the document would be beneficial to the user.

It was noted by the group that there are additional tools for calculating measurement uncertainty. The procedure Gert Asmund presented during MCWG2002 (Agenda Item 8.1.2), and in more detail at the QUASIMEME conference in Barcelona (October 2002), is an example of a practical approach to uncertainty of measurement (based on proficiency testing data), which may also give more information. This method accounts for the concentration (Horwitz) effect.

How, or indeed whether, uncertainty of measurement could be used in any data assessments (for instance temporal trend assessments) is not addressed in the document. However, analytical uncertainty data could potentially be incorporated in assessments of monitoring data (e.g., through weighting) for temporal trend assessments or comparing concentrations against reference levels (e.g., background concentrations). The document does not address handling of corrections for recovery and the incorporation of the uncertainty associated with recovery factors. Further information on this can be found in Thompson *et al.* (1999).

It is generally accepted by MCWG that the top-down approach, or a combined approach, is preferable to using only the bottom-up approach (uncertainty budgets) for calculating uncertainty. However, when CRMs are used, care has to be taken that uncertainties are not underestimated. It is also important to take account of the uncertainty associated with the CRMs used. Use of LPT (laboratory proficiency testing) data may help ensure that laboratories determine uncertainty of measurement on a similar basis.

ISO/AOAC/IUPAC Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement. Edited by M. Thompson, S. L R. Ellison, A. Fajgelj, P. Willetts, and R. Wood, Pure Appl. Chem., 1999, No 71, 337–348.

8.1.5 Consider and finalise draft guidelines for integrated chemical and biological effects monitoring (with WGBEC and WGMS) and report the outcome

Prior to MCWG2003, the Chair had contacted the Chair of WGBEC, Ketil Hylland, to discuss this topic. At the meeting MCWG had hoped to be able to discuss draft guidelines from both the UK and the Netherlands, but, unfortunately, these did not become available in time for them to be considered this year. Both countries are currently evaluating this approach for their national monitoring programmes, and further developments are expected in 2003.

Integrated chemical and biological effects monitoring was used and evaluated during the BECPELAG pilot study, and this experience was reported at the ICES 2002 ASC. The results will be discussed further at WGBEC2003, and could have an important impact on the development of the guidelines.

Several countries are evaluating this approach in national programmes. There are, for instance, a number of examples of this approach being taken by oil companies in Norway. Canada has made simultaneous determinations of EROD activity and contaminants in fish liver for the last 5 years. In Germany, integrated cruises have been organised for four years where chemists and biological effects specialists have coordinated their work on the same samples. France has also been combining chemical measurements with biological effects data (e.g., genotoxicity in relation to chemistry in the Seine estuary and bay). Belgium has a long-term study on combined EROD induction and chemical monitoring in dab.

It is clear that most, if not all, of the work carried out thus far represents research and development rather than routine monitoring. Establishing firm guidelines may therefore be rather ambitious at this stage. The rationale for integrated monitoring also needs to be established. Integrating biological effects and chemical measurements surely has benefits, but only in a very few cases might significant, simple, correlations be expected. This has proved to be the case for imposex and the concentrations of organotins, and also, up to a certain point, for scope for growth measurements. During the *Sea Empress* oil spill incident the immune function of oil-exposed mussels was depressed, and later recovered as environmental levels of PAH declined. Nevertheless, this type of simple correlation may not be observed in all cases. Natural factors, such as oxygen levels and temperature, may have a greater influence on certain biological effects measurements than the causative chemicals. However, this should not prevent the setting up of integrated monitoring programmes, as the combined information from the two together will provide a better assessment of the status of the marine environment than either alone.

At the present stage of development, the rationale for integrating chemical and biological effects monitoring seems to be to gain a better understanding of the way in which each biomarker responds to the chemicals to which animals are exposed. Also, to gain a better understanding of the variability in response that arises from other causes, e.g., temperature, reproductive status, and oxygen.

The Chair proposed that this work be handled intersessionally in collaboration with WGBEC. Patrick Roose will attend WGBEC2003, and agreed to advise the group of our discussions. All MCWG members should send new information to Patrick Roose (in particular Marc Raemaekers on the Belgian programme, Michel Lebeuf on the Canadian programme, Robin Law on the UK programme, Ton van der Zande on the Netherlands programme) in advance of MCWG2004. Patrick Roose will present the information at MCWG2004 and this topic will be reconsidered at that meeting.

8.1.6 Review the new version 3.2 of the Environmental Data Reporting Formats from ICES

Robin Law gave a PowerPoint presentation supplied by Marilynn Sørensen on the new developments in data reporting formats for ICES contaminant data and related information. Only limited discussion of the data formats was possible as no one present had any real familiarity with the database. ICES had requested that individual members send examples of their data to ICES in order that the current database format could be tested (to see which types of data will cause it to fail) and 4 members of MCWG (Patrick Roose, Ton van der Zande, Gert Asmund, Evin McGovern) agreed to do so. The Chair had asked those within CEFAS who submit data to the database to comply with the request before the meeting. Subsequently, two specific questions were posed during a phone call to ICES. The first related to occasions using version 2.2 for biota samples, where both fat weight and extractable lipid values were reported for single samples. As these are both operationally defined measurements and the methods applied are different, the values are generally not the same. The ICES request concerned assigning the individual lipid determinations to specific methods and determinands (organic or inorganic), in order that corrections should be assigned specifically. Some members of MCWG expressed concern regarding the normalisation of data on a lipid basis, although this topic was not discussed in detail. MCWG recommended that lipid content be determined using a total lipid method, either that of Bligh and Dyer (1959) or a compatible method (Smedes (1999)). Serious errors can result when “extractable lipid” is determined, particularly in lean fish tissues (lipid content < 10 %) (Herbert and Keenleyside, 1995).

Bligh, E. G. and Dyer, W. J. 1959. A rapid method of total lipid extraction and purification. Canadian Journal of Biochemistry and Physiology, 37: 911–917.

Herbert, C. E. and Keenleyside, K. A. 1995. To normalize, or not to normalize. Fat is the question. Environmental Toxicology and Chemistry, 14: 801–807.

Smedes, F. 1999. Determination of total lipid using non-chlorinated solvents. Analyst, 124: 1711–1718.

8.2 Trace Metal Subgroup

8.2.1 Advise on the availability of suitable analytical methods to allow the determination of environmental concentrations of the substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome. This should include references to the sources of methods and data [OSPAR request 2003/1]

MCWG considered the draft guidance prepared at MCWG2002 and revised the table accordingly. The revised table is attached as Annex 4, and also includes input under Agenda Item 8.3.1.

For the brominated diphenylethers, a number of recent references are provided for both the analytical methodology and environmental distribution of these compounds. If OSPAR requires fuller detail and citations for specific compounds these can be prepared on request, but a number of the well-established determinands have already been the subjects of overviews or review notes.

References

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Wade, T.L., Sericano, J.L., Gardinali, P.R., Wolff, G., and Chambers, L. 1999. NOAA's "Mussel Watch" Project: current use organic compounds in bivalves. Marine Pollution Bulletin, 37: 20–26.

8.2.2 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 2003/3.2]

MCWG discussed the possibilities of monitoring using seabird eggs. Anders Bignert from the Museum of Natural History, Stockholm is an acknowledged expert in this field and he gave a presentation at the MCWG meeting in Stockholm, 1998. More information on this topic can be found in the report of MCWG1998, under Agenda item 7.2. This information is fully relevant today.

Analysis of bird's eggs has advantages because of the homogeneous matrix and the good mutual comparability of samples. Whole egg contents are normally used for analysis, both for mercury and organochlorines. Sampling is an important stage, as it can cause additional variability. This can be solved by, e.g., always taking eggs from the first clutch. Migration is also a crucial factor to take into account, and variability will be reduced if eggs are collected from birds which have a limited migratory behaviour, depending on the aims of the monitoring programme. There are practical difficulties in sampling, e.g., it may be necessary to climb cliffs. There is experience within MCWG with bird egg sampling for environmental purposes in Sweden, Germany and Canada. In Greenland, eggs have been sampled since the 1980s and archived material may still be available at NERI, Roskilde, Denmark. There is information available on the concentrations of organobromine compounds also in bird's eggs from Canada, Sweden, and possibly Greenland. BDE209 (and other congeners) is currently being analysed in bird's eggs for the EU risk assessment on the deca-mix PBDE formulation. MCWG recommends that more groups include analysis of organobromine compounds such as BDEs and HBCD (hexabromocyclododecane), as these contaminants are becoming more important due to rising levels in the environment (within the ICES area; the former in North America and the Arctic, the latter in Europe). The analysis of mercury and organohalogens in eggs does not require a specific approach which would differ significantly from that applied to fish samples.

It should also be noted that the background concentration of mercury in eggs may not be zero because of the natural presence of mercury in the marine environment. There was no experience in the group relating to the analysis of mercury in feathers. However, following the meeting, MCWG was informed of a project which is now under way at NERI, Denmark, entitled FOMA (Fate of Mercury in the Arctic): a simple model of transfer of atmospheric mercury to carnivores. This study will establish a link between the mercury levels in the abiotic environment (e.g., historical records of mercury data in peat bogs, the ice sheet or marine sediments) with levels in carnivore species (polar bear development of the mercury loads in high trophic-level biota). This will show whether changes in mercury levels in the atmosphere are reflected in species at higher trophic levels of the Arctic ecosystem. As mercury data in biota from Greenland are recent, covering only the past two decades, we do not know whether the increase in mercury levels seen in peat cores and marine sediments during the last century are reflected in biota. To date, the AMAP temporal trend projects have focused on recent time trends with a short five-year period, from 1999 to 2003 for selected contaminants and media. The use of power analysis has shown that many years (often ten or more) are required to provide reliable and powerful conclusions on temporal trends, and this project will expand the time-series of mercury concentrations in biota to about 150 years by analysing museum samples of bird feathers (gyrfalcon, peregrine falcon, and white-tailed sea eagle) and polar bear hair and teeth. The project is due to report by May 2004.

Ton van de Zande will collect information from members of MCWG on levels of mercury and organohalogens in bird eggs and present that at the next meeting.

8.2.3 Review information on trace element speciation and its effects on behaviour and toxicity, and report the outcome

Evin McGovern reported a problem in Ireland following the finding of high concentrations of total arsenic (about 40 mg/kg) in seaweed taken for animal feed. In EU regulations concerning animal feed, the maximum allowable concentrations for arsenic are 2, 4, or 10 mg/kg, for different kinds of feed, and the seaweed samples breached the regulations on basis of total arsenic. The arsenic in the seaweed was then analysed using a speciation method (HPLC-MS), and this showed that the arsenic was predominantly present as arseno-sugars with inorganic forms not detected (<0.5 mg/kg). The seaweed was collected on the west coast of Ireland and the source of the arsenic is considered to be natural.

It is long known that arsenic can occur naturally at relatively high levels in marine biota. In marine biota samples, arsenic is usually present in organically bound forms, such as arsenobetaine in fish and arsenosugars in marine algae (although there are exceptional species where more toxic forms of arsenic occur), and these organic forms are generally considered harmless. Total arsenic determinations are not, therefore, appropriate for assessing the toxicological significance of arsenic in marine biota. Concentrations in marine biota are generally higher than those in freshwater biota.

There are no current EU regulations for arsenic in food, although an EU SCOOP task is under way, for the SCF (Scientific Committee for Food) to gather relevant information.

Other members of MCWG confirmed the high concentrations of arsenic in marine fish and shellfish, and Evin McGovern agreed to collate information on this topic for MCWG2004.

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

No new data were available under this specific agenda item, but see the related discussion under Section 8.3.5.

8.2.5 Review new information on the use of ICP-MS analysis for trace elements, and experience within RIKZ

Ton van der Zande presented a comparison of trace element analyses performed using ICP-MS (inductively-coupled plasma / mass spectrometry) with analyses performed by a variety of atomic absorption techniques. Based on the experience within his laboratory and within the QUASIMEME LPS scheme, ICP-MS can replace all the atomic absorption techniques currently in use, yielding resulting of similar or better quality. Within QUASIMEME, z-scores were in practically all cases < 1, and a majority of z-scores were < 0.5. Chromium concentrations were, for some biological samples, close to or below the detection limit of the instrument. This problem could probably be solved by the use of a reaction or collision cell in the ICP-MS, as is available on new instruments. Lead analyses in some QUASIMEME samples were also a problem, but that was due to high blank values obtained, and not an instrument problem. The calibration of the instrument is linear over the entire measuring range and the repeatability of measurements was 5 % to 10 % for most elements, but 15 % for chromium at low levels. Direct comparison of AAS and ICP-MS analyses showed some systematic differences for Pb, Cd, Ni and Cu, but calculation of the rescaled sum of z-scores for the AAS analyses showed that it is the ICP-MS results that are the most reliable. Seawater analyses cannot be performed directly. Seawater has to be diluted with ultra clean water before analysis, or after matrix removal (either on-line or off-line) and preconcentration. The analysis of mercury can also be conducted using ICP-MS, if the solutions are stabilised with gold. This application is described in more detail in the presentation made at the QUASIMEME Conference referred to above.

At RIKZ, 24 samples are analysed together with standards, blanks and control samples during a single day, which includes five hours of instrument time.

8.3 Organics Subgroup

8.3.1 Advise on the availability of suitable analytical methods to allow the determination of environmental concentrations of the substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome. This should include references to the sources of methods and data [OSPAR request 2003/1]

See Section 8.2.1, and Annex 4.

8.3.2 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 2003/3.2]

See Section 8.2.2.

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

Jacob de Boer advised MCWG that these compounds are now included within a routine fish monitoring programme in the Netherlands, and he will advise MCWG of the results. Michel Lebeuf proposed that MCWG continue with the collaborative programme that has previously been under way on the global distribution of *tris*(4-chlorophenyl)methanol and *tris*(4-chlorophenyl)methane in flatfish (Lebeuf *et al*., 2002), and this was agreed. He also advised that a standard solution containing these compounds is now available from Wellington Co. in Canada.

Lebeuf, M., de Boer, J., Haarich, M., Ikonomou, M. G., Law, R. J., and Roy, R. 2002. Global distribution of *tris*(4-Chlorophenyl)methanol and *tris*(4-Chlorophenyl)methane in flatfish – is technical DDT the most likely source? Organohalogen Compounds, 58: 445–448.

8.3.4 Review new information on the analysis of PAH metabolites in bile, critically review the robustness of the methods, and report the outcome

Comprehensive information on this topic was provided to MCWG2002. Two CRMs certified for PAH metabolites are due to become available during 2003, but this launch may be delayed due to the loss of the certification committee which previously operated within the Measurement and Testing Programme of the EC.

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

Ton van der Zande informed MCWG that his laboratory has a current research programme which is investigating the use of silicone membranes for passive sampling. He agreed to report their findings to MCWG2004.

Two new papers containing valuable information on passive samplers have been published recently, and they also include some information on the sampling of trace metals.

Kingston, J. K., Greenwood, R., Mills, G. A., Morrison, G. M., Bjorklund Persson, L. 2000. Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments. Journal of Environmental Monitoring, 2: 487–495.
Gorecki, T. and Namiesnik, J. 2002. Passive sampling. Trends in Anayltical Chemistry, 21: 276–291.

8.3.6 Review new information on the monitoring and analysis of toxaphene, and report the outcome

Newly published information on analytical methodology is available (de Boer *et al*., in press; Gouteux *et al*., 2002). Few new data were available at the meeting, but studies are currently under way in Canada on temporal trends of toxaphene concentrations in beluga whales, and within AMAP on toxaphene concentrations in birds and mammals, both of which will become available during 2003. Michel Lebeuf and Gert Asmund agreed to present these data for discussion at MCWG2004.

A report on a toxaphene research project (preliminary results) funded by the Canadian TSRI (Toxic Substances Research Initiate) programme was made available to MCWG members by Michel Lebeuf.

de Boer, J., Leonards, P. E. G., Klungsøyr, J., McHugh, B., Nixon, E., McGovern, E., and Rimkus, G. G. (In press). Comparative tests to improve the gas chromatographic analysis of chlorobornanes in fish samples. JAOAC, 86.
Gouteux, B., Lebeuf, M., Trottier, S., and Gagné, J.-P. 2002. Analysis of six relevant toxaphene congeners in biological samples using ion trap MS/MS. Chemosphere, 49: 183–191.

8.3.7 Review new information concerning polybrominated diphenylethers (PBDEs) and report the outcome

Jacob de Boer presented new information on PBDEs and other brominated flame retardants taken from the DIOXIN 2002 Conference held in Barcelona, the current EU risk assessment on decabromodiphenyl ether (BDE209; the deca-mix PBDE formulation) and the European research project FIRE – Risk assessment of brominated flame retardants (BFRs) as suspected endocrine disrupters for human and wildlife health.

New data on human exposure to BFRs, their occurrence in the environment and the results of the BSEF/QUASIMEME BFR Interlaboratory study were presented. In Japan, a 44-fold increase in total BDE concentrations in adipose tissue was observed between 1970 and 2000. The total BDE concentration in human milk from Vancouver, Canada was 43 ng/g lipid weight. This was 10 times higher than concentrations observed previously in Sweden, and furthermore had increased by a factor of 15 from 1992 to 2000. Most blood samples from Sweden contained 1–6 ng/g, but 5 % of the samples had BDE concentrations above 30 ng/g. High concentrations of BDE209 were found in the blood of rubber industry workers in Sweden. PBDE data for human milk were reported from the Czech Republic and Japan, data for PBDEs in blood from Korea, and for polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) in blood from Japan. High concentrations of BDE47 (47 ng/g lipid weight) were found in human serum from California. In addition to food, house dust might be another important exposure route for humans to PBDEs as shown by data from Germany. A Swedish study indicated a three-fold higher human uptake of HBCD from food than was seen for PBDEs.

Investigations in sediment cores from Japan have shown a correlation between the production data for PBDE formulations and the BDE concentrations found in the cores. Extremely high concentrations of PBDEs (up to 2,000 µg/kg lipid weight) were found in fish samples from Minnesota. Preliminary results from Germany indicate the occurrence of BDE209 in freshwater fish.

36 laboratories from 13 countries took part in the QUASIMEME interlaboratory study on BDEs, HBCD (hexabromocyclododecane), TBBP-A (tetrabromobisphenol-A) and Me-TBBP-A in fish, mussels, sediment, sediment extract, human milk and standard solutions of unknown concentrations. The results can be summarised as follows: results for BDE-7 were satisfactory for all matrices (CV = 15–25 %). For BDE99 there was a considerable improvement compared to the first worldwide intercomparison study (CV = 22–35 %, exception milk CV = 65 %). Analysis of BDE209 was once again not under control in most laboratories. Only a few results were submitted for TBBP-A, Me-TBBP-A and HBCD. Laboratories need more time to set up methods for the latter three flame retardants before comparable data can be generated.

The EU risk assessment of the deca-mix PBDE formulation will be completed in June 2003. BDE209 was detected for the first time in peregrine falcon eggs from Sweden in 2001. Samples (eggs, muscle, liver) of peregrine falcons from the U.K. and of other bird species are currently being analysed to confirm these findings. First results indicate the presence of BDE209 in peregrine falcons from the UK as well as Sweden.

The EU-project FIRE: risk assessment of brominated flame retardants as suspected endocrine disrupters for human and wildlife health, with 19 partners from seven European countries, started in 2002. More than 25 brominated flame retardants, including BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209, TBBP-A, α-, β- and γ-HBCD, FR 720, 2,4,6-tribromophenol, 6-OH-BDE47, and TB-DEPH (tetrabromophthalic acid, diethylhexyl ester), will be tested using *in vitro* screening assays to select five BFRs for further *in vivo* studies. Human and aquatic wildlife hazards will be identified by *in vivo* studies on rats and on zebrafish and flounder, respectively. Moreover, human exposure and aquatic ecosystem exposure assessment will be performed. Finally, all data will be used for an integrated risk assessment for humans and wildlife.

During the discussion, Jacob de Boer stated that members should be aware of serious potential blank problems with BDE209 due to its tendency to adsorb strongly to glass surfaces and be released only after long contact with organic solvents. This experience was shared by CEFAS within the deca-mix risk assessment study. Another source of high blanks for BDE209 can be dust. To reduce blank problems, it was recommended to use completely different sets of glassware for the analysis of BDEs in sediment and biota samples, and never to mix the two. Michel Lebeuf said that from his experience, the time window for collecting the eluate during GPC clean-up must be specifically adjusted when analysing for BDE209, otherwise it can be partly or completely lost due to non-elution from the GPC column. ASE (accelerated solvent extraction) may be an alternative to Soxhlet extraction for BDEs from environmental samples. Peter Lepom noted that comparable extraction efficiencies were obtained for both techniques when extracting BDEs from sediments, provided that conditions are well optimised in each case. There were some discussions on whether bioaccumulation of BDE209 in fish might be possible or not. Peter Lepom informed MCWG that he plans to verify the results on the occurrence of BDE209 in fish by independent analysis of these samples in the laboratory of RIVO. During the discussion, it was also noted that there are some indications from feeding studies of biotransformation of BDEs in fish, e.g., for BDE99. There is a need for further research on this topic.

Jacob de Boer informed MCWG that during DIOXIN 2003, 25 to 29 August in Boston, a one-day session on brominated flame retardants will take place and that the next conference on BFRs will be held from 13 to 16 June 2004 in Toronto, Canada.

These compounds are persistent organohalogen compounds, which show increasing concentrations in biota and which are undergoing long-range transport to the Arctic. They merit further study. Jacob de Boer and Michel Lebeuf will present new data next year, the latter on beluga whales.

A report on a PBDE research project (preliminary results) funded by the Canadian TSRI (Toxic Substances Research Initiate) programme was made available to MCWG members.

8.3.8 Consider a new review note on phenylurea herbicides (diuron and isoproturon) and report the outcome

Norbert Theobald presented a review note on these two phenylurea herbicides in the marine environment. The production volumes, physico-chemical properties, toxicity, analytical techniques and occurrence of diuron and isoproturon (mainly in the North and Baltic Seas) were included. The review note is appended to this report as Annex 5.

The production data for these compounds needs to be updated and is difficult to obtain. For instance, values for the EU production of isoproturon in 1995 range from 10 to 50 kilotonnes per year (ktpa) and German usage is over 1 ktpa. Six phenylurea herbicides were monitored in all. These compounds are of medium polarity, and because of their relatively high water solubility they are present in the dissolved phase and transported to the marine environment mainly in the water phase. The water phase occurrence and phytotoxic mode of action of the phenylurea herbicides suggest that algae should be one of the primary toxic end-points for these compounds.

It appears also that water is the principal matrix in which phenylurea herbicides should be monitored. As these chemicals are thermolabile as well as relatively polar, they are not directly amendable to gas chromatography and so the preferred analytical technique is HPLC with different detectors. The need for selective and very sensitive detection techniques for the identification and detection of phenylurea herbicides in seawater samples was stressed. The best results were obtained using an HPLC-MS/MS technique.

Data on the occurrence of phenylurea herbicides in the marine environment are still relatively scarce. Recent results from the German monitoring programme of 2000 to 2002 demonstrate the large geographical extent of contamination of the coastal and offshore waters by phenylurea herbicides in the Elbe estuary, German Bight, Baltic Sea and North Sea, including the English Channel. Isoproturon and diuron were detected more frequently and at higher concentrations than the other compounds determined, but other herbicides such as chlortoluron, linuron and fenuron were also detected. The geographical distributions in the German Bight show pronounced gradients for all herbicides, with declining concentrations with increasing distance offshore linked to mixing and dilution processes. The occurrence of diuron and isoproturon in the waters of the North Sea and Baltic Sea is distinct and probably reflects the different uses of these compounds, at least in part. The contamination of coastal waters by diuron close to harbours could be related to its use as a booster biocide in antifouling paints, whilst the geographical distribution of isoproturon is probably more strongly influenced by riverine inputs.

The reported concentration levels of the dissolved phenylurea herbicides in the North and Baltic Seas, which are within the range of < 1 to > 10 ng/L, are higher than those of organochlorine insecticides such as the HCH isomers, at the same sampling stations. Diuron and isoproturon are included in the list of priority pollutants given in the Water Framework Directive (WFD) and should be considered as candidate contaminants for future monitoring programmes within the marine environment.

Ton van der Zande, Britta Pedersen and Jacek Tronczynski will send additional data from their institutes to Norbert Theobald, to allow the distribution in other maritime zones to be assessed. Norbert Theobald will report to MCWG2004.

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

Jacob de Boer gave a presentation on two ongoing EU funded projects, both of which aim to assess alternative and more cost-effective methods of dioxin analysis, rather than the only currently accepted method of gas chromatography/high-resolution mass spectrometry (GC-HRMS). The DIAC project is investigating the use of comprehensive (2-dimensional) gas chromatography (GCxGC) with electron capture detection (ECD) for the analysis of PCDD/Fs and CBs, including WHO “dioxin-like” CB congeners. This involves using a modulator to continuously stop and focus eluate from a first GC column and then release it for analysis using a second column. Thermal desorption and cryogenic modulators are commercially available, with the latter being generally favoured. Using this technique, separation of all relevant (17 WHO) PCDD/F and “dioxin-like” CBs was attained, including OCDD and OCDF. The quantification capability of this technique is currently being assessed. There are issues with respect to quantification software, which is only now becoming available.

The DIFFERENCE project is assessing a number of methods for the screening of dioxin concentrations in food samples, as a cost-effective alternative to GC-HRMS. The objectives are to:

- develop cost-effective bio- and chemical analytical screening methods to distinguish compliant and non-compliant samples in accordance with the requirements of EU Directive 2002/69/EC;
- obtain rapid selection of positive suspect samples;
- attain low detection capabilities to reduce the number of false positive values.

It was noted that, in approximately two years, the EU maximum limits for dioxins in food will be lowered and maximum limits for “dioxin-like” CBs will also be set (Commission Regulation 2375/2001/EC).

The methods being investigated include chemical methods: GC-HRMS and GC coupled to low resolution mass spectrometry (GC-LRMS), GCxGC with ECD detection; and two bioanalytical methods: Calux-DR and a new Ah-PCR technique. GC-HRMS is used as the standard reference method. Nine laboratories are involved in this project. Some laboratories have also experimented with the use of ASE for extraction and clean-up.

Although for GCxGC there were some problems at the lowest concentrations (possibly an issue of upper bound reporting), the method has shown good progress. There were significant differences between laboratories in the calibration of the Calux assay, and this method needs further study. GC-LRMS performed quite well, and may provide an alternative approach. The ASE extraction/clean-up also shows promise. However, sensitivity at the action level may still prove to be a problem for some methods.

GCxGC coupled to time-of-flight electon capture negative ion chemical ionisation MS (Tof ECNI-MS) may provide a solution in the longer term. Although more expensive than the other methods being investigated, it is less costly than GC-HRMS.

A feasibility study on CRM preparation for PCDD/Fs and “dioxin-like” CBs is also being carried out as part of the DIFFERENCE project. Five food or feed materials have been prepared (milk, pork, fish, compound feed and fish oil). With the disbanding of the EU Measurements and Testing group, it remains to be seen whether this can be implemented within a full CRM production project, following successful completion of the feasibility study. The responsibility for that now lies with the Institute for Reference Materials (IRMM) of the EU Joint Research Centre in Geel, Belgium.

Jacob de Boer will provide an update on these programmes at MCWG2004.

8.4 Chemical Oceanography Subgroup

8.4.1 Data available in the ICES databanks will be used to prepare illustrative data products under the OSPAR Common Procedure, and this term of reference will assist in defining the data products. This is further consideration of an OSPAR request concerning EcoQOs for eutrophication. The subgroup will consider more appropriate EcoQOs

As there were not a sufficient number of members of the COSG present at the meeting, it was not possible to undertake the task above. There was only a brief plenary discussion about this agenda item, which is presented below. The item will be reconsidered at MCWG2004.

Concerning the OSPAR request concerning EcoQOs for eutrophication, it was recognised that EcoQOs have to be developed at a local scale, as knowledge of water mass dynamics and of the actual nutrient regime are of major importance for establishing proper EcoQOs for any area. As the content of nutrients in a water mass is strongly connected to plankton blooms and the biological development in the water mass, the use of any specific nutrient concentration for determination of the quality status is also time-dependent.

It was strongly advocated not to use simple numbers for the concentration of the various nutrients as indicators for establishing the quality status concerning eutrophication of a specific area. Examples were given of misleading use of simple numbers where, for example, a surface water mass containing 10 µmol NO_3 per litre was classified as being in bad condition in the context of eutrophication, for an area influenced by Atlantic deep water containing 12–14 µmol NO_3 per litre. The importance of establishing regional specific natural background concentrations and the variability associated with these must also be taken into account in design of monitoring programmes. This is influenced by natural inputs, geochemical and oceanographic factors and mixing patterns. These factors are considered in a report from the Marine Institute, Dublin, which was provided to MCWG members by Evin McGovern.

McGovern, E., Monaghan, E., Bloxham, M., Rowe, A., Duffy, C., Quinn, A., McHugh, B., McMahon, T., Smyth, M., Naughton, M., McManus, M. and Nixon, E. 2002. Winter nutrient monitoring of the western Irish Sea – 1990 to 2000. Marine Institute, Dublin, Ireland. ISSN no. 1649-0053, 73 pp.

(This is available for download from: http://www.marine.ie/information+services/library+services/marine+institute+publications/marine+environment+and+health+services/mehs4.pdf)

Attention was also drawn to the more than twenty years of monitoring nutrients in the Kattegat and the difficulties of drawing conclusions concerning nitrogen sources and fluxes from this extensive monitoring.

9 Plenary discussion of subgroup work

This agenda item was redundant as the MCWG met in plenary throughout.

10 Election of MCWG Chair for the period 2004–2006

There were no nominations for the post of MCWG Chair. Robin Law offered to continue for a further year, and the MCWG agreed. The group discussed the difficulty of finding an alternative Chair this year, and also the lack of members in both the Trace Metal and Chemical Oceanography Subgroups in 2001 and 2003.

11 Any other business

11.1 CD-Rom

The Chair asked whether MCWG had found it useful for a CD-ROM to be circulated after the meeting, containing the background papers circulated prior to the meeting, the draft MCWG2003 report as submitted to ICES, and copies of all those presentations made during the meeting using PowerPoint. This was done for the first time following MCWG2002, and many photographs of the MCWG meeting were also included. MCWG members agreed that this was useful, and another will be made this year. All collections of photographs from the meeting which are e-mailed to the Chair prior to production of the CD-ROM will also be incorporated.

11.2 Silver Jubilee

The Chair noted that MCWG2003 was the 25th meeting of the MCWG, and that 2004 will represent the Silver Jubilee of the group – 25 years after the initial meeting in Lisbon in 1979 under the leadership of Margarida de Barros. Members should find for themselves and solicit from their colleagues any available photographs and other reminiscences of early meetings. The Chair will also contact past Chairs and prominent members for their insights and recollections.

11.3 CREAM programme

Britta Pedersen informed MCWG about a new project, CREAM, presently running at NERI. CREAM, the Center for Research and Monitoring in the Marine Environment, is a Marie Curie training site hosted by the National Environmental Research Institute (NERI) in Denmark and funded by the European Commission. PhD students enrolled in member states including the Baltic states are invited to apply for fellowships of 3–12 months at the CREAM training site to conduct research as a part of their PhD studies.

For more information concerning, e.g., the training, projects, supervisers and finance see the web site of NERI (www.dmu.dk) and search for CREAM.

11.4 Chemical data

Lars Føyn reminded the MCWG that chemical data provided through monitoring and research were highly appreciated and used by other groups of ICES. He felt it therefore important for MCWG members to attend working groups and other ICES fora where chemical data are interpreted. Particularly important is the meeting of the parent committee for MCWG, the Marine Habitat Committee, MHC, at the ICES Annual Science Conference, ASC. To be able to have a proper discussion on the implementation of the results from MCWG it is important that MCWG members attend the ASC and participate in MHC. It was, however, noted that in most institutes the participation for chemists at the ASC was not given the necessary priority.

In the context of the use of chemical data, Lars Føyn drew the MCWG members' attention to the ecosystem approach to management that is to be implemented with ICES' provision of advice. The basis for this approach will be worked out on a regional scale, and as a beginning ICES has established a new study group on the ecosystems of the North Sea. This group, the ICES Regional Ecosystem Study Group for the North Sea, REGNS, will meet in Nantes from 4–7 April 2003 under the Chairmanship of Andrew Kenny from CEFAS, UK.

One of the ToRs for REGNS is of particular interest for the members of the MCWG and that is item c), as follows:

"in joint session with PGNSP [ICES-EuroGOOS Planning Group on the North Sea Pilot Project (NORSEPP)], consider the role of ICES in improving the coordination, harmonisation and efficiency of current national and international monitoring to serve the assessment processes;"

A major part of national and international monitoring is the monitoring of chemical components from nutrients to contaminants. Therefore, participation in REGNS of the chemists who have produced monitoring data in the marine environment will be of great value for the implementation of such data in the assessment processes.

11.5 Preferred matrices for WFD priority compound monitoring

Following the plenary lecture on the work of the AMPS group reported at Section 7.1, above, MCWG discussed possible future collaboration between the two groups. Following MCWG2002, Robin Law had made contact with the Chair of the AMPS group, Georg Hanke, and had attended their second meeting in Ispra, Italy in January 2003. It was agreed that there was expertise on marine monitoring within MCWG which would be of use to AMPS, and links between the two groups are being maintained by Robin Law and Peter Lepom, who is also a member of AMPS. The MCWG discussed the preparation of a table outlining which of the WFD compounds are best determined in the dissolved phase. This table is attached as Annex 6, and the information will be sent to the AMPS Chair in advance of their third meeting, to be held during April 2003. QUASIMEME will provide AMPS with a key overview summarising what they can offer in ensuring QA within the WFD monitoring programme. It was also suggested that the Chair make contact with the Steering Group on Environmental Quality Standards, which is another of the groups working towards WFD implementation.

12 Recommendations and action list

These are appended to the report as Annexes 7 and 8.

13 Date and venue of the next meeting

MCWG discussed the venue and dates of the next meeting. One of the members, Jacek Tronczynski, kindly offered to host the next meeting of the MCWG at IFREMER in Nantes, 15–19 March 2004, subject to confirmation by the host institute. MCWG acknowledged the invitation with appreciation. Another member, Teresa Nunes, made a tentative offer to host MCWG2005 in Vigo, Spain.

14 Closure of the meeting

The members of the MCWG expressed their appreciation to Anne Talvari, and to Pille Unt, who had assisted Anne so effectively in making arrangements for the meeting. The Chair thanked all the participants for all their hard work and support during his third meeting as Chair, and closed the meeting at 16.30 hrs on 6 March 2003.

15 Annexes

Annex 1 List of participants

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Name	Address	Telephone	Telefax	E-mail
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Annex 2 Agenda for the ICES Marine Chemistry Working Group

1 Opening of the meeting

2 Adoption of the Agenda

3 Report of the 90th ICES Statutory Meeting

4 Reports on related activities

  4.1 OSPARCOM and HELCOM
  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 UNEP Global POPs Monitoring Network

5 Report 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 Peter Lepom
  The work of the AMPS group.

  7.2 Ott Roots
  POPs monitoring in the Baltic Sea ecosystem: Estonian data.

  7.3 Jarle Klungsøyr
  Reproductive effects of C_4-C_7 alkylphenols in cod.

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 Review the relevant aspects of the implementation table of the OSPAR Joint Assessment and Monitoring Programme and indicate activities that could be proposed to be carried out by MCWG.

    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.

    8.1.5 Consider and finalise draft guidelines for integrated chemical and biological effects monitoring (with WGBEC and WGMS) and report the outcome.

    8.1.6 Review the new version 3.2 of the Environmental Data Reporting Formats from ICES.

    8.1.7 Links between MCWG and the AMPS group

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

8.2 Trace Metal Subgroup

8.2.1 Advise on the availability of suitable analytical methods to allow the determination of environmental concentrations of the substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome. This should include references to the sources of methods and data. [OSPAR request 2003/1].
8.2.2 Assist the Working Group on Seabird Ecology in commencing the devlopment 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 2003/3.2].
8.2.3 Review information on trace element speciation and its effects on behaviour and toxicity, and report the outcome.
8.2.4 Review new information on the use of membrane systems for sampling and report the outcome.
8.2.5 Review new information on the use of ICP-MS for trace element analysis.

8.3 Organics Subgroup

8.3.1 Advise on the availability of suitable analytical methods to allow the determination of environmental concentrations of the substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome. This should include references to the sources of methods and data. [OSPAR request 2003/1].
8.3.2 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 2003/3.2].
8.3.3 Review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish, and report the outcome.
8.3.4 Review new information on the analysis of PAH metabolites in bile, critically review the robustness of the methods, and report the outcome.
8.3.5 Review new information on the use of membrane systems for sampling and report the outcome.
8.3.6 Review new information on the monitoring and analysis of toxaphene, and report the outcome.
8.3.7 Review new information concerning polybrominated diphenylethers (PBDEs) and report the outcome.
8.3.8 Consider a new review note on phenylurea herbicides (diuron and isoproturon) and report the outcome.
8.3.9 Review new information concerning the analysis of dioxins and the preparation of reference materials for these compounds (DIFFERENCE project), and report the outcome.

8.4 Chemical Oceanography Subgroup

8.4.1 Data available in the ICES databanks will be used to prepare illustrative data products under the OSPAR common procedure, and this term of reference will assist in defining the data products. This is further consideration of an OSPAR request concerning EcoQOs for eutrophication. The subgroup will consider more appropriate EcoQOs.

9 Plenary discussion of subgroup work

10 Election of MCWG Chair for the period 2004–2006

11 Any other business

12 Recommendations and action list

13 Date and venue of the next meeting

14 Closure of the meeting

Annex 3 Activities under QUASIMEME

SIME 03/
Original: English

English only

OSPAR CONVENTION FOR THE PROTECTION OF THE MARINE ENVIRONMENT OF THE NORTH EAST ATLANTIC

WORKING GROUP ON CONCENTRATIONS, TRENDS AND EFFECTS OF SUBSTANCES IN THE MARINE ENVIRONMENT (SIME)

LONDON (SECRETARIAT): 18–20 MARCH 2003

Quality Assurance of Information in Marine Environmental Monitoring (QUASIMEME)
Summary and Future Work Programme
Presented by the UK[1]

Introduction

QUASIMEME(1992–2003) (Quality Assurance of Information in Marine Environmental Monitoring) has completed 10 years of support for the External Quality Assurance for Marine Institutes for Chemical Measurements.

The project was initiated with EU funding (1992–1996) and continued by subscription of the participating institutes. Participation in the QUASIMEME Laboratory Performance Study Scheme is open to all institutes, worldwide, that make chemical measurements in seawater, sediment and biological materials.

The QUASIMEME scheme is updated annually and made available to all current and former participants and to third parties that have a close interest in the project and its outcome, e.g., OSPAR, HELCOM, MEDPOL and ICES.

Performance Studies

QUASIMEME is more than a proficiency testing scheme. At the heart of the project is an holistic *learn-by-doing* spiral. The routine laboratory performance studies provide the basis of the external quality assurance for institutes that make regular chemical measurements. Most studies have two rounds per annum with a minimum of two test materials containing the analytes at two different concentrations. The output from these studies are reviewed annually by the Scientific Assessment Group which comprises of experts in each of the main areas of the QUASIMEME programme (Table 1). As a result of the review it is possible to identify areas of poor performance which would benefit from a more detailed scrutiny. An improvement programme may be initiated through a workshop run at an institute with sound expertise, and with a series of Development Exercises to provide detailed tuition, information and a series of test materials tailored to the specific needs of the problem.

The content of the current scheme is given in Table 1. Most Laboratory Performance Studies are conducted twice per annum, with a minimum of two test materials per study (Round). Additions to the routine exercises for 2003–2004 are:

- Chlorophyll *a* in seawater (Formerly a development exercise)

Development Exercises

The development exercises for 2003–2004 have a new approach.

- Organotin compounds will have a fresh focus. The regular exercises will also include investigation on the different steps in the analysis to identify the main sources of error. This will be over 2–3 years. There will also be sufficient matrices included for institutes to offer routine external QA to underpin the national and international marine monitoring programmes.

- Shellfish Toxins. QUASIMEME is commencing a development programme to underpin the measurement of shellfish toxins. In the first instance the programme will focus on the measurement of amnesic shellfish poisoning (ASP) toxins and later extend to diarrhetic shellfish poisoning (DSP) toxins and paralytic shellfish poisoning (PSP)

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[1] This report has also been presented to the ICES MCWG, Tallinn, 3 – 7 March 2003.

toxins. This is being done in conjunction with the EU Reference Laboratory in Vigo, Spain, the Marine Institute, Galway Ireland and FRS Marine Laboratory, Aberdeen (UK National Reference Laboratory for Biotoxins).

- Brominated Flame Retardants will continue to be measured in biological tissues and be extended to include sediments.

Assessment

QUASIMEME operates to the ISO Guide 43–1 for proficiency test providers and is currently seeking UKAS accreditation under this standard through the ILAC G13:2000 guidelines.

The assessment of the Laboratory Performance Studies is undertaken using Robust Statistics (ISO 13528) and the Cofino Model Statistics[2]. A similar approach is used for the Development Exercises for the initial assessment. There is also an additional evaluation and recommendation for the stepwise improvement. Most of the advice relating to improvement is made available at the QUASIMEME Workshops which are held regularly for both developing topics and troublesome analyses.

QUASIMEME Workshops held in 2002

BE-1	Imposex and intersex in Marine Snails, May 2002 FRS, Aberdeen, UK.
DE-6	Chlorophyll *a* in seawater, July 2002 MUMM, Oostende, Belgium.
DE-3, 5, 7	Organotin compounds in sediment, water and biota, July 2002, IVM, Free University, Amsterdam, NL.
DE-8	Brominated Flame Retardants, October 2002, CSIC, Barcelona, Spain.

In addition, the QUASIMEME Conference (10th anniversary) was held during October 2002 at the University of Barcelona, Spain.

QUASIMEME Workshops 2003–2004

Organochlorine Pesticide Residues in biota and water (Proposed)

Particulates and Filtration – Metals in water (Proposed)

Shellfish Toxins, Galway, Ireland, June 2004

Imposex and Intersex in Marine Gastropods, The Netherlands, September / October 2003 (Proposed – joint QUASIMEME – RIKZ – OSPAR workshop)

Reports on the QUASIMEME Workshops are prepared on CD and are available to participants through the QUASIMEME Project office.

QUASIMEME continues to provide a comprehensive external QA programme primarily for chemical measurements. Any request for additional determinands and/or matrices may be made, by participants or Agencies and Commissions which are third parties requiring external QA for their national or international monitoring programmes.

QUASIMEME Project Office, FRS Marine Laboratory, PO BOX 101, 375 Victoria Road, Aberdeen AB11 9DB,
United Kingdom,

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[2] *A new model for the interference of population characteristics from experimental data using uncertainties in data. Application to interlaboratory studies.* Wim P. Cofino, Ivo H.M. van Stokkum, David E. Wells, Freek Aries, Jan-Willem M. Wegener, Renée A.L. Peerboom. Chemometrics and Intelligent Laboratory Systems. 53, (2000), 37-55.

(Table 1) Laboratory Performance Study Programme for 2003–2004

Round	**Group Number**	**Number of test materials per exercise**	**Determinand Group**	**Matrix**
AQUEOUS				
34 & 36	AQ-1	2	Nutrients	Seawater
34 & 36	AQ-2	3	Nutrients (low salinity, 2 high & 1 low concentration)	Estuarine and low salinity open water
35 & 37	AQ-3	3	Metals, other than Hg (includes 1 low salinity test material)	Seawater
35 & 37	AQ-4	2	Mercury	Seawater
35 & 37	AQ-5	3	Chlorinated organics (includes 1 low salinity test material)	Seawater
35 & 37	AQ-6	2	Volatile organochlorines	Seawater
35 & 37	AQ-7	2	Pentachlorophenol	Seawater
35 & 37	AQ-8	3	Triazines & organophosphorus organics (includes 1 low salinity test material)	Seawater
SEDIMENTS				
34 & 36	MS-1	2	Trace metals	Silty sediment
34 & 36	MS-2	2	Chlorinated organics	Silty sediment
34 & 36	MS-3	2	PAHs	Silty sediment
BIOTA - Stabilised wet biological tissue				
34 & 36	BT-1	2	Trace metals	Fish & shellfish
34 & 36	BT-2	2	Chlorinated organics	Fish & shellfish
36	BT-3	2	Non *ortho* CBs, PCDDs and PCDFs	Fish & shellfish
34	BT-4	2	PAHs	Shellfish
36	BT-5	3	Chlorobornanes (toxaphene)	Wet tissues & fish oil
36	BT-6	2	Trace metals	Fucus
37	BT-7	2	Chlorophyll *a*	Filtered test materials
37	BE-1	2 species	Imposex in marine snails	Marine snails
DEVELOPMENT EXERCISES				
37	DE-3	3	Organotins in biota	Solution & shellfish
37	DE-5	3	Organotins in seawater	Solution & seawater
37	DE-7	3	Organotins in sediment	Solution & sediment
37	DE-8	3	Brominated flame retardants	Solution & biota
37	DE-9	2	Shellfish toxins	Solution & biota

Annex I
QUASIMEME – RIKZ - OSPAR Workshop on Intersex / Imposex

From:	Schipper, C.A. (OSC)[SMTP:C.A.Schipper@rikz.rws.minvenw.nl]
Sent:	26 February 2003 14:50
To:	'quasimeme@marlab.ac.uk'
Subject:	EM6216 OSPAR-SIME intersex and imposex Workshop

Dear,
The Netherlands have functioned in recent years in OSPAR-SIME as lead country for organotins. The Netherlands were asked to coordinate the assessment criteria for *Littorina littorea, Nucella lapilus, Buccinum* and *Hinia.* At the last QUASIMEME intersex/imposex workshop in Aberdeen (May 2002) already an interlaboratory comparison test and a teaching project were organized. Since OSPAR-SIME mandatory monitoring of TBT biological effects intersex/imposex starts in 2003, The Netherlands will ask QUASIMEME the possibilities to organize in September/October 2003 in cooperation with RIKZ an international Intersex/imposex workshop.

Topics could be to share knowledge of **assessment criteria** for several gastropod species, QA/WC, SOPs, results of pilot intersex/ imposex surveys, interlaboratory comparison, etc.

Please soon a reaction at my question, due to the OSPAR-SIME London meeting.

Cor Schipper

Projectmanager Specie*Bio
National Institute for Coastal and Marine Management/RIKZ

28 February 2003

Dear Cor,

QUASIMEME – RIKZ - OSPAR Workshop on Intersex / Imposex

In principle, QUASIMEME can organise a workshop on intersex and imposex in co-operation with RIKZ to underpin the QA requirements for OSPAR – SIME monitoring of TBT biological effects. The details of the workshop can be planned during May 2003 with regard to the content and timetable.
I will also confirm with the UK delegation that this joint proposal is tabled at SIME 2003.

With kind regards

David Wells

David E Wells
QUASIMEME Project Manager

Annex 4 Analysis of chemicals on the OSPAR List of Chemicals for Priority Action

Preliminary response to the potential OSPAR request for views on the possibility to analyse the substances on the OSPAR List of Chemicals for Priority Action, and whether there are levels of these substances reported from the marine environment.

Chemical (CAS number and/or name)	**Analysis**[a]	**Presence**[b]	**Comment**
85–22–3 Benzene, pentabromoethyl	1	−	
36065–30–2 Benzene, 1,3,5-tribromo-2-(2,3-dibromo-2-methylpropoxy)	1	−	
732–26–3 2,4,6-tri-*tert*-butylphenol (phenol, 2,4,6-tris(1,1-dimethylethyl))	1	−	Blank problems
98–51–1 4-*tert*-butyltoluene (benzene, 1-(1,1-dimethylethyl)-4-methyl-))	1	−	
Brominated flame retardants	3	+	For penta-mix BDE congeners
	1	+	For octa-mix BDE congeners
	1	+	For BDE209
	1	+	For HBCD and polybrominated biphenyls (PBBs)
77–47–4 1,3-cyclopentadiene, 1,2,3,4,5,5-hexachloro-	2	+	
Certain phthalates (dibutylphthalate and diethylhexylphthalate**)**	2	+	Blank problems
115–32–2 Dicofol (benzenemethanol, 4-chloro-α-(4-chlorophenyl)- α-(trichloromethyl)-)	2	+	
115–29–7 Endosulphan (6,9-methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-,3-oxide)	2	+	
2104–64–5 EPN (phosphonothioic acid, phenyl-, O-ethyl O-(4-nitrophenyl) ester)	0	−	
70124–77–5 Flucythrinate (benzene acetic acid, 4-(difluoromethoxy)- α-(1-methylethyl)-, cyano(3-phenoxyphenyl)methyl ester)	0	−	
28680–45–7 and 2440-02-0 Heptachloronorbornene (bicyclo[2.2.1]hept-2-ene, heptachloro-)	3	+	For some congeners (P26, P50, P62)
	1	+	For other toxaphene congeners
Hexachlorocyclohexane **(**HCH) isomers	3	+	For α-, β- and γ-isomers
107–46–0 HMDS (disiloxane, hexamethyl-)	1	−	
465–73–6 Isodrin (1,4:5,8-dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-, (1.α.,4.α.,4a. β.,5. β.,8. β.,8a. β.)-)	2	−	Environmental levels very low
Organic lead compounds	2	+	For tetra-alkyl lead
Organic mercury compounds	2	+	
72–43–5 Methoxychlor (benzene,1,1'-(2,2,2-trichloroethylidene)bis(4-methoxy)	3	+	
Musk xylene	2	+	
Chlorinated naphthalenes	2	+	Individual isomers should be determined

Chemical (CAS number and/or name)	Analysis[a]	Presence[b]	Comment
51000–52–3 Neodecanoic acid, ethenyl ester	0	−	
Nonylphenol/ethoxylates (NP/NPEs) and related substances	2	+	
140–66–9 Octylphenol (phenol, 4-(1,1,3,3,tetramethylbutyl)-)	2	+	
Organic tin compounds	3	+	For trialkyl- and triphenyltin
1825–21–4 Pentachloroanisole	2	+	
Pentachlorophenol (PCP)	3	+	
603–35–0 Phosphine, triphenyl-	0	−	
Polycyclic aromatic hydrocarbons (PAHs)	3	+	
Polychlorinated biphenyls (PCBs)	3	+	
Polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs)	3	+	
Short-chained chlorinated paraffins (SCCP)	1	+	
79–94–7 TBBA (phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo]-)	1	+	
2227–13–6 Tetrasul (benzene, 1,2,4-trichloro-5-[(4-chlorophenyl)thio]-)	2	+	
87–61–6 Trichlorobenzene (benzene, 1,2,3-trichloro-)	2	+	
120–82–1 1,2,4-trichlorobenzene (benzene, 1,2,4-trichloro-)	2	+	
108–70–3 1,3,5-trichlorobenzene (benzene, 1,3,5-trichloro-)	2	+	
55525–54–7 Urea, N,N'-bis[(5-isocyanato-1,3,3-trimethylcyclohexyl)methyl]-	0	−	
Cadmium	3	+	
Lead	3	+	
Mercury	3	+	
Organic mercury compounds	2–3	+	
Organic tin compounds	2–3	+	

[a] MCWG believes that (3) there are good validated methods available; (2) there are methods described in the literature; (1) it is possible for some laboratories to analyse the compound; or (0) no methods are known to the group.

[b] MCWG knows that there are environmental levels reported (+), or MCWG members do not have knowledge of any environmental data (−).

Recent references relating to the analysis and environmental distribution of the brominated diphenylethers

de Boer, J., Allchin, C., Law, R., Zegers, B., and Boon, J.P. 2001. Method for the analysis of polybrominated diphenylethers in sediments and biota. Trends in Analytical Chemistry, 20: 591–599.

Law, R.J., Allchin, C.R., Bennett, M.E., Morris, S., and Rogan, E. 2002. Polybrominated diphenyl ethers in two species of marine top predators from England and Wales. Chemosphere, 46: 673–681.

Boon, J.P., Lewis, W.E., Tjoen-A-Choy, M.R., Allchin, C.R., Law, R.J., de Boer, J., ten Hallers-Tjabbes, C.C., and Zegers, B.N. 2002. Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. Environmental Science and Technology, 36: 4025–4032.

Additional papers are in press, for both Dioxin 2003 and the special issue of Environment International on Brominated Flame Retardants, due to be published in June 2003.

Some additional useful references include:

de Boer, J., and Law, R.J. 2003. Developments in the use of chromatographic techniques in marine laboratories for the determination of halogenated contaminants and polycyclic aromatic hydrocarbons. Journal of Chromatography A, 1000. In press.

Clark, J.R., Goodman, L.R., Borthwick, P.W., Patrick J.M. jr., Cripe, G.M., Moody, P.M., Moore, J.C., and Lores, E.M. 1989. Toxicity of pyrethroids to marine invertebrates and fish: a literature review and test results with sediment-sorbed chemicals. Environmental Toxicology and Chemistry, 8: 393–401.

Muir, D.C.G., and Norstrom, R.J. 2000. Geographical differences and time trends of persistent organic pollutants in the Arctic. Toxicology Letters, 112–113: 93–101.

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

Staples, C.A., Parkerton, T.F., and Peterson, D.R. 2000. A risk assessment of selected phthalate esters in North American and Western European surface waters. Chemosphere, 40: 885–891.

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Butyltin methodology
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Mercury
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Annex 5 Review Note on Phenylurea Herbicides in the Marine Environment

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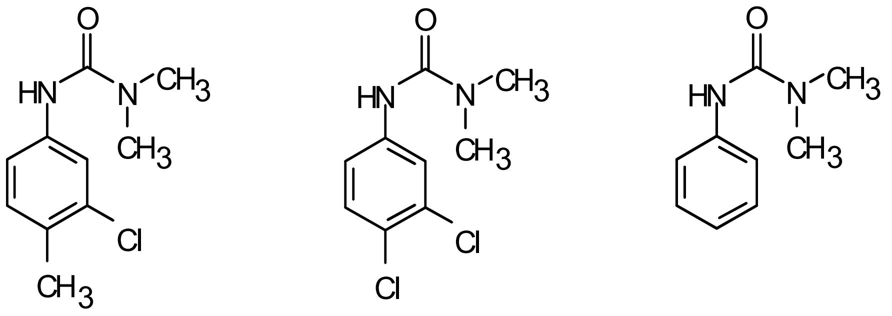
Abstract

The occurrence of phenylurea herbicides in the North Sea and Baltic Sea is described. In addition, the concentrations observed in the river Elbe, the major input source for the German Bight, are presented. It is shown that especially the compounds Diuron and Isoproturon can be detected in the whole area under investigation. As a generally applicable analytical procedure for the determination of phenylurea herbicides in water, a method is described that is based on a solid phase extraction (SPE) and a HPLC-MS-MS quantification method. This procedure is sensitive and selective enough to determine the low concentrations found in the open sea (down to 0.1 ng l^{-1}).

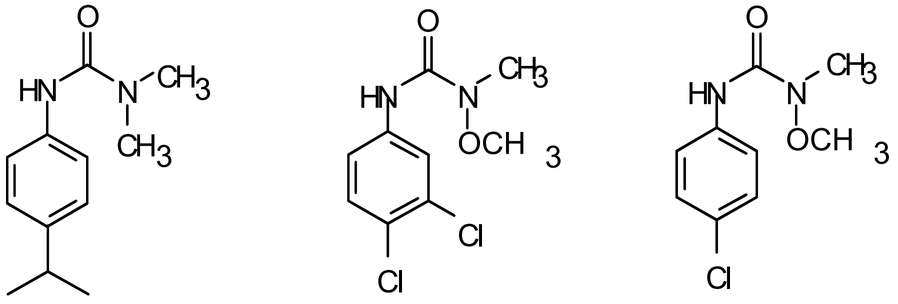
1 Introduction

Phenylurea herbicides are an important class of modern herbicides that are produced and used in Europe in large quantities. Due to the large quantities used and the fact that some of these compounds exhibit quite a slow degradation rate in the environment, they deserve special attention in environmental monitoring. Diuron and Isoproturon are therefore on lists of possible priority pollutants (EU, OSPAR). Because of their good water solubility and their persistence, they can reach the marine environment.

In this review, the following compounds are dealt with: Diuron, Isoproturon, Chlortoluron, Fenuron, Linuron, and Monolinuron. The chemical structures are depicted in Figure. 1; some relevant properties are listed in Table 1.



Chlortoluron **Diuron** **Fenuron**



Isoproturon **Linuron** **Monolinuron**

Figure 1. Chemical structures of the phenylurea herbicides under investigation.

Table 1. Properties of phenylurea herbicides.

Compound	Log P_{OW}	Degradation in water (half-life)	Degradation in soil (half-life)
Chlortoluron	2.41		
Diuron	2.82	stable	3 to 5 m
Fenuron	0.96		
Isoproturon	2.5	stable	6–23 d
Linuron	2.76		
Monolinuron	2.3		

Table 2 summarises some production and application amounts.

Table 2.

Compound	Production in EU [t yr^{-1}]	Use in Germany [t yr^{-1}]
Chlortoluron		
Diuron	3,000–15,000	200–500
Fenuron		
Isoproturon	10,000–50,000	> 1000
Linuron		
Monolinuron		

Because of their herbicidal properties, the phenylureas exhit high toxicities especially against algae and water plants. Therefore, in Table 3 these toxicities are listed. Diuron and Isoproturon were shown to be toxic for fishes and small crustaceans also.

Table 3. Toxicity data on phenylurea herbicides.

Compound	NOEC -Algae (µg l^{-1})	LC50 fish	EC50 invertebrate
Chlortoluron		30–50 mg l^{-1}	
Diuron	0.46	5–25 mg l^{-1}	1–12 mg l^{-1}
Fenuron			
Isoproturon	2	30–100 mg l^{-1}	507 mg l^{-1}
Linuron		3	120 µg l^{-1}
Monolinuron		56–74 mg l^{-1}	32 mg l^{-1}

2 Analysis of phenylurea herbicides

Because of their good water solubility and their polarity (low log P_{OW} values < 3), the water phase is the preferred monitoring matrix. Extraction from water samples is preferably done by solid phase extraction (SPE). Not all phenylurea herbicides can be analysed by GC-MS. Therefore, HPLC is used as a more general analysis technique. As UV-detection is not very sensitive and selective, MS or MS-MS detection is the preferred technique.

Water samples are sampled in 10 l glass bowls. The water is acidified with 10 ml of hydrochloric acid (25 %) to a pH of 2 to 3, and a solution of deuterated internal standards (d_6-Diuron) is added. 6 l of this sample are pumped in batches of 2 l over 3 separate cartridges each filled with 600 mg of Chromabond HR-P resin (Macherey-Nagel, Düren, Germany). After washing with pure, deionised water and drying in a stream of nitrogen, the cartridges are eluted with 10 ml dichloromethane and 10 ml acetone each.

After concentrating the combined extracts to 75 µl, the sample solution is mixed with 50 µl of water. 20 µl of this solution is injected into the HPLC-MS-MS system (Agilent 1100 Series autosampler, binary pump, column oven 23 °C and Applied Biosystems API 2000 LC-MS-MS system, ESI source). A phenyl phase column (Synergi Polar-RP, Phenomenex) is used (2 mm, 7.5 cm) with a flow rate of 200 to 250 µl min^{-1}. Eluent A consists of water with 10 mM ammonium acetate and 10 mM acetic acid, pH 4.5, eluent B is Methanol with the same concentrations of buffering compounds. The following gradient is used:

0 min, 80 % A, 200 µl min^{-1}
12 min, 50 % A, 250 µl min^{-1}
25 min, 30 % A, 250 µl min^{-1}
36 min, 5 % A, 250 µl min^{-1}
45 min, 5 % A, 250 µl min^{-1}

The mass spectrometric parameters, the overall recoveries, and limits of determination are summarised in Table 4.

Table 4. Analytical parameters.

Compound	**MS-MS Transitions**	**Overall Recovery %**	**Limit of determination (ng l^{-1})**
Chlortoluron	212.9 / 72.1	80	0.35
Diuron	232.9 / 72.1	90	0.10
Fenuron	165.0 / 72.0	75	0.06
Isoproturon	207.0 / 72.1	90	0.04
Linuron	249.0 / 160.2	90	0.14
Monolinuron	215.0 / 126.1	90	0.08

The procedure was validated and controlled by internal and external QA procedures. Internal QA covers determination of procedural blanks (smaller than LOD), recoveries by standard addition (75 to 90 %), tests for calibration linearity and determination of the detection limit (s/n 10). External QA was proven by participation in two QUASIMEME ring tests; all Z scores were < 2.

3 Results

The data presented here were obtained within the German monitoring programme and cover the years 2000 to 2002. Table 5 summarises the overall data, covering data from the river Elbe, German Bight, North Sea and Baltic Sea. As expected, the maximum values are observed in the river Elbe. The two most important compounds are Diuron and Isoproturon followed by Chlortoluron, Linuron and Fenuron. Monolinuron is found in the Elbe only.

Table 5. Overview of the concentrations observed (ng l^{-1}).

	Area	Count	Average	Median	Minimum	Maximum
Chlortoluron						
	Elbe	17	4.20	3.85	2.03	7.58
	North Sea	52	1.32	1.34	< 0,35	3.20
	Baltic Sea	8	0.30	0.22	0.15	0.77
Diuron						
	Elbe	25	22.19	13.56	7.74	124.16
	North Sea	89	3.63	3.70	0.10	14.32
	Baltic Sea	18	3.04	0.97	0.42	13.34
Fenuron						
	Elbe	16	2.88	2.62	1.39	5.39
	North Sea	28	0.18	0.17	<0,06	0.46
	Baltic Sea	1	0.39	0.39	0.39	0.39
Isoproturon						
	Elbe	25	11.46	6.92	2.67	36.90
	North Sea	86	2.33	2.14	0.05	8.28
	Baltic Sea	18	0.61	0.43	0.20	2.49
Linuron						
	Elbe	19	1.44	1.07	0.13	3.67
	North Sea	7	0.23	0.21	<0,14	0.54
Monolinuron						
	Elbe	5	0.36	0.30	0.13	0.87

The spatial distribution of the different compounds is quite similar and parallels in coastal areas the freshwater content of the sea water. As Figure 2 indicates there are differences concerning the steepness of the gradient, possibly indicating differences in the degradation. Chlortoluron, Diuron and Isoproturon seem to be more stable because of the less steep gradient. However, data are not strong enough for a clear statement.

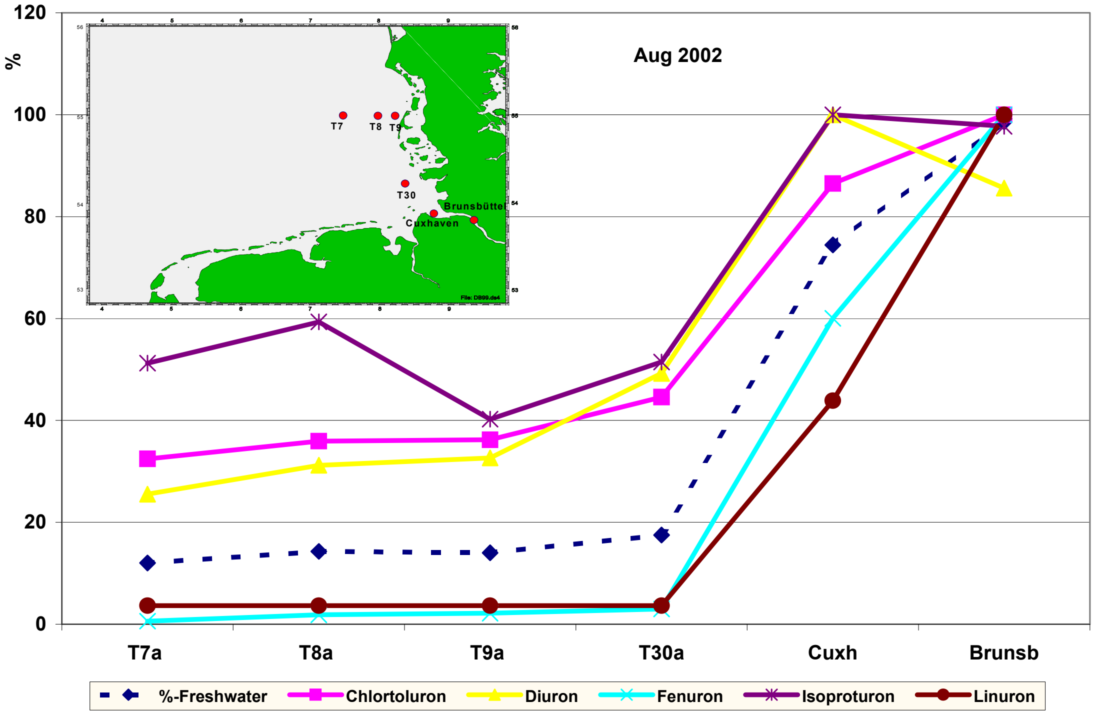


Figure 2. Spatial concentration gradients of herbicides in the Elbe plume (% of the maximum concentration in the Elbe).

The geographical distributions of Diuron and Isoproturon in the North Sea are shown in Figures 3 and 4. Both compounds are found in relatively high concentrations in coastal areas, especially at the estuaries of the big rivers Elbe and Rhine (Diuron 1–10 ng l^{-1}, Isoproturon 1–5 ng l^{-1}). In the central North Sea or the Atlantic (Bay of Biscay), concentrations are very low (Isoproturon 0.05 ng l^{-1}, Diuron 0.2 ng l^{-1}).

In deep water (500 m) samples of the Atlantic and Skagerrak, significantly lower values are observed compared to surface water samples.

Diuron has been analysed in the marine environment in the past 5 years in several studies in connection with its use as a booster biocide in antifouling paints for small ships (References 1 to 9). Most studies were performed in marinas of the UK and Spanish coasts, where concentrations ranged from 3 to 2000 ng l^{-1}. In summer generally higher values are observed than in winter, due to a higher ship density. In the Ebro delta, concentrations of < 10 to 117 ng $l^{-1}$are reported (Ferrer, 1999). Concentrations in the open sea have not been determined as yet.

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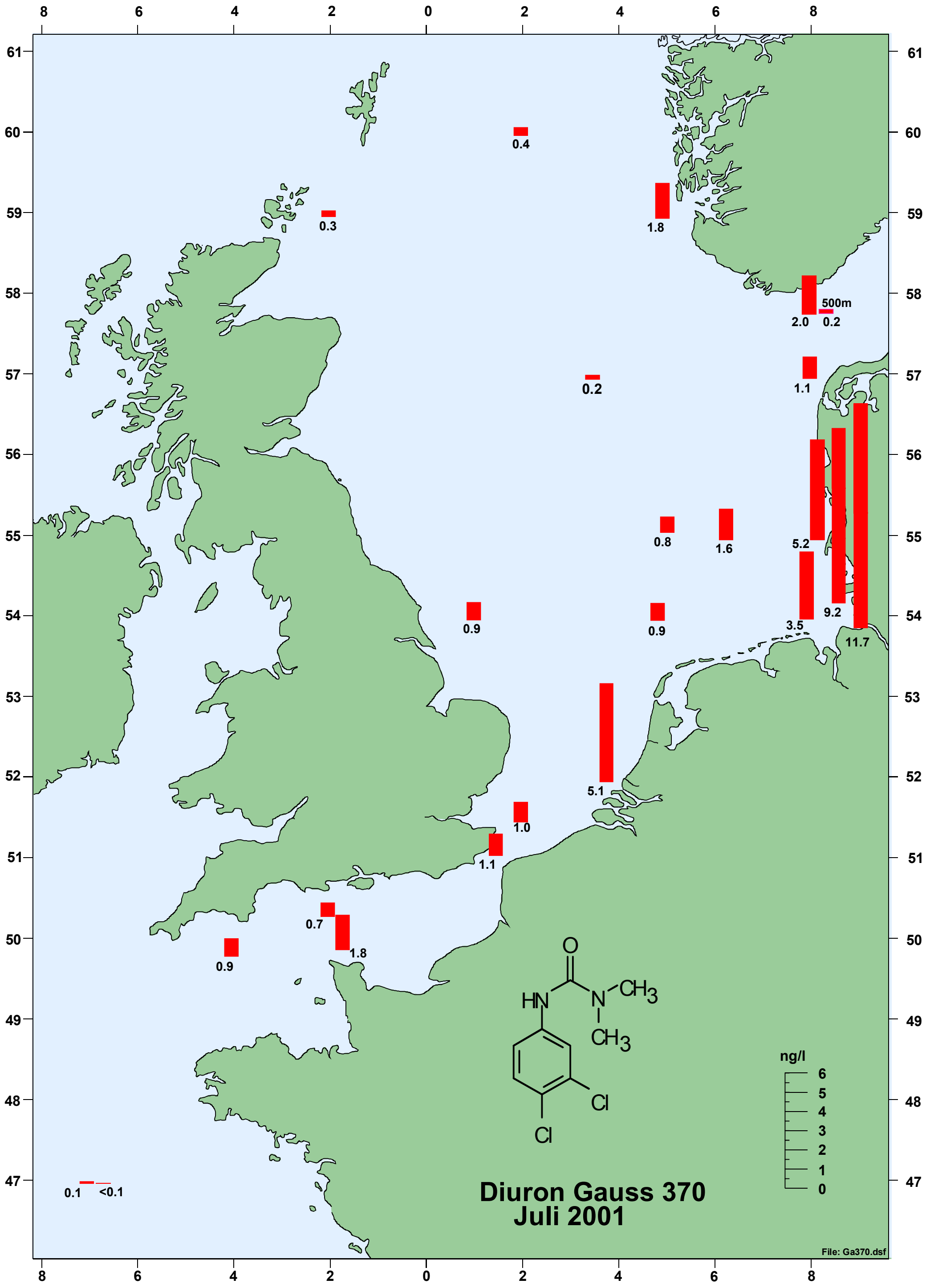

Figure 3. Concentrations of Diuron in the North Sea in July 2001 (unless other stated surface water (5 m)).

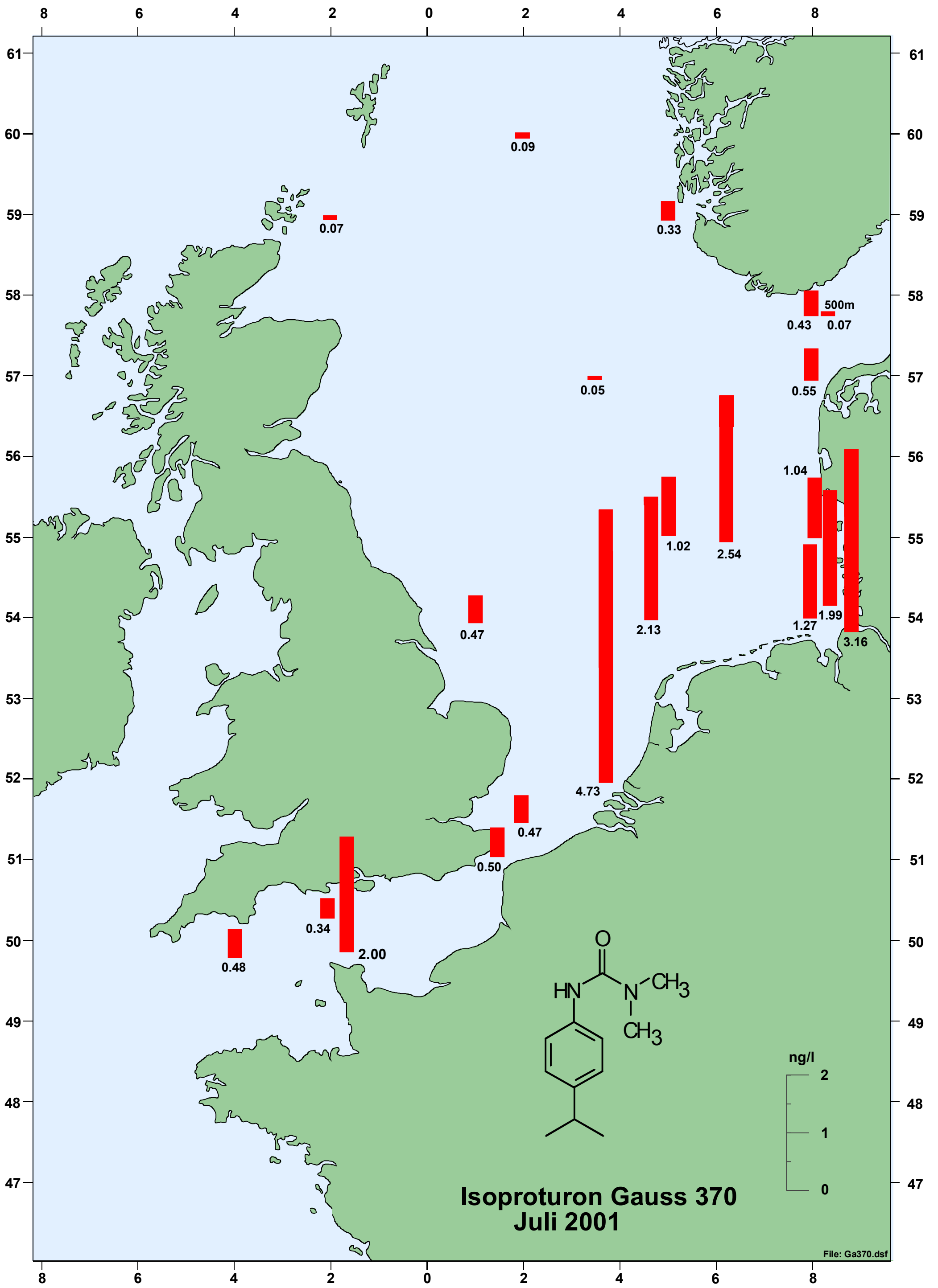

Figure 4. Concentrations of Isoproturon in the North Sea in July 2001 (unless other stated surface water (5 m)).

In the Baltic Sea (Figures 5 and 6), concentrations are in a similar range as in the North Sea. Concentrations in the Baltic do not reach the low values observed in the open North Sea or Atlantic; this can be explained by the more enclosed sea area of the Baltic Sea. In coastal areas there seem to be regional differences between Isoptroturon and Diuron. While Isoproturon shows the highest values (up to 2.5 ng l^{-1}) in the mouth of the river Odra indicating this as an input source, Diuron is found in the highest concentrations in the western part of the Baltic, in the Kiel and Flensburg bights. Whether these elevated concentrations are caused from its possible use as an antifouling agent in pleasure boats can be speculated but was not proved by measurements.

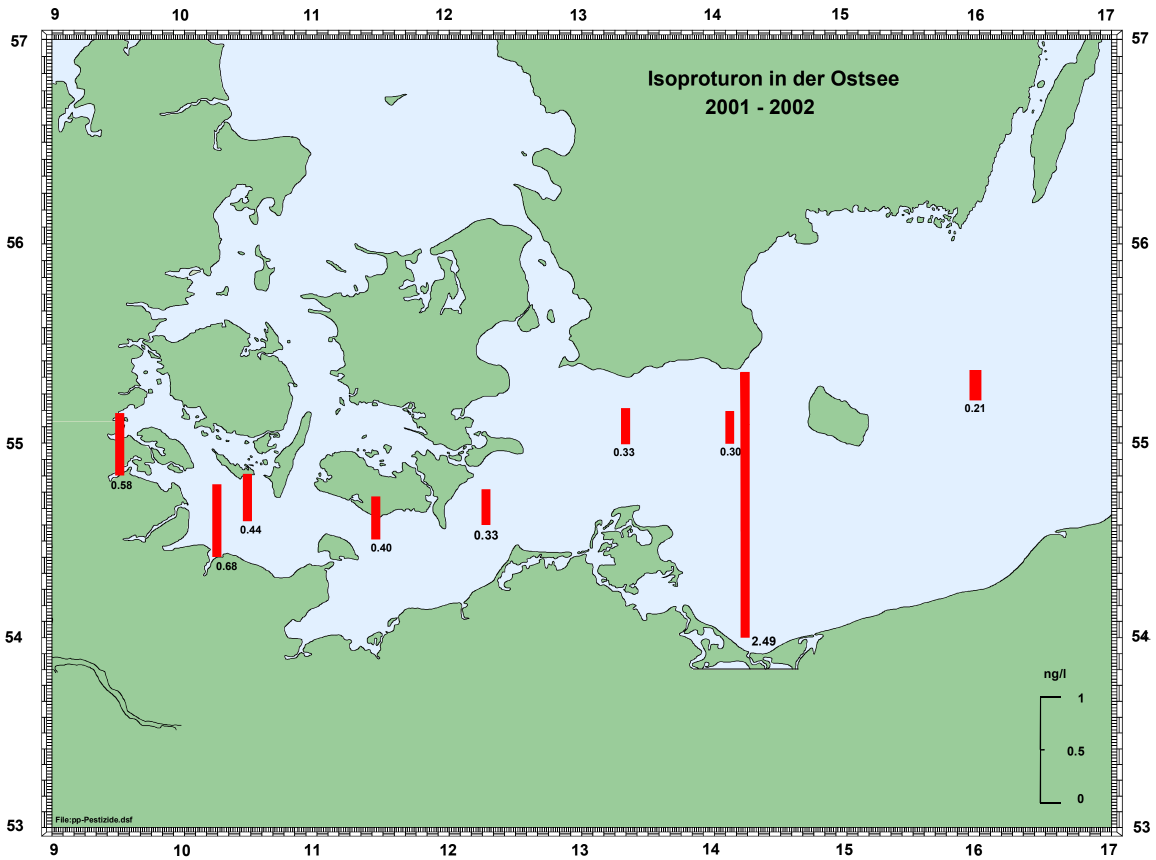

Figure 5. Concentrations of Isoproturon (ng l^{-1}) in the Baltic Sea - average values of Aug. 2001 and 2002 (5 m).

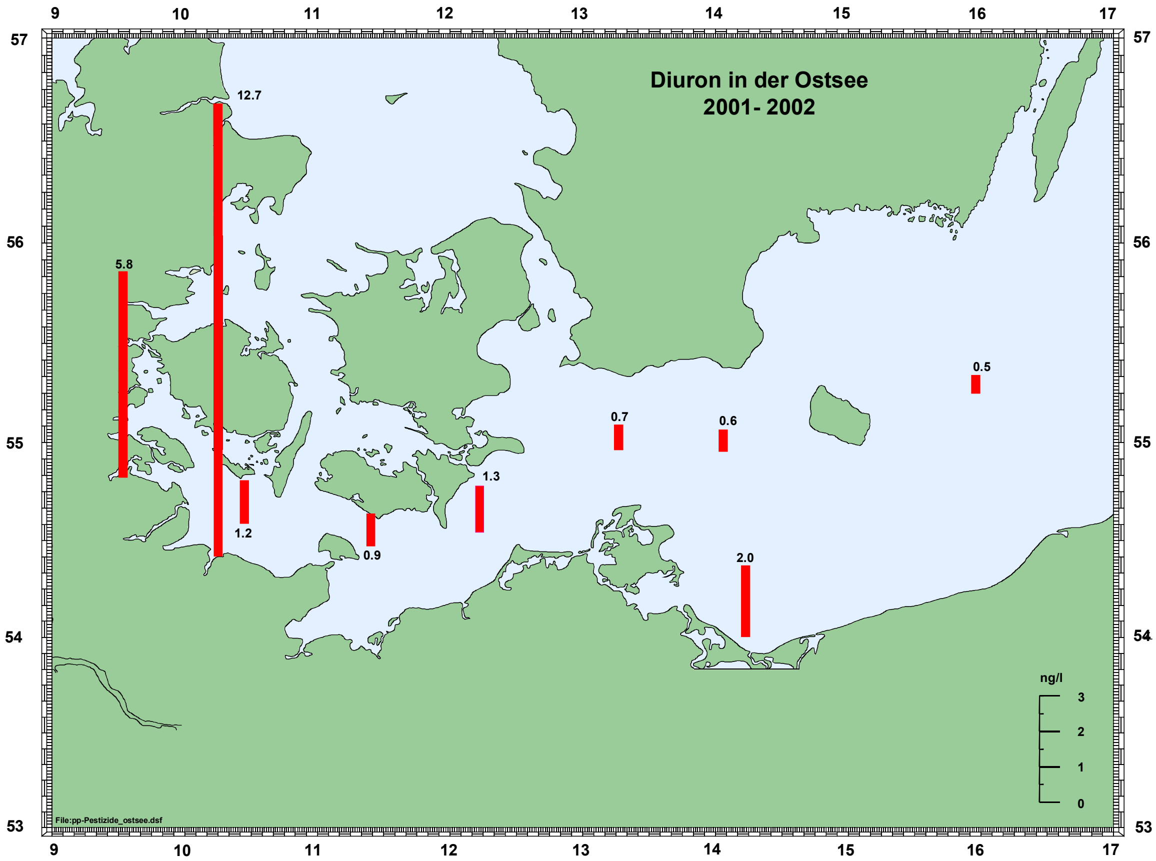

Figure 6. Concentrations of Diuron (ng l^{-1}) in the Baltic Sea - average values of Aug. 2001 and 2002 (5 m).

The time course in the German Bight over the years 2000 to 2002 for Diuron and Isoproturon is shown in Figure 7 and Figure 8. The values show quite a high variability and the time series are too short to observe any statistically relevant trend. The same is true for seasonal fluctuations within a year.

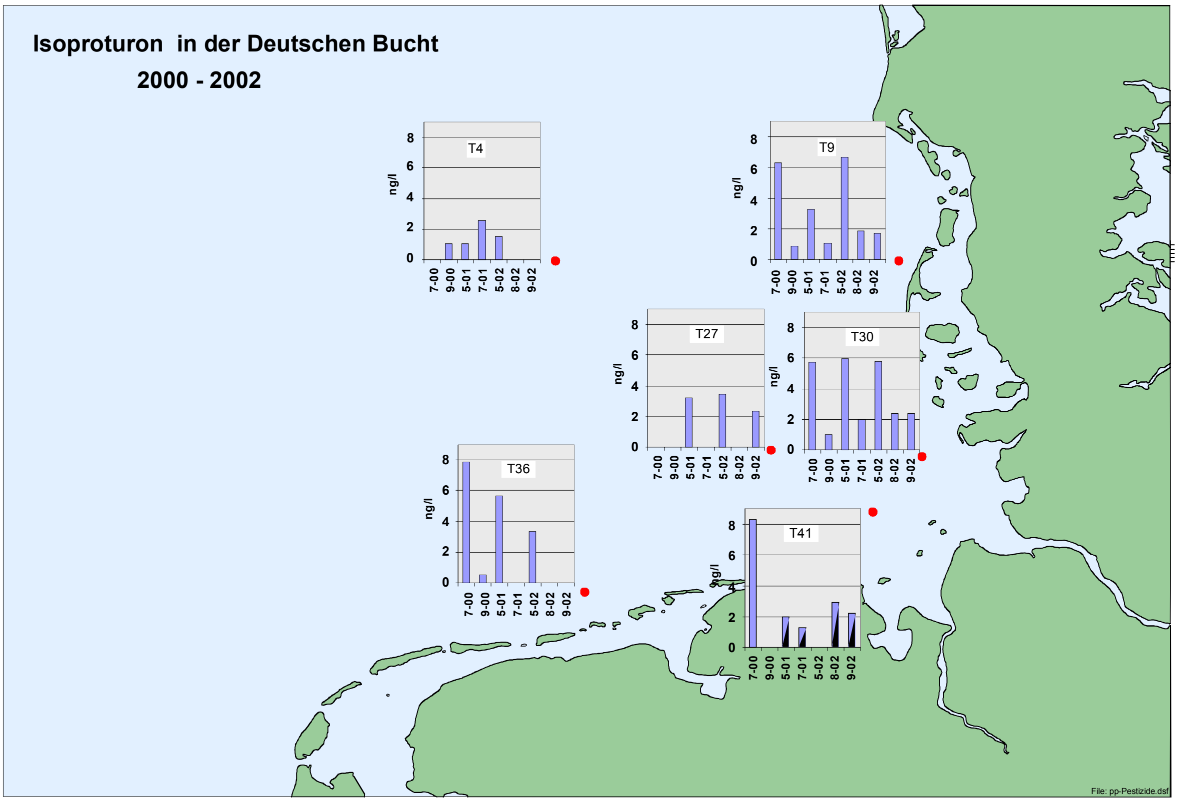

Figure 7. Concentrations of Isoproturon in the German Bight in 2000 to 2002 (surface water (5 m)).

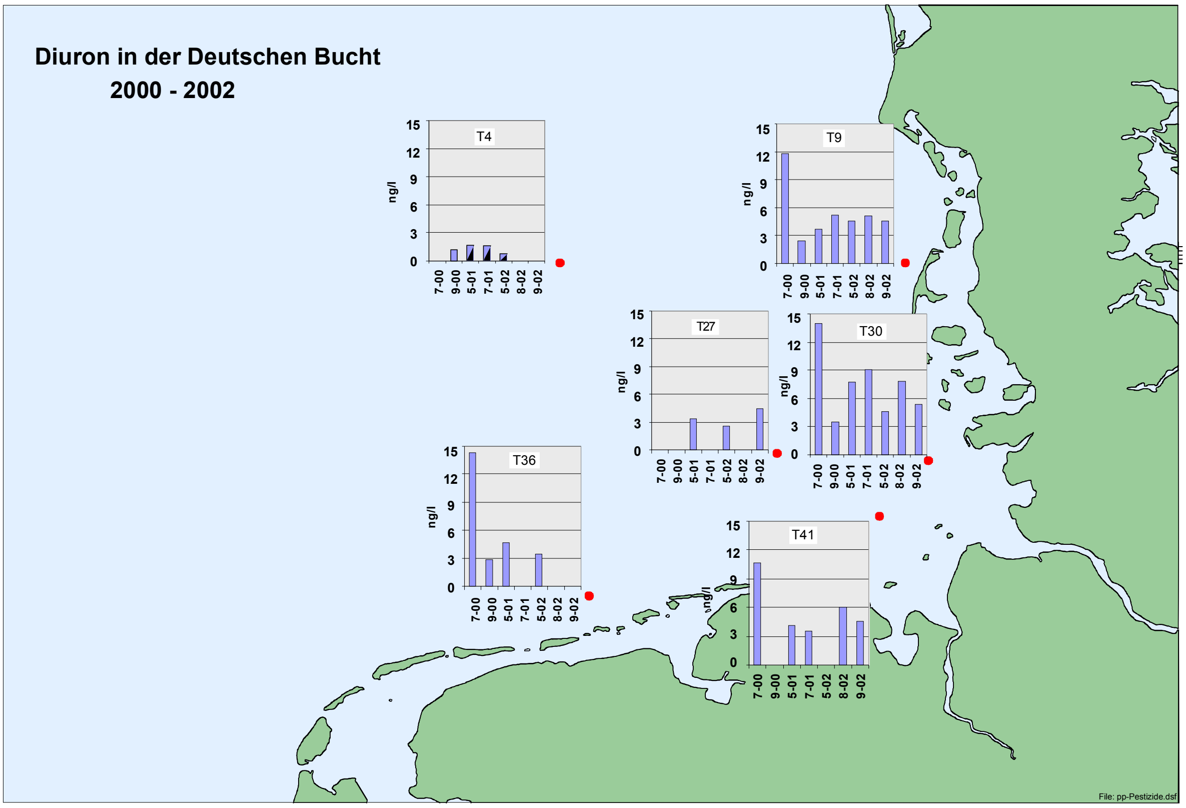

Figure 8. Concentrations of Diuron in the German Bight in 2000 to 2002 (surface water (5 m)).

The phenylurea herbicides have been determined in many land-based monitoring programmes and positive findings were reported both for surface water and groundwater. Unfortunately, in many reports only information on positive findings (< LOD), samples above a limit of 0.1 µg l^{-1} and maximum values are reported.

In the river Rhine, Chlortoluron, Linuron, Diuron and Isoproturon have been monitored; in 2000 they all showed average values of less than 50 ng l^{-1} (LOD). For Diuron a maximum of 70 ng l^{-1}, and for Chlortoluron and Isoproturon maxima of 120 ng l^{-1} were observed (Anon. 2002).

4 Conclusion

Several phenylurea herbicides have been detected in the marine environment. Especially Diuron and Isoproturon are found in sea water of the North Sea and Baltic Sea at concentrations which are higher than those of "classical" contaminants like HCH isomers. Compared to lipophilic pollutants like PCB or PAH they even show 10 to 100 times higher values. As Diuron and Isoproturon are often found in surface water and are considered as priority pollutants in the EU Water Framework Directive they should be determined in future marine monitoring surveys. For Diuron there is, in addition to land-based sources, a "marine" source possibly because of its use as an antifouling paint constituent.

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Annex 6 Preferred matrix for monitoring priority compounds under the Water Framework Directive.

Priority substance	**Is water the preferred matrix ?**
Alachlor	Yes
Anthracene	No
Atrazine	Yes
Benzene	Yes
Brominated diphenylethers	No
Cadmium and its compounds	No
C_{10}-C_{13} chloroalkanes	No
Chlorfenvinphos	Yes
1,2-Dichloroethane	Yes
Di(2-ethylhexyl)phthalate	No
Diuron	Yes
Endosulphan & alpha-endosulphan	Yes
Hexachlorobenzene	No
Hexachlorobutadiene	No
Hexachlorocyclohexane & lindane	Yes
Isoproturon	Yes
Lead and its compounds	No
Mercury and its compounds	No
Naphthalene	No
Nickel and its compounds	No
Nonylphenols & 4-nonylphenol	No
Octylphenols & *p*-*tert*-octylphenol	No
Pentachlorobenzene	No
Pentachlorophenol	Yes
Polycyclic aromatic hydrocarbons	No (considered individually, as a group)
Benzo[*a*]pyrene	No
Benzo[*b*]fluoranthene	No
Benzo[*k*]fluoranthene	No
Benzo[*ghi*]perylene	No
Fluoranthene	No
Indeno[1,2,3-*cd*]pyrene	No
Simazine	Yes
Tributyltin compounds and cation	No
Trichlorobenzenes (& 1,2,4-TCB)	Yes
Trichloromethane	Yes
Trifluralin	Yes

The water matrix referred to is the dissolved phase. If the answer above is “no”, then other matrices should be considered (sediment, SPM, biota). These decisions should take account of the characteristics of the area to be monitored, as well as the aims of the monitoring programme. For instance, SPM concentrations may be very low in some areas due to geological variations, and some biota may rapidly biotransform the chemicals of interest so that their determination in tissues is not possible. In many cases this may mean that sessile bivalve molluscs are preferred as sentinel species over fish.

Annex 7 Action list

David Wells: to update MCWG on developments within the QUASIMEME LPS programme.

Jacek Tronczynski: to enquire within IFREMER about the possibility of MeHg analysis to set assigned values in QUASIMEME test materials.

Robin Law, Jacob de Boer, Bo Jansson: to provide MCWG with an update of the UNEP Global POPs Monitoring Network.

Jarle Klungsøyr: to report to MCWG the results of further studies on the effects of alkylphenols from produced water.

Marc Raemakers and Patrick Roose: to present at MCWG2004 information on the integrated Belgian chemical and biological effects programme. Michel Lebeuf to present information on the Canadian programme. Robin Law to present information regarding the UK programme. Ton van der Zande to present information on the Dutch programme. Patrick Roose to carry our discussion points from MCWG2003 to WGBEC2003, which he will be attending.

All members: to send information relating to the development of guidelines or rationale for integrated chemical and biological effects monitoring to Patrick Roose, who will report to MCWG2004.

Patrick Roose, Ton van der Zande, Gert Asmund, Evin McGovern: to send data from their own programmes to Marilynn Sørensen at ICES, for the purpose of testing the new data reporting format.

All members: to send information on levels of mercury and organohalogens in birds' eggs to Ton van de Zande, and he will present these data to MCWG2004.

All members: to send information on arsenic in marine fish and shellfish, and its speciation, to Evin McGovern, and he will present these data to MCWG2004.

Jacob de Boer: to advise MCWG of new data for TCPM and TCPMe arising from the Dutch fish monitoring programme. All members: to advise Jacob when they have new data. Michel Lebeuf: to compile data on DDTs, TCPM and TCPMe in flatfish, and report to MCWG2004.

Ton van der Zande: to report on new findings concerning the use of silicone membranes for passive sampling.

Michel Lebeuf and Gert Asmund: to present data on temporal trends of toxaphene concentrations in beluga whales in Canada, and on toxaphene concentrations in birds and mammals from the AMAP programme, at MCWG2004.

Jacob de Boer and Michel Lebeuf: to present new data on brominated diphenylethers and other brominated flame retardants at MCWG2004.

Ton van der Zande, Britta Pedersen and Jacek Tronczynski: to send additional data from their institutes to Norbert Theobald, to allow the distribution in other maritime zones to be assessed. Norbert Theobald: to report to MCWG2004.

Jacob de Boer: to provide an update on the analysis of dioxins and related programmes at MCWG2004.

Annex 8 Recommendations

MCWG recommends that ICES work to develop the producer/website links for reference materials suitable for use in marine monitoring programmes as a matter of priority, and as originally recommended at MCWG2001.

MCWG reminds ICES of the paramount importance of CRMs to international collaborative marine monitoring programmes, and recommends that ICES contact the director of IRMM, Geel (Hendrik Emons) to express its concern that the closure of the EU Standards, Measurement and Testing Programme will not result in delays to the production of these invaluable materials.

MCWG recommends that more groups include analysis of organobromine compounds such as BDEs and HBCD, as these contaminants are becoming of more concern due to rising levels in the environment (within the ICES area; the former in North America and the Arctic, the latter in Europe).

The **Marine Chemistry Working Group** [MCWG] (Chair: R. Law, UK) will meet in Nantes, France, from 15 to 19 March 2004 to:

A. Chemical Oceanography Subgroup

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

B. Organics Subgroup

a) update information on the availability of suitable analytical methods to allow the determination of environmental concentrations of organic substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome [OSPAR 2003/1];

b) 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 2003/3.2];

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

d) review new information on the use of membrane systems for sampling and report the outcome;

e) review new information on the monitoring and analysis of toxaphene and report the outcome;

f) review new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants, and report the outcome;

g) review new information concerning the analysis of dioxins and the preparation of reference materials for these compounds, and report the outcome;

h) review developments within the UNEP Global POPs Monitoring Network, and report the outcome;

i) review new information on the impact of alkylphenols from produced water;

j) review new information on the herbicides isoproturon and diuron, and report the outcome.

C. Trace Metals Subgroup

a) provide information on the availability of suitable analytical methods to allow the determination of environmental concentrations of inorganic substances listed on the OSPAR list of chemicals for priority action, and whether any information exists on the presence of these chemicals in the marine environment, and report the outcome [OSPAR 2003/1];

b) 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 2003/3.2];

c) review information on arsenic speciation, and report the outcome;

d) review new information on the use of membrane systems for sampling and report the outcome;

D. Plenum

a) undertake activities relating to the implementation of the OSPAR Joint Assessment and Monitoring

Programme in the light of discussions at MCWG2003 and as required by OSPAR;

b) 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;

c) 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;

d) review any new ICES/HELCOM SGQAC Annexes on Quality Assurance and report the outcome;

e) review the revised ICES Environmental Data Reporting Format (Version 3.2) and provide comments to the ICES Marine Data Centre;

f) consider and finalise draft guidelines for integrated chemical and biological effects monitoring (with WGBEC and WGMS);

g) discuss matters referred from the three subgroups, as necessary.

MCWG will report by 5 April 2004 for the attention of the Marine Habitat and Oceanography Committees and ACME.