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## Report of the Marine Chemistry Working Group (MCWG)

7–11 March 2005

Vigo, Spain



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

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## Executive summary

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The Marine Chemistry Working Group [MCWG] (Co-chairs Robin Law, UK, and Jacek Tronczynski, France) met in Vigo, Spain, from 7–11 March 2005. The key outcomes from the terms of reference are described below.

### **Laboratory Performance Study QUASIMEME**

QUASIMEME has continued its regular studies with rounds 37–40 during the period April 2004 to January 2005. There have been no major changes to these studies as they have fulfilled the key requirements for the OSPAR, HELCOM and MEDPOL monitoring programmes. QUASIMEME has continued with a suite of development exercises, for organotins in biota, sediments and water, amnesic shellfish poisoning toxins and brominated flame retardants in biota and sediment. In April 2005, QUASIMEME will transfer its operation from the Fisheries Research Services, Marine Laboratory, Aberdeen, to Wageningen University and Research Centre (Wageningen UR), The Netherlands, based at the Centre of Water and Climate at Alterra under the direction of Professor Wim Cofino (a past chair of MCWG). The Netherlands Institute for Fisheries Research (RIVO), in the person of Professor Jacob de Boer as head of the Department of Environment and Food Safety, will join Alterra in this operation.

### **With WGMS and WGS AEM, develop draft advice on appropriate strategies for undertaking one-off surveys for 2,4,6-tri-*tert*-butylphenol, endosulphan and short-chain chlorinated paraffins in the OSPAR area.**

Review notes were prepared for 2,4,6-tri-*tert*-butylphenol and short-chain chlorinated paraffins, and recent data for endosulphan were reviewed during the meeting. Advice was passed to ACME confirming that one-off surveys for these compounds were feasible, particularly if a single laboratory conducted all the analyses in each case. Further advice on analytical methods and environmental occurrence was also provided.

### **Continue to report on new information concerning polybrominated diphenyl ethers (PBDEs) and other brominated flame retardants.**

A number of novel studies on brominated flame retardants were described. A retrospective time trend study (1981–2003) on organohalogen compounds in mussels from the Seine estuary, the Mediterranean Sea and the Atlantic showed an increase in PBDE concentrations from 1981 until 1991–1995, after which the concentrations levelled off and eventually began to decrease. The rates of increase were found to be similar to those found in other studies from Europe and the USA. It was noted that it is not clear how future trends in concentration for these compounds could be anticipated, given the different environmental behaviour of the BDE congeners and current changes in their industrial applications and in the regulatory measures applied to the various products. Data on the temporal trends in biological samples of the BDEs are still relatively sparse and these studies require good sample sets of archived samples (such as those held in specimen banks in a few countries), a prerequisite that is often difficult to achieve. In another study, thirty-four marine mammals of twelve species stranded in the UK between 1992 and 2002 were analysed for BDEs. The highest sum BDE concentration of 16.2 mg kg<sup>-1</sup> wet weight was found in a killer whale, a juvenile female stranded on the coast of the Shetland Islands.

**Review the draft MON assessment report, particularly the way in which Background Concentrations and Environmentally Acceptable Concentrations have been used.**

A tremendous amount of work has obviously been involved in the assessment process, and it represents good progress in the development of these assessments. Many data have been presented in the report (including those for time trends in sediments in biota) but the dataset will benefit from further study and synthesis over time. In particular, statistical significance in time trends is not sufficient of itself, and these trends also need to be examined for chemical and biological relevance. Trends for sediments and biota can differ at the same site, also many chemicals which share similar sources (e.g., combustion-derived PAH) show different behaviours. This may reflect differences in the length of time-trends available for different compounds, but merits further study.



## **1 Opening of the meeting**

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The co-Chairs (Robin Law (UK) and Jacek Tronczynski (France)) opened the meeting at 10.00 am on Monday 7 March 2005. The Director of the host organisation, the Centro Oceanográfico de Vigo of the Instituto Español de Oceanografía, Dr Alberto González-Garcés, welcomed the participants and wished them well in their deliberations. The participants then introduced themselves and their affiliations and described their specific interests within the field of marine chemistry. The List of Participants is given in Annex 1, and the Agenda in Annex 2. Recommendations are listed in Annex 4, and the Action List is appended as Annex 5.

## **2 Adoption of Agenda**

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The agenda was adopted with additions made just prior to the meeting (Agenda Item 8.22) and during the meeting (Agenda Item 8.23) following requests from both ICES and OSPAR, and best efforts were made to respond to these.

## **3 Report of the 92<sup>nd</sup> ICES Statutory Meeting**

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Lars Føyn and Teresa Nunes attended the 92nd ICES Statutory Meeting and Annual Science Conference, and presented a short report of the meeting. They drew attention to the fact that scientific input to MHC and ACME benefits from the activities of ICES working groups. During the years, MCWG work has fed into advice provided by the Advisory Committee on the Marine Environment (ACME), and has contributed to its reports and ICES official advice to Member Countries and Regulatory Conventions, such as OSPAR. With respect to the parent Science Committee, the Marine Habitat Committee (MHC), time pressures within their schedule result in very little time being allocated to discussion of MCWG work and that of other WGs, within the present ICES system – only about 3 to 4 hours available for MHC meetings in the Statutory Meeting/ASC. Taking into account the Committee's wide range of subjects, and the large number of WG Reports that they have to review, concern was raised about this situation, and it is suggested that this is taken into account within the changes which are currently being made in the ICES structure and function. Finally, the function and objectives of the ICES Sciences Committees need further clarification, as outlined by the Chair of MHC. It also appears that routine attendance at the Statutory Meetings by WG chairs is often problematic due to funding difficulties within their host institutes.

## **4 Reports on related activities**

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### **4.1 OSPAR and HELCOM**

All official requests from OSPAR and HELCOM received prior to the meeting have been incorporated in the agenda.

### **4.2 Intergovernmental Oceanographic Commission (IOC)**

In the past MCWG have received a report of relevant activities within the IOC from the ICES Hydrographer. In the absence of this input, information was sought from the IOC website. No recent relevant activities were noted. As no members of MCWG have regular contacts with IOC, we request advice from ICES regarding the mechanism for updating us on IOC activities in the future in order that we may comment on them and take account of them within our work. Otherwise this standing agenda item should be removed from future agendas, and only reinstated if specific requests can be made, with reference to appropriate documentation.

### 4.3 Laboratory Performance study QUASIMEME

David Wells provided an update on activities within QUASIMEME.

QUASIMEME has continued its regular studies with rounds 37–40 during the period April 2004 to January 2005. There have been no major changes to these studies as they have fulfilled the key requirements for the OSPAR, HELCOM and MEDPOL monitoring programmes. The details of laboratory performance are available in the QUASIMEME quarterly reports (available on the QUASIMEME website) and from the QUASIMEME office. Overall performance has been maintained and was similar to that in previous years.

Chlorophyll-*a* transferred from the development studies to the routine Laboratory Performance Studies (LPS) in 2003–2004, and continues to be undertaken twice annually.

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

QUASIMEME has continued with the development exercises for organotins in biota, sediments and water. In the programme of three development exercises, followed by a workshop, the first two development exercises have been completed, with the report on the second to be issued during March 2005. The third development exercise will be part of Round 41 (April to July 2005) with a workshop to discuss the progress in October 2005 to be held at NERI, Roskilde, Denmark.

Following the first two development exercises for amnesic shellfish poisoning toxins, QUASIMEME held a one-day workshop in Galway, Ireland in June 2004, following the International Conference on Molluscan Shellfish Safety. At the workshop, it was agreed that there should be another two development exercises during 2004–2005, with a move to a routine LPS study for the measurements of ASP toxins in 2005–2006.

The development exercises for the measurement of brominated flame retardants in biota and sediment continue, with one study during the current QUASIMEME year (April to July 2004) with another development exercise planned as part of the 2005–2006 programme. Jacob de Boer continues to assess the data in conjunction with the QUASIMEME office.

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

The model can be applied to data other than laboratory performance studies and has been used successfully to obtain information on the Background Concentrations (BCs) for determinands in sediment and biota as required by OSPAR for assessment purposes.

QUASIMEME worked actively with ICES to enable laboratories to accurately and more speedily report their external QA data to the ICES database during 2004 in good time for the OSPAR MON assessment. QUASIMEME provided all participating laboratories with their assessed QA data on CD for checking and forwarding to ICES with their ICES institute code on the CD label. All data transferred in this way is non-attributable to the QUASIMEME coding.

In all QUASIMEME LPS Study reports since Round 34, laboratories are identified only by a specific round identifier rather than by their permanent code. This is to improve confidentiality in line with the requirements of G13:2000 and ISO 43.

In April 2005, QUASIMEME will transfer its operation from the Fisheries Research Services, Marine Laboratory, Aberdeen to Wageningen University and Research Centre (Wageningen UR), The Netherlands, based at the Centre of Water and Climate at Alterra under the direction of Professor Wim Cofino (a past chair of MCWG). The Netherlands Institute for Fisheries Research (RIVO), in the person of Professor Jacob de Boer as head of the Department of Environment and Food Safety, will join Alterra in this operation. This change was announced in the QUASIMEME Newsletter, issue 31 (February 2005).

As part of the transfer to Alterra, QUASIMEME is currently improving the database by migrating it from PARADOX to SQL/VB.net. The new database will also improve the use of method codes that may link more effectively to the numerical data, providing better information to participants and third parties, such as ICES/OSPAR/HELCOM/MEDPOL with regard to method improvement and the choice of analytical methodologies.

As an extension of the QUASIMEME programme, a number of workshops are planned for 2005–2007, to provide an opportunity for more detailed discussion of the analysis of some of the priority substances listed under the Water Framework Directive. Initially, in 2005–2006 the following workshops are planned:

- Organotin, in October 2005 at NERI, Roskilde, Denmark;
- Organochlorine pesticides, in November 2005 or early 2006 at FRS Marine Laboratory, Aberdeen, UK, following an expert review of methods in March–April 2005;
- Chemical measurement of shellfish toxins, especially the okadaic acid group of DSP toxins, early in 2006 at the Marine Institute, Galway, Republic of Ireland, following a development exercise on the chemical measurement of the okadaic acid toxin group.

Other workshops planned for 2006–2007 include: Alkylphenols and their ethoxylates, brominated flame retardants, organophosphorus pesticides, polycyclic aromatic hydrocarbons, and volatile organochlorine compounds. Details of workshops will be sent to all QUASIMEME participants once the workshop programme is confirmed, and will be included in QUASIMEME newsletters.

The QUASIMEME programme for 2005–2006 is now available.

After discussions the following suggestions were made. These should be relayed to the new management group at Alterra, and David Wells agreed to do this.

Although dried sediment samples are adequate for the assessment of analytical variability, the use of wet sediments will be necessary in studies on sampling, sieving, homogeneity, and (bio)availability.

The work on chlorophyll-*a* could be extended to include studies of sampling and patchiness.

Chlorinated paraffins should be included on the list of topics for QUASIMEME workshops, in view of the likely interest arising as a result of the inclusion of short-chain chlorinated paraffins within the requirements of the Water Framework Directive.

The expected concentrations of contaminants in samples circulated within the Laboratory Proficiency Scheme (indicative values, for instance, based on known spikes added) should be given if no assigned values are available due to low levels of participation in any round.

The number of participants taking part in the exercises for, e.g., toxaphene should ideally be expanded to include more participants to ensure better value and information for these exercises. QUASIMEME has investigated the reasons for low participation for some determinand groups – often this is a result of laboratory rationalisation or changes in work programmes. Also, interest in toxaphene in Europe is rather peripheral as the material has never been used there – the major European interest is in Arctic areas to which toxaphene is transported *via* the atmosphere from the major usage areas in North America.

In view of the coming changes in the management of QUASIMEME activities the MCWG Chairs will contact Wim Cofino and Jacob de Boer to arrange an update for MCWG2006.

#### **4.4 Other activities**

Peter Lepom provided information on the work of the EU AMPS (Analysis and Monitoring of Priority Substances) group in implementation of the EU Water Framework Directive.

Peter Lepom updated the group on the work of AMPS and the planned follow-up activities.

Peter Lepom made available to the members of MCWG the Draft Final Report of the Expert Group on the Analysis and Monitoring of Priority Substances (AMPS), which has been completed and published in June 2004, and informed MCWG that the AMPS group has been terminated.

Upon completion of the draft final report of AMPS, the DG ENV announced to establish a new working group “Chemical Monitoring“ by March 2005 to develop clear technical guidance, guidelines or technical specifications on monitoring, which could include legally-binding provisions adopted by the WFD Committee.

For this purpose a working group bringing together experts on surface and ground water monitoring, to ensure a coherent view and to avoid duplication of effort on issues of joint concern, should be established. Key issues are monitoring strategies in relation to compliance checking of good chemical status, as they should be applied to the different types of waters covered by the WFD, and issue working documents including aspects of quality assurance.

The starting point for the work will be the existing requirements of the Water Framework Directive, and the proposed “daughter Directives” on Groundwater and on Priority Substances, and the work carried out in different working groups and expert groups of the Common Implementation Strategy (CIS) of the WFD, which resulted in the development of a guidance document on monitoring (CIS Guidance N°7). For surface water, specific discussions have taken place in the framework of the AMPS expert group with regard to monitoring of priority substances in surface waters, sediments and biota. For groundwater the work of Working Group 2C regarding groundwater will be the starting point. Specific monitoring guidance already developed by international or national organisations, and research-related activities are to be taken into account.

The work mainly to be carried out in 2005–2006, will be divided in three major topics, (i) issues of common concern and (ii) issues specific to groundwater and (iii) issues specific to surface water monitoring. In the context of the above timeframe, the activities will consist of drafting activities and workshops to share information/experience according to the following timeframe:

- Workshop of the WG to define specific roles and tasks of the subgroups and the provisional content of the technical guidance in March 2005;
- WG meeting in November 2005;
- WG meeting in spring 2006;
- Final WG meeting in autumn 2006.

The activities of the working group should focus on all monitoring issues relevant to the WFD, e.g.:

- Monitoring strategies including frequency and location of monitoring;
- Trend monitoring;
- Discharge monitoring;
- Areas of impact;
- Metal background concentrations;
- Matrices recommended for monitoring;
- Analytical protocols including sampling / sample pre-treatment, laboratory methods, and alternative methods;
- Quality assurance;
- Data to be reported.

The Working Group will be chaired by DG JRC (IES Ispra) and composed of Member States representatives and stakeholders. Member States are asked to nominate experts competent in both ground and surface water. ICES will be invited to be formally involved in the planned working group on chemical monitoring, and has been asked to provide advice in relation to the developing EU marine strategy. Drafting subgroups will be established to develop the sections of the technical guidance document. These groups will be composed of small teams of experts mandated by the WG with developing specific parts of the guidance document. For specific purposes, groups of external experts may be involved.

Unfortunately, no official information on whether and when the new working group on chemical monitoring will be established was available for MCWG 2005.

## **5 Reports on projects and activities in Member Countries**

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No activities were reported which were not covered under the other agenda items.

## **6 Requests from ACE, ACME and Regulatory Agencies**

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All requests which arose prior to the preparation of the Agenda have been included.

## **7 Plenary presentations**

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### **7.1 Lucía Viñas**

Monitoring and assessment of the pollution caused by the *Prestige* oil spill on the Spanish coast.

The single-hulled product tanker *Prestige* sank off the west coast of Spain on the 19<sup>th</sup> of November 2002, releasing a large proportion of her cargo of 77,000 tonnes of heavy fuel oil (IFO380). Oil came ashore in Galicia (NW Spain), along the Spanish coast of the Bay of Biscay, and on the Atlantic coast of France. The presentation described the work undertaken by the Instituto Español de Oceanografía in the wake of this incident. A more detailed summary of this presentation is given in Annex 5.

### **7.2 Ricardo Beiras (University of Vigo)**

Integrative assessment of pollution on the Galician coast using sediment chemistry, bioaccumulation in mussels and embryo-larval bioassays.

The classical paradigm of assessing pollution by measuring a long and ever growing list of pollutants is currently challenged by the integrative approach combining chemical and biological methods, namely ecological indicators, molecular and cellular markers and toxicological bioassays. Specifically, ICES ACME advocated in 2002 that "... it is important that each method [of monitoring] is not used alone and that a strategy using integrated chemical and biological effects measurements is developed".

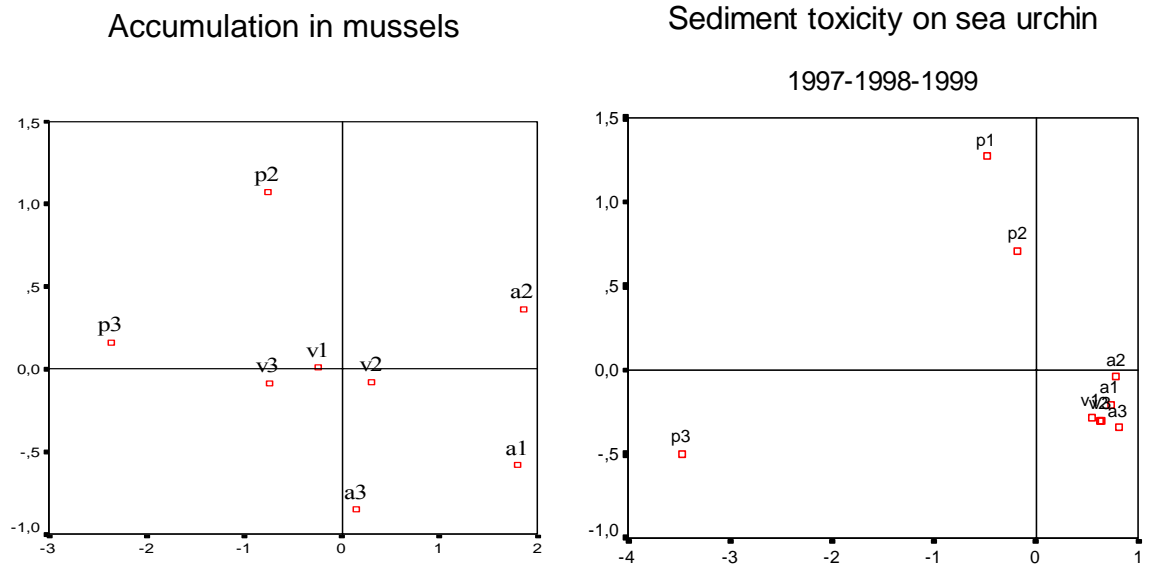
The research group at the University of Vigo has been working for the past decade in collaboration with the Spanish Institute of Oceanography (IEO) in order to include embryo-larval bioassays in the programme of monitoring of coastal pollution in the Atlantic coast of Spain. This work has focussed mainly on the Galician Rias (NW Iberian Peninsula), highly productive ecosystems whose resources have both economic and social relevance. The species chosen for the bioassays are representative of the main taxa of marine invertebrates: bivalves, crustaceans and echinoderms. The sea-urchin embryogenesis bioassay combines sensitivity, ecological relevance and simplicity of standardisation. Its sensitivity to metals and hydrocarbons is similar to that of the classical fresh-water *Daphnia* test; also, it is more sensitive to detergents but much less sensitive, as expected, to selective pesticides. This limitation can be overcome by the use of a battery of species including a crustacean (to cover insecticides) and a photosynthetic organism (herbicides). Availability of biological material is another important limitation. The sea-urchin in Galician waters is mature from early spring to early autumn. In winter some clam species (*Tapes rhomboideus* and *Venerupis pullastra*), which are available from aquaculture farms, can provide an alternative. The bivalve embryos have very similar sensitivity to the main types of marine pollutants as do sea-urchins.

After two years of sampling in four different Galician Rias it has been shown that the patterns of pollution revealed by bioaccumulation in wild mussels are similar to those seen for the sea-urchin ecotoxicological data (Beiras *et al.* 2003a,b). Using non-metric multidimensional scaling with two data sets, one consisting of bioaccumulation in mussels and another from concomitant sediment toxicity tests with sea-urchin embryos, the same sampling stations were discriminated, indicating a good agreement between the two types of information (Figure 7.2.1).

The next step is to introduce within the monitoring programme measurements of molecular markers (e.g., metallothioneins and oxidative stress enzymes in wild mussels), and benthic community indices. The former provide early warning regarding sublethal exposures, and the later provide ecological relevance to the monitoring results.

Beiras, R., Bellas, J., Fernández, N., Lorenzo, J.I., and Cobelo-García, A. 2003a. Assessment of coastal marine pollution in Galicia (NW Iberian Peninsula); metal concentrations in seawater, sediments and mussels (*Mytilus galloprovincialis*) vs. embryo-larval bioassays using *Paracentrotus lividus* and *Ciona intestinalis*. *Marine Environmental Research*, 56: 531–553.

Beiras, R., Fernández, N., Bellas, J., Besada, V., González-Quijano, A., and Nunes, T. 2003b. Integrative assessment of marine pollution in Galician estuaries using sediment chemistry, mussel bioaccumulation, and embryo-larval toxicity bioassays. *Chemosphere*, 52: 1209–1224.



**Figure 7.2.1. Non-metric Multidimensional Scaling ordination of sampling sites on the basis of mussel bioaccumulation (left) and sea-urchin embryo ecotoxicological data. In both plots sites from Pontevedra (P) are discriminated. Site P1 was not included in the bioaccumulation data-set since mussels are not available there.**

### 7.3 Jarle Klungsøyr

The analysis of alkylphenols in produced water and their biological effects on fish.

The presentation consisted of three main parts.

1. Information about the development of a selective and sensitive technique for the analysis of alkylphenols in water and biota.
2. Results from a risk assessment of reproductive effects of alkylphenols in produced water on fish stocks in the North Sea.
3. Effects on development, sex differentiation and reproduction of cod (*Gadus morhua*) exposed to produced water during early life stages.

A short discussion took place after the presentation concerning possible technological solutions intended to reduce the inputs of contaminants in produced water to the marine environment. Re-injection of produced water is a solution which is used for some oil/gas fields, but is not applicable to all fields for technical or geological reasons. New technical solutions are also under development and their implementation could further reduce the amounts of contaminants in produced water. However, in the North Sea, large volumes of produced water will still be discharged during the coming years, as the ratio of produced water to oil rises in aging fields as the production zone moves closer to the oil/water interface in the reservoir. Produced water may also contain residues of production chemicals added to the production stream and other natural compounds from the reservoir which are not fully characterized. The question was raised whether there is a need also to screen these contaminants for possible oestrogenic activity? For production chemicals used on the UK Continental Shelf, any products containing compounds identified as possible endocrine disruptors have already been removed from the list of available products, and an active substitution process is in place to encourage less toxic alternatives to all chemicals used. The issue relating to naturally produced compounds can probably be handled with *in vitro* screening techniques which have already been developed. The offshore petroleum

industry also discharges significant amounts of cuttings which are contaminated with chemicals used in drilling operations, although restrictions have been placed on those drilling muds which are not water-based (i.e., based on oils or synthetic fluids).

## **8 Main agenda**

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### **8.1 Continue to provide guidance and assistance relating to the development of a series of data products to illustrate eutrophication status within the ICES area**

There is nothing to report on this item, and unless a specific targeted request is received this item will be removed from the agenda for MCWG2006.

MCWG then discussed the future of chemical oceanography in the context of the ICES science strategy. In the terms of reference for the MCWG 2005 meeting there are almost no agenda items that can be considered chemical oceanography, defined as using chemical methods to describe and understand processes in the marine environment. The main focus, as also has been the case in the past few years, is on marine pollution and, in particular, the organic contaminants and monitoring questions raised by OSPAR and HELCOM.

This focus has resulted in a low level of participation from chemical oceanographers for several years, as they find little of specific interest in the meeting. MCWG asks the Marine Habitat Committee to consider, together with the Oceanographic Committee, a new initiative which will allow ICES, its Commission customers and the Member Countries to make full use of the expertise of the chemical oceanographers within the ICES community. The rationale for this is based on the fact that ecosystem-based management advice will be crucially important for the effective future management of both national and international marine areas, and that it will therefore be important to consider such basic processes as:

- Processes for the remineralisation of nutrients and other biologically important components;
- Availability of nutrients and other substances that can promote plankton growth and blooms;
- Circulation and deposition of CO<sub>2</sub> in the marine environment;
- The role of nutrients (eutrophication) in processes regulating transport and bioavailability of contaminants;
- Provide new tools in marine chemistry and/or additional parameters to meet new demands (e.g., higher resolution in time and space, automatic measurement devices such as chemical or biological sensors).

and to fully integrate these components into future ICES advice.

### **8.2 Examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2]**

OSPAR had not been able to make the anticipated progress with the preparation of the draft guidelines, and so there was no document on which MCWG could comment.



### **8.3 Continue to report on new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish**

No new data were reported on this agenda item during the meeting. However, some new data on TCPM/Me in biota were produced during the past year in the Netherlands (Stefan van Leeuwen, RIVO) and provided to Michel Lebeuf. In addition, flatfish samples from Belgium (Marc Raemaekers) were collected and sent to Michel Lebeuf and flatfish samples already collected in Spain (Teresa Nunes) are in preparation before being sent to Canada for analysis. Michel Lebeuf mentioned that his laboratory will analyse the Belgian and Spanish flatfish samples for TCPM/Me and DDTs within this project and that any relevant new data from other members of the MCWG are still welcome. Michael Haarich indicated that he is presently validating TCPM/Me data produced by his laboratory between 1999 and 2004 in flatfish tissues from Germany in order to provide that information to Michel Lebeuf. Michel Lebeuf has volunteered to collate all the data made available to him by the MCWG members in order to present the results at the next MCWG meeting in 2006.

### **8.4 Continue to report on new information on the use of membrane systems for sampling**

This subject was introduced by Foppe Smedes in two presentations. One explained once more the basic principle of the use of passive samplers and the second providing an update on the monitoring taking place at the RIKZ using passive samplers (PS) in parallel with deployed mussels. The presentations are summarized below.

#### **Principle of passive sampling**

A passive sampler can be seen as the glass level indicator often fitted to a large coffee container. The level in the glass reflects how full the coffee container is and at the same time the “pressure” which will drive the coffee out of the container if the tap is opened. The aqueous environment can also be seen as a compilation of different compartments connected with each other through the water phase. In equilibrium, all compartments will be filled to the same degree. Using the fugacity or partition theory it can be derived that in equilibrium the ratio of the concentration of a compound in a matrix (activity) to its uptake capacity is equal for all of the compartments. The uptake capacity is equivalent to solubility for water and for a sediment it is the sorption capacity. The ratio between concentration and uptake capacity will also be reflected by any reference phase connected to these compartments and used as a passive sampler. When seeking a compartment in which a compound can be accurately measured and whose uptake capacity is well defined, it is apparent that this is only the case for the reference phase. So, the reference phase can act as a gauge to measure the “pressure”, i.e., pollution level in a compartment. One condition is, of course, that the reference phase is in equilibrium with the compartment in question. Principally, a reference phase can be used in any watery matrix to measure the pollution level, provided that equilibrium can be attained. The results from, for example, two sediments with different compositions, or a soil and a sediment sample, can be compared directly. Ideally, everybody using passive samplers should use the same reference phase and appropriate assessment criteria should be developed, so as to avoid problems with units when comparing data. There is however a need to recalculate to an already existing phase with a known fugacity capacity, since different materials are already in use as the reference phase (at least six have been observed in literature already) and others may be developed in the future. The suggested approach is to determine the water-reference phase partition coefficient of the compound of interest and recalculate to the free dissolved concentration in the water phase. Reference phases can be used in both water and sediments to give an estimate of the level of exposure.

### **Passive sampling in parallel with the deployment of mussels**

The RIKZ is currently conducting a monitoring programme in which passive samplers and mussels are exposed alongside one another. This programme has been running for four years now and is slowly evolving into a routine sampling technique. Passive samplers made from silicone rubber sheets were exposed in duplicate together with 100 mussels for a period of six weeks around November and February each year. In comparing the uptake in mussels with the uptake within the passive samplers, at some stations the mussels showed a significantly larger uptake of contaminants due to their greater growth at those stations. In addition to the variable growth of mussels, the different dynamics at each station influences the thickness of the boundary layer and therefore the sampling rate of the passive samplers at that location. Passive samplers were spiked with a number of performance reference compounds that dissipate from the sampler during exposure. The degree of dissipation allows the calculation of the sampling rate. From the partition coefficients and the sampling rate, the free dissolved concentrations of contaminants in the water phase can be calculated. The results demonstrated the effectiveness of performance reference compounds in allowing the estimation of the sampling rate. Obviously, for compounds that are either fully lost or not released at all from the passive samplers it is not possible to estimate the sampling rate. However, different compounds that were released at different rates yielded similar estimates of sampling rate. Depending on the detection limits achievable for each compound, the sampling rate can most optimally be estimated when 50–90% is released during the 6 week deployment. Sampling rates varied from 10 l/d for areas where flows were low, up to 40 l/d for areas which are highly dynamic.

Plotting the estimated free dissolved concentration in the water phase (for CB153 as example) with the concentration in the mussels a strong correlation was observed. The mussels that doubled in size during the deployment were not outliers in the dataset, indicating that the extra growth of the mussels paralleled their additional uptake. Essentially, it shows that the bioaccumulation factor was not affected by the growth of the mussels.

The final variability in the bioaccumulation factor was 0.1 log unit (or 20%) across all stations, indicating that the passive sampling method reflects the exposure level. A correction for the dynamics of the sampling location is necessary to obtain such a small level of variability.

Foppe's conclusions were that:

- Passive sampling reflects the exposure of mussels to contaminants;
- The dynamics at the sampling location are relevant to uptake and need to be corrected for;
- Silicon rubber was a practical material for manufacture of passive samplers;
- The methodology is almost ready for routine use.

### **Discussion**

The group felt that passive sampling is a very promising technique giving an insight into the availability of contaminants. Several questions after the presentation were concerning the details of the methodology, but most of the discussion focused on the possibility of using it in routine monitoring. In the discussion some obstacles for implementation were identified:

- No standardization yet;
- Validation is missing;
- No known intercalibration studies for this type of passive sampler, although some studies have been undertaken for other devices, such as SPMEs (solid-phase micro-extraction).

Foppe responded that in his view the mussels were the best validation in relation to the intentions of the monitoring programme. An analytical validation is not easy as, for the very hydrophobic contaminants, the free dissolved concentration cannot be isolated from the fraction

bound to dissolved organic carbon by filtration, while at the same time sorption of hydrophobic contaminants to the filter can also occur. In relation to intercalibration, Foppe pointed out that the variability of the analytical component is very small and it is the sampling system that would then need to be intercalibrated by different laboratories, each sampling at a single location. A mesocosm system would not be a practical alternative, as a passive sampler extracts about 1600 l water during a standard deployment and the mesocosm would need to be at least 10 times that volume to prevent exhaustion of the aqueous phase. With 10 laboratories participating, a 10x larger volume of water would be needed. Field intercalibrations are much more straightforward and likely to be easier to organise.

Many within the group felt, however, that before application of passive samplers is considered for routine use a comparison with other sampling and extraction technique is required for validation purposes, and to allow comparison with earlier datasets. This is best addressed by using both sets of methodologies in parallel for a number of years. Some participants were interested to take it further but no concrete proposals were made during the meeting. Within some of the participants' laboratories, there are already proposals to include passive sampling in their routine monitoring programmes. A prerequisite to this is adequate training, validation and intercalibration of this technique. In some laboratories also, proposals which have been made to include passive sampling in monitoring studies have not received funding, so the case for their use also needs to be made with funding organizations.

There are plans for a training workshop on passive sampling to be held in June 2005, and further information can be obtained from Foppe Smedes. This topic will be carried forward to the agenda for MCWG2006.

**8.5 With WGMS and WGS AEM, develop draft advice on appropriate strategies for undertaking one-off surveys to provide new information about the following chemicals identified by OSPAR for priority action: 2,4,6-tri-*tert*-butylphenol (exploratory survey to establish whether the substance is found in sediments in the OSPAR area); endosulphan (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define "hot-spots" of the substance, in sediments of the OSPAR area); and short-chain chlorinated paraffins (survey to establish baseline in sediments in the OSPAR area against which to measure progress towards the goal of the OSPAR Hazardous Substances Strategy) according to specific OSPAR requests, taking into account sources and modes of dispersion/transport**

For 2,4,6-tri-*tert*-butylphenol, a short review note of recent information was produced (Annex 6). Currently, no data are available for this compound in any environmental matrix. As the lead country, the UK has commissioned a small-scale survey in sediments from a number of major industrialised UK estuaries, which is underway and should be completed during March 2005. Although the OSPAR background document indicates that the chemical is used in the manufacture of plastics and rubber, industry sources in the UK indicate that it is not used in making rubber, and the only registered manufacturer in the UK makes additives for petroleum products. A one-off survey is feasible in the OSPAR area, and MCWG advises that the analyses be undertaken within a single laboratory. Limits of detection will be supplied from the UK survey, along with the data. OSPAR should examine the results from the UK survey and take account of these when deciding whether or not to proceed with a wider survey. An outline of the analytical method used is given in Annex 7. No reference materials are available

which are certified for this compound. On the basis of available information sediment seems an appropriate matrix, although no studies have been undertaken to date.

Norbert Theobald presented a short overview and new information on the presence of endosulphan in the marine environment. The new data were for water and sediments from the North and Baltic seas. These studies were conducted within a research program and the German monitoring program.

The solid phase and microwave extractions were made for water and sediment samples respectively and after clean up and fractionation, the extracts were analysed for endosulphan by gas chromatography mass spectrometry in electron capture negative ionisation mode (GC-MS-ECNI).

The limit of determination of endosulphan in water samples was  $20 \text{ pg l}^{-1}$ . The concentrations of endosulphan were below the limit of detection at many stations in the North and Baltic seas. The concentrations ranged between  $< 20$  and  $43 \text{ pg l}^{-1}$  and between  $< 20$  and  $37 \text{ pg l}^{-1}$  for endosulfan I and II respectively in the North Sea. For this area the highest concentrations were determined at some off-shore stations indicating atmospheric inputs. Slightly higher concentrations in the Baltic Sea ranged between  $< 20$  and  $62$  and between  $< 20$  and  $49 \text{ pg l}^{-1}$  for endosulphan I and II respectively. The levels in the North and Baltic seas were compared to the literature data (e.g., Bering Sea between  $1$  and  $5 \text{ pg l}^{-1}$ , Canadian Arctic lake  $40 \text{ pg l}^{-1}$ , rainwater in Belgium  $1$  to  $224 \text{ ng l}^{-1}$ ).

The limit of determination of endosulphan in  $20\text{g}$  sediment samples from these studies was  $0.03 \text{ } \mu\text{g kg}^{-1}$ . Most of the samples analysed were below this concentration, and in only a few samples from the Baltic Sea were concentrations up to  $0.067 \text{ } \mu\text{g kg}^{-1}$  observed.

There is a geographical variation in the European use of endosulphan, with most being used in the south (Spain, Greece, Italy, and France).

Sediment is an appropriate matrix for endosulphan surveys. However detectable levels in sea water were clearly shown as well. The possible use of passive samplers (such as plastic membranes) was also briefly discussed. Finally, endosulphan has a high bioconcentration potential and biota such as mussels might also be a good alternative for endosulphan monitoring.

A sediment reference material with certified values for endosulphan has been produced by the IAEA.

Peter Lepom presented a review note on short chain chlorinated paraffins (SCCPs) (Annex 7). SCCPs are on the OSPAR list of chemicals for priority action and are listed as priority hazardous substances under the Water Framework Directive Annex X (EU Dec. 2001/2455/EC). While there are other uses, its primary use has been in metalworking fluids. The production level has been relatively high (4000 tonnes in 1998).

The complexity of the substance (with over 7000 theoretical positional isomers) makes analysis very challenging. Various techniques have been applied, primarily Gas Chromatography-Mass Spectrometry (GC-MS). Variations of GC-MS with negative chemical ionisation (NCI-MS) have been used although there are various drawbacks, such as ion source temperature dependence of mass spectra and response differences, up to a factor of 10, depending on the degree of chlorination. Use of high-resolution MS gives advantages in terms of sensitivity and selectivity. While no separation is achieved, use of short GC columns can also offer increased sensitivity. It was noted that GC-EI-MS/MS offers potential for cost-effective analysis, although issues in relation to interference from aromatic compounds need to be resolved. Lack of a harmonised approach to calibration and quantification as well as lack of calibration and reference materials is currently a major contributing factor to poor laboratory performance and comparability.

Although there is limited information on levels of SCCPs in the marine environment, it is evident that they are very widespread, including remote arctic areas. Water is not considered an appropriate matrix for monitoring in the marine environment. SCCPs concentrations have been determined in sediment, SPM, fish & shellfish, seabirds and marine mammals and recent data are presented in the review note. For instance, SCCPs in sediments from the Drammensfjord, Norway, ranged from 94–1300  $\mu\text{g kg}^{-1}$  dw. Concentrations recently reported for SCCPs in sediments from the North Sea/German Bight and the Baltic Sea were similar when expressed on an organic carbon basis, (3.7–9.1 and 2.1–8.4  $\text{mg kg}^{-1}$  OC respectively). In marine organisms, the highest levels (up to 1.4  $\text{mg kg}^{-1}$  wet weight) were recorded for Beluga from the St. Lawrence River in Canada.

As it is known that these substances are widespread in the marine environment, the one-off survey is required to establish baseline levels in the OSPAR area against which future progress can be assessed. Several recommendations were made specifically on the proposed baseline survey for SCCPs:

- Given the difficulty of analysis and problems of between-laboratory comparability, one expert laboratory should carry out all the analysis;
- GC-NCI-HRMS currently offers the best available technique and should be used for analysis;
- Sediment is an appropriate matrix for such a one-off survey;
- Although there are no sediment CRMs available for SCCPs, within-laboratory reproducibility should be established by analysing laboratory quality control sediment materials;
- MCWG recognised the urgent need for calibration standards and appropriate reference materials.

Foppe Smedes informed MCWG of the outcome of a joint discussion between WGMS and WGSAAEM on this topic, focusing on survey design.

In their discussions a pragmatic approach was adopted. For 2,4,6-tri-*tert*-butylphenol and endosulphan an exploratory design should be adopted, with the endosulphan surveys also focusing on hotspots. Currently there is no data on 2,4,6-tri-*tert*-butylphenol (although data from the UK should be available soon) and the one-off exploratory survey is required to establish if these contaminants are present in marine sediments. Data for endosulphan is mainly in water with limited sediment data. SCCPs are known to be present in the marine environment and have been detected in sediments, although data is limited. Therefore, for SCCPs a baseline study is required.

Matrix: All three compounds are hydrophobic and should accumulate in sediment. Therefore, surveys should focus on sediment. Analysis of biota may be considered as an alternative, however, if compounds are metabolised they would not give a good indication of presence in the environment. Passive samplers may also be a good alternative but need to be more widely used and methods fully validated.

Sampling design: WGMS used the DIFFCHEM survey design as a basis for the design of the current surveys. Samples for the DIFFCHEM survey were collected in estuarine areas only, with one station from each estuary being sampled and analysed in triplicate for PAHs, SCCPs and BFRs. A report is available in an OSPAR document, although this does not contain the analytical data. Only the PAH data could be obtained at the time of the meeting and these data were used to establish whether this approach was adequate. In general, the best approach to identify hotspots is to use a grid design for sampling, but this is not practical over the whole OSPAR area. Therefore, for the baseline survey three samples should be collected at three stations; one at the mouth of the river, one in the middle of estuary and one at the mouth of the estuary. A steep gradient in concentrations would suggest that a hotspot was present. Fur-

thermore, samples should be taken at a place where the fine sediment is deposited as hydrophobic contaminants will accumulate to a greater extent in these areas. Depositional areas in the open sea should also be included. Samples should be collected at depths representative for the last five years of deposition and should take into account the sedimentation rate in each area. For each of the chemicals, an experienced lab should be identified to undertake the sieving and analysis of all samples, particularly for the analysis of SCCPs for which fully validated quality assured methods are not available.

WGMS did not address analytical methodology, limits of detection or quality assurance, as these were to be covered by MCWG.

As the SCCPs will be the subject of a baseline survey then there is clearly a plan to resurvey at a later date. MCWG suggests, therefore, that larger samples than are needed for this survey be collected and a portion stored in a freezer at  $-20^{\circ}\text{C}$ . These subsamples can be analysed alongside the samples from the later survey, for a direct comparison of concentrations using whatever is the most appropriate methodology available at that time.

Further information on survey design and statistical aspects is available within the report of WGMS 2005.

### **8.6 Continue to report on the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and its availability via the ICES website**

Following discussions with Neil Fletcher of ICES and further consideration at the meeting, MCWG decided that the best way forward would be to provide links to the websites of organisations producing certified reference materials. Ideally, this would be from the ICES website, but if that proves impractical then it could probably be hosted on the QUASIMEME website with appropriate links.

### **8.7 Comment on any new annexes on quality assurance from the ICES/HELCOM SGQAC (Annexes 4 to 6 in the report of SGQAC 2005)**

MCWG was supplied with the draft report of SGQAC 2005 and asked to comment on draft guidelines given in Annexes 4–6 of that report.

**Annex 4** Technical note on QA of the determination and documentation of cofactors.

This paper primarily gives a listing and description of cofactors used to normalise quantification of pollutants in different matrices. In its present form it will have limited use. There is little information on the measurement of cofactors or on their QA and a very limited list of references. In its present form it is a ‘non-paper’ and only serves a brief summary for the reader new to the field.

There is a need for detailed guidelines on the QA requirements for the measurement of cofactors that should take full account of the current developments within this field e.g. the Smedes approach to normalisation procedures for contaminants in sediment, accelerated solvent extraction (ASE) v Smedes method for the determination of total lipids. There is a wide range of studies on the methodologies for the determination of cofactors that should be reviewed and evaluated if these guidelines would have added value to the laboratories involved in marine environmental monitoring.

#### **Annex 5** Routine Quality Control within the Laboratory

Recommendations on which types of control chart should be used alongside which measurements should be added to the text.

#### **Annex 6** Limit of Detection, Limit of Quantification, Limit of Application

There is much more information available on this subject in standard texts and references could be added to these.

In general some aspects of the above Annexes may be of value if developed from standard text to incorporate practical and detailed issues on a method by method basis. If such a task were undertaken then this group should draw on the wide and considerable experience of the wider ICES scientific community. Intersessionally, the co-Chairs and MCWG Members interested in this topic will explore ways in which to make the links between SGQAC and MCWG closer in order that these technical annexes can be prepared in a more effective manner so as to better meet the needs of the monitoring laboratories within HELCOM.

### **8.8 Continue to determine priorities for assistance from WGSAEM with statistical analyses and develop with WGSAEM a plan for the necessary collaboration.**

Recently, most discussions between the Chairs of MCWG and WGSAEM have been in relation to the OSPAR request concerning one-off survey design (Agenda Item 8.5) on which they are collaborating, also with WGMS. If the three groups meet together in 2006, this will provide an opportunity for joint consideration of projects current at that time.

### **8.9 Compile data (notably winter nutrients) for the North Sea (in Excel spreadsheet format), taking account of the work already being undertaken by WGMS in response to the OSPAR MON request/meeting in December 2004. The data should be compiled (averaged) for ICES rectangles where possible, for the period 1984 to 2004 and submitted to the secure REGNS website in preparation for the REGNS Integrated Assessment Workshop to be held from 9–11 May 2005.**

Clarification of the requirements of this agenda item were sought from both ICES and REGNS in advance of the meeting. ICES supplied draft plots of the nutrient data available from the ICES database, and a summary listing. REGNS advised that what they required primarily for the workshop was a list of available datasets which could be used for the assessment in addition to the ICES information, and provided a template on which this could be recorded.

MCWG discussed the request to identify the datasets they feel will be of most value for REGNS in their integrated assessment of contaminants in the North Sea, and initially for the planned workshop in May 2005. It was pointed out that the latest OSPAR MON assessment report contains probably the most complete database on contaminants within the OSPAR region, and this could form the basis on which the 2006 REGNS quality status report of the North Sea could build. This database includes many geographically referenced data on contaminants (both metals and organic compounds, in sediments and biota) including time trend information in sediments and in biota. It was suggested that the best way forward was for MCWG members to identify experts from each member state who will attend the integrated assessment workshop to be held at ICES HQ in Copenhagen on the 9<sup>th</sup> to 11<sup>th</sup> May 2005 and guide the REGNS group to those national databases appropriate for integrated assessment.

The chemical oceanographers within MCWG were unable to identify additional nutrients datasets for the purposes of REGNS beyond the ICES database. A summary map of nutrient information held by ICES for 1994–2004 is given as Annex 9.

### **8.10 Continue to report on new information concerning polybrominated diphenyl ethers (PBDEs) and other brominated flame retardants**

Jacek Tronczynski, Patrick Roose, Robin Law, and Evin McGovern presented new information on PBDEs.

Jacek Tronczynski presented a retrospective time trend study (1981–2003) on organohalogen compounds in mussels from the Seine. In the meantime, the study has been extended to include mussels from the Mediterranean Sea and the Atlantic and a further paper has been accepted for publication. The study showed an increase in PBDE concentration from 1981 until 1991–1995, after which the concentrations levelled off and eventually began to decrease. The rates of increase were found to be similar to those found in other studies from Europe and the USA. The highest concentrations of about 10 ng g<sup>-1</sup> dry weight for BDE47 were found in mussels from the Seine Estuary collected in 2001, whilst concentrations in the mussels from the other locations were about 10 times lower. BDE209 was also included in the analyses; concentrations of this compound were low, with the highest concentration observed being 0.4 ng g<sup>-1</sup> dry weight.

Johansson, I., Heas-Moisan, K., Guiot, N., Munsch, C., and Tronczynski, J. (in press 2005). Polybrominated diphenyl ethers (PBDEs) in mussels over the past twenty years at selected sites on the French coast. *Chemosphere*.

Johansson, I., Moisan, K., Guiot, N., Truquet, I., Munsch, C. and Tronczynski, J. (2004). Levels and trends of organohalogen compounds in mussels from the Seine estuary in 1981–2003. *Organohalogen Compounds*, 66, 1844–1852.

Comment from the group: Clean-up procedures based on gel permeation chromatography can adversely affect the recovery of BDE209, however, with appropriate validation of the method this problem can be avoided.

Patrick Roose told the group that brominated diphenyl ethers have been analysed in mysid (*Mysidaceae*) samples from the Scheldt Estuary, as part of an ongoing monitoring programme, which also includes pesticides, PAHs, TBT and other compounds. BDE47 was the main congener found in mysids, with concentrations varying between less than the limit of detection to 100 ng g<sup>-1</sup> dry weight. BDE209 was also included in the programme, but all concentrations were below the limit of detection. The most remarkable result was a maximum concentration of 3000 ng g<sup>-1</sup> dry weight for TBT, which is well above the levels at which toxic effects could be expected. More results will be presented at MCWG2006.

Robin Law had provided two papers on brominated flame retardants with the background material for the meeting. The first one is a paper just published in *Marine Pollution Bulletin*, the second one is a review on brominated flame retardants in the European environment presented at the BFR 2004 workshop (Law *et al.*, 2004, 2005). Robin initially presented the results from the study recently published in *Marine Pollution Bulletin*, which describes BDEs in 12 species of marine mammals collected within the UK Marine Mammals Stranding Programme. Altogether, 34 animals stranded between 1992 and 2002 were analysed, comprised of bottlenose dolphin, killer whale, hooded seal, Sowerby's beaked whale, pygmy sperm whale, Cuvier's beaked whale, fin whale, minke whale, sei whale, northern bottlenose whale, humpback whale and Risso's dolphin. The highest  $\Sigma$ BDE concentration of 16.2 mg kg<sup>-1</sup> wet weight was found in one of killer whales, which was about one order of magnitude higher than the concentrations in the other four killer whale samples. The animal with the highest concentration was a juvenile female stranded on the coast of the Shetland Islands. BDE47 was the main individual



congener in all samples and accounted for 23–100% of  $\Sigma$ BDE. (Comment from the group: 100% means that BDE47 was the only congener found at above the limit of detection). BDE209 was not included in the analyses since it has never been detected in earlier studies concerning marine mammals, and BDE183 (often considered a marker for the octa-mix PBDE formulation) was not detected in this study. No time trend could be observed in the data.

Discussion: Can the POP concentrations in marine mammals be related to immunosuppression? According to Robin, there are no studies available which directly investigate effects of POPs on the immunosystem in marine mammals. In their studies, they observed that the animals that died of infectious diseases had the higher levels of PCBs and Hg than those which died of trauma (mostly fishery bycatch), and the PCB concentrations in the infectious disease group exceeded a tentative toxicity threshold derived from experimental studies in other mammal species (such as mink) (Jepson *et al.*, 2005).

Jepson, P.D., Bennett, P.M., Deaville, R., Allchin, C.R., Baker, J.R. and Law, R.J. 2005. Relationships between PCBs and health status in harbour porpoises (*Phocoena phocoena*) stranded in the United Kingdom. *Environmental Toxicology and Chemistry*, 24, 238–248.

Law, R.J., Allchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S. and de Wit, C.A. (2004). Levels and trends of brominated flame retardants in the European environment. *Proceedings of the Third International Workshop on Brominated Flame Retardants BFR2004*, 6–9 June 2004 Toronto, Canada. 79–104.

Law, R.J., Allchin, C.R., and Mead, L.K. 2005. Brominated diphenyl ethers in twelve species of marine mammals stranded in the UK. *Marine Pollution Bulletin*, 50: 356–359.

Evin McGovern told the group about an Irish survey of dioxins, PCBs, PBDEs and HBCD in various fish species which is currently being conducted and will be completed in 2005. In 2004, a smaller study dealt with PBDEs and HBCD in seven individual farmed salmon samples collected from seven aquaculture sites in Ireland. The mean upperbound  $\Sigma$ BDE concentration was  $3 \pm 0.58 \text{ ng g}^{-1}$  wet weight, and the upperbound HBCD concentration was  $1.2 \pm 0.26 \text{ ng g}^{-1}$  wet weight. The results were compared with a previous study on trout and eel from the Skerne-Tees river system (UK), which had  $\Sigma$ BDE and HBCD levels of respectively one and three orders of magnitude higher than the salmon from the Irish study. The UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment concluded that the estimated dietary intake for PBDEs and HBCD were unlikely to present a health risk, based on consumption of a weekly single portion of fish from the Skerne-Tees river system. Therefore it is concluded that, based on current information, levels of PBDEs and HBCD in Irish farmed salmon are unlikely to pose a health risk to consumers.

On behalf of Jacob de Boer, Heather Leslie handed out copies of the following three papers with new information on brominated flame retardants:

de Boer, J. 2004. Brominated flame retardants in the environment – the price for our convenience? *Environmental Chemistry*, 1, 81–85.

Korytár, P., Covaci, A., de Boer, J., Gelbin, A. and Brinkman, U.A.Th. 2005. Retention-time database of 126 polybrominated diphenyl ether congeners and two Bromkal technical mixtures on seven capillary gas chromatographic columns. *Journal of Chromatography A*, 1065: 239–249.

Morris, S., Allchin, C.R., Zegers, B.N., Haftka, J.J.H., Boon, J.P., Belpaire, C., Leonards, P.E.G., van Leeuwen, S.P.J. and de Boer, J. (2004). Distribution and fate of HBCD and TBBPA flame retardants in North Sea estuaries and aquatic food webs. *Environmental Science and Technology*, 38: 5497–5504.

Other references to new information:

Zegers, B.N., Mets, A., van Bommel, R., Minkenberg, C., Hamers, T., Kamstra, J.H., Pierce, G.J. and Boon, J.P. (2005). Levels of hexabromocyclododecane in harbor porpoises and common dolphins from western European seas, with evidence for stereoisomer-specific biotransformation by cytochrome P450. *Environmental Science and Technology*, in press.

### **8.11 Continue to report on new information concerning the analysis of dioxins and the preparation of reference materials for these compounds**

Heather Leslie provided MCWG members with a CD-ROM disc “A World of Difference: New techniques for dioxin analysis” which presented a video summary of the findings of the project. A copy will be provided to ICES for information by the co-Chairs. Three references were also noted as presenting new information of relevance to MCWG and ACME:

Korytár, P., Danielsson, C., Leonards, P.E.G., Haglund, P., de Boer, J. and Brinkman, U.A.Th. (2004). Separation of seventeen 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and dibenzofurans and 12 dioxin-like polychlorinated biphenyls by comprehensive two-dimensional gas chromatography with electron-capture detection. *Journal of Chromatography A*, 1038, 189–199.

Munsch, C., Moisan, K. and Tronczynski, J. (2004). Levels and patterns of PCBs and PCDD/Fs in different tissues of the marine flatfish dab (*Limanda limanda*) from the English Channel, France. *Organohalogen Compounds*, 66, 1672–1680.

Van Loco, J., van Leeuwen, S.P.J., Roos, P., Carbonelle, S., de Boer, J., Goeyens, L. and Beernaert, H. (2004). The international validation of bio- and chemical-analytical screening methods for dioxins and dioxin-like PCBs: the DIFFERENCE project rounds 1 and 2. *Talanta*, 63, 1169–1182.

### **8.12 Continue to report on new information concerning the monitoring and analysis of toxaphene**

Toxaphene is included in the basic monitoring programme which the Danish Environmental Protection Agency and NERI conduct in Greenland as part of the Arctic Monitoring and Assessment Programme. Besides toxaphene, the programme includes PCBs, HCHs, HCB, DDTs and chlordane-related compounds. In the past 5 years (1999–2004) annual analyses have been performed on shorthorn sculpin liver, ringed seal blubber and black guillemot eggs (“Time Trend Programme”). Furthermore, Arctic char were included from the freshwater environment. In 2004, the so-called Core Programme with a two-year interval was started, which, however, will be subject to revision in 2006. The programme has three main elements:

1. Analysis of organochlorine compounds (including toxaphene) in 20 ringed seals from East Greenland collected in 1986, to extend the time series backwards.
2. Retrospective time trend analysis (1986–today) of other compounds of concern, i.e., PFOS, dioxins and PBDEs, in ringed seals from East Greenland. The analyses of PBDEs are proposed for 2006.
3. Monitoring of organochlorine compounds (including toxaphene) in the following animals/matrices: East Greenland: Shorthorn sculpin, black guillemot eggs, ringed seal, glaucous gull, Arctic char. West Greenland: Shorthorn sculpin, black guillemot liver, ringed seal, Arctic char. Northwest Greenland: Ringed seal. Of each sample type, 20 individuals will be analysed, except for the black guillemot eggs which will only include 10 individuals.

The analyses within elements 1 and 2 have been completed. These results will form part of the final report after completion of part 3, which is expected at the end of 2005. Katrin Vorkamp will present the toxaphene results at MCWG2006.

Michel Lebeuf informs that the following paper on toxaphene in seals has been published:

Gouteux, B.; Lebeuf, M.; Hammil, M.O.; Muir, D.C.G.; Gagné, J.-P. 2005. Comparison of toxaphene congener levels in five seal species from Eastern Canada: What is the importance of biological factors. *Environmental Science & Technology*, 39: 1448–1454.

### **8.13 Continue to report on developments within the UNEP Global POPs Monitoring Network**

Attention was drawn to two new developments within this developing programme, information on which is available on the UNEP POPs website at:

<http://www.chem.unep.ch/gmn/gmnlabs/default.htm> and

<http://www.chem.unep.ch/gmn/GuidanceGPM.pdf>

(Accessed on 16 March 2005).

The first outlines the development of a list of POPs monitoring laboratories; the second, the development of guidelines for the monitoring programme itself.

#### **Relevant references**

Bordaland, L.R., Korytár, P., de Boer, J. and González, M.J. 2005. Enantiomeric separation of chiral polychlorinated biphenyls on  $\beta$ -cyclodextrin capillary columns by means of heart-cut multidimensional gas chromatography and comprehensive two-dimensional gas chromatography: application to food samples. *Journal of Separation Science*, 28: 163–171.

Boer, J. de. 2005. Polychlorinated biphenyls. *In* Encyclopedia of Analytical Science 2nd edition. Ed. by P. Worsfold, A. Townshend and C. Poole. Elsevier Science Ltd., Oxford, UK, pp. 214–225.

Lebeuf, M., and Nunes, T. 2005. PCBs and OCPs in sediment cores from the lower St. Lawrence estuary, Canada: Evidence of fluvial inputs and time lag in delivery to coring sites. *Environmental Science & Technology*, 39: 1470–1478.

### **8.14 Continue to report on new developments on the impact of alkylphenols from produced water**

New information is presented within the summary of the plenary presentation at Agenda Item 7.3.

### **8.15 Report on new information on contaminant concentrations in marine fish and other marine food products**

Marc Raemaekers reported on a Belgian intake assessment project entitled “Integrated evaluation of marine food products: nutritional value, safety & consumer acceptance”. Duration: 2 year, now half-way through. Four different research units: three from the University of Ghent, one governmental research institute (the Sea Fisheries Department, Oostende). The major objective is to estimate the intake of contaminants and nutritional factors associated with the consumption of fish and other marine food products. In order to estimate the intake of these constituents, a mathematical research model has been developed. The variables that are used in the model are consumption pattern, origin of the marine food product, its concentration of contaminants/nutrients, body weight of the consumer and period of time during which the marine food items were consumed. In order to feed the model, various databases have been set up: a database of marine food consumption patterns and databases of contents of dioxins, di-

oxin-like CBs, marker CBs and Hg, vitamin D, long-chain omega-3 fatty acids in various marine species from different origins, all based on previously published measurements. The Sea Fisheries Department assisted in collecting data to feed the latter database. The major task of the SFD was the estimation of the origin of all marine food products entering the Belgian market (import and own landings). A national database containing import figures per product group and country of origin was used, in combination with an FAO database containing production figures per country and per production area. Problems encountered when combining this information were highlighted. Before the databases can be used as input for the model, distribution curves of contaminant concentrations have to be set up for each product group and each production area. If too few data exist, product groups and/or production areas have to be merged. Merging can also be done if concentrations show similar distributions in different production areas and/or product groups. In order to fit distributions, it is important that individual measurements are used, and not average values of results from pooled samples. It is stressed that only measurements carried out on marine organisms of well-known origins (not simply taken from the “market”) are valuable as input for the model.

As a final research result, intake distributions with confidence intervals of the various contaminants and nutrients from the consumption of marine food products will be obtained. Marc will report further findings to MCWG2006.

### **8.16 Report on new information regarding perfluorinated compounds**

Norbert Theobald reported the levels of a suite of eight environmentally relevant perfluorinated compounds perfluorooctanoic acid (PFOA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNoA), perfluorodecanoic acid (PFDeA), perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonamide (PFSOA) in water samples collected in the north-west Atlantic between the eastern coast of Greenland and Svalbard, Norway. Samples were taken using a 10 l glass bottle sampler. Perfluorinated compounds were extracted by solid-phase extraction (SPE) and analysed by electro-spray ionisation LC-MS/MS operated in the negative ion mode. Observed blanks were between 2 and 18 pg l<sup>-1</sup> and primarily associated with sampling and elution, but with a small contribution (only for PFOA) from the LC-MS/MS instrument due to the use of Teflon. LOQs for the various PFCs ranged from 2 to 30 pg l<sup>-1</sup>. Perfluorinated carboxylic as well as sulfonic acids, were detected in all samples from the north-west Atlantic. Measured concentrations were mostly close to the limit of quantification. PFOA was the predominating compound in almost all samples. Highest levels of both PFOA and PFOS (100–120 pg l<sup>-1</sup>) were seen off the Norwegian coast near Tromsø. PFC levels near Svalbard and the coast of Greenland were higher than those along the 75° N transect. PFOS concentrations seemed to decline from east to west along this transect.

Perfluorinated compound concentrations in the German Bight ranged from a few hundred to 8,000 pg l<sup>-1</sup> with the highest concentrations observed in the estuary of the River Elbe at Stade and along the German coast, and the lowest concentrations occurring in the open North Sea.

These results indicate that PFCs are a new class of substances of possible marine concern

Katrin Vorkamp informed MCWG about a preliminary screening study of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, bird and marine mammals from Greenland and the Faeroe Islands, which has been accepted for publication in *Environmental Pollution*. Moreover, a retrospective time trend study (1986–2005) on PFCs in ringed seal from East Greenland is ongoing at NERI. She will present the details of both studies at the next MCWG meeting to be held in Copenhagen in March 2006.

### Relevant references

- Holmström, K.E., Järnberg, U. and Bignert, A. (2005). Temporal trends of PFOS and PFOA in Guillemot eggs from the Baltic Sea, 1968–2003. *Environmental Science and Technology*, in press.
- Tomy, G.T., Budakowski, W., Halldorson, T., Helm, P.A., Stern, G.A., Friesen, K., Pepper, K., Tittlemeier, S.A. and Fisk, A.T. (2004). Fluorinated organic compounds in an eastern Arctic marine food web. *Environmental Science and Technology*, 38: 6475–6481.

#### **8.17 In relation to guidelines on frequency and spatial coverage of monitoring for nutrients and eutrophication parameters (phytoplankton, zoobenthos, phytobenthos), together with WGSaEM examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2]**

OSPAR had not been able to make the anticipated progress with the preparation of the draft guidelines, and so there was no document on which MCWG could comment.

#### **8.18 With WGBEC, consider the current developments within OECD/EU regarding endocrine disruptors and whether this is adequate for the marine environment, and draft advice on any further work considered necessary to address issues specific to the marine environment [OSPAR 2005/8]**

OECD studies are directed towards ring-testing (interlaboratory testing intended to determine the reproducibility of a new test method) of biological effects methods. EU documents COM(1999)706 final and COM(2001)262 outline the Community strategy in relation to endocrine disrupting chemicals. The approach appears comprehensive, but is mainly directed towards human health effects. The EU-funded EDEN project is addressing the effects of mixtures of endocrine-disrupting chemicals, and includes some studies in fish. Lists of candidate causative chemicals will be produced from within these studies and from the suite of test methods to be finalized by the EU in 2005. Once these lists are available they should be used as the basis for exposure assessments in the marine environment (sources and volumes; via discharges from land, atmospheric inputs, shipping and the offshore oil and gas industry) in order to direct future studies which will directly address concerns for effects in the marine environment. In addition, WGBEC should consider the suite of methods recommended by the EU and consider whether they are appropriate for the marine environment. MCWG notes that there is a broad range of studies currently in progress and being reported in the scientific literature, and considers that it may be useful to review this material for a future meeting of MCWG or WGBEC.

#### **8.19 With BEWG and WBGEC, contribute to an assessment of the long-term impact of oil spills on marine and coastal life, based on a list of issues from OSPAR [OSPAR 2005/7]**

The list of issues from OSPAR was provided by Richard Emmerson just prior to the meeting.

An assessment of the long-term effects of oil spills should consider:

- a. the distinction between the effects of the oil and what is caused by natural changes;

- b. the impacts of oil on different types of habitats (i.e., the nature of the coastline) and ecosystems (variability in rates of recovery);
- c. the impacts of oil in different marine regions subject to different climatic influences;
- d. the impacts of different types of oil, both toxic impacts (toxic effects and accumulation) and non-toxic impacts (physical properties creating nuisance and hazardous conditions - physical contamination and smothering);
- e. the impacts of remedial activities such as the use of heavy equipment and high pressure hosing to clean up oil spills;
- f. whether the current framework of environmental risk assessment and toxicology is sufficient to take account of the long term effects of oil pollution.

He also provided some additional clarification, to the effect that the background to this item is to build up a more collective view of what is known about the long-term impacts of oil spills, taking account of the work that has been done following a number of recent incidents (*Braer*, *Sea Empress*, *Erika*, *Prestige*, *Tricolor*). Are there particular issues that we should be worried about? or need to take action about at a generic level? OSPAR would like to have the material for presentation to the North Sea Intermediate Ministerial Meeting to be held in April 2006. MCWG noted that the ICES ASC has a theme session on oil spills in 2005 (theme session S) and proposed that a group of MCWG members with relevant experience of these incidents (Robin Law, Jacek Tronczynski, Lucia Viñas, Lynda Webster and Patrick Roose) should prepare a paper for the theme session which could also be sent to ACME 2005 for approval and onward transmission to OSPAR.

### **8.20 Review the outcome of the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-sea Areas (WKIMON) to resolve any outstanding issues and, together with WGBEC and WGSAM, finalise a draft set of guidelines for integrated monitoring for OSPAR [OSPAR 2005/6]**

Following Agenda Item 7.2, the plenary presentation by Ricardo Beiras which also addressed some of these issues, there was a discussion session in which all MCWG members took part as an addition to a topic subgroup discussion which took place earlier in the day. The first point made was that toxicity bioassays and chemical determinations of concentration were seen as complementary. A number of topics were discussed, the first that of short-lived and non-bioaccumulating compounds – how are they handled by bioassays? If discharges of short-lived compounds are continuous or nearly so they are viewed as “*pseudo-persistent*”, as the toxic concentrations are essentially being continuously renewed despite degradation. Acute toxicity thresholds were also addressed – there is a possibility for additive and/or synergistic effects where individual compounds are each below their toxicity level, but toxicity may result because of their total concentration and similar modes of action – the example given was in produced water discharges from offshore oil and gas installations. Another topic raised was “by measuring chemical concentrations are we already too late?” When high concentrations are found have the effects already occurred, and how can we be more proactive in order to protect the environment?” Regulators need to be convinced of harm before they will act to control chemicals, and the political realities are that others will be lobbying against controls and a strong case must be made. It was also suggested that a change in population structure of a species in the absence of other adverse signals from bioassays and/or chemical measurements could be a warning signal, but we must be able to distinguish man-made (pollutant) effects from natural changes.

Specifically concerning the WKIMON report, MCWG felt that the current draft guidelines are at a relatively early stage of development. They go some way towards defining the underlying philosophy of integrated monitoring, though even this could benefit from some additional de-

velopment, but do not currently contain sufficient detail to qualify as guidelines useful to direct monitoring programmes. MCWG and WGBEC will need to work together initially to prepare assessment criteria for integrated monitoring, after which the guidelines can be fleshed out. The co-Chairs will consult with John Thain (Chair of WGBEC) in advance of the meeting of that group later in 2005. As a first stage of integration, possibly the creation of a pilot project would be an achievable aim. For a single contaminant or group of contaminants relevant effects would need to be identified and specific biomarkers of those effects would need to be developed and validated, as well as integrated assessment criteria. A concentration hotspot or single point source would also need to be identified for study. Within ongoing national and international monitoring programmes the first step should be to synchronise sampling for chemical and biological effects monitoring (with any necessary cofactors) so that the same samples are taken, at the same time and place, for both purposes.

### **8.21 Report on the feasibility of merging WGMS and MCWG**

As requested by MHC, the MCWG considered the possible outcomes of the suggested merger of the two groups. The first likelihood is that the overall number of representatives funded to attend by their parent laboratories would be reduced. Where many institutes currently send individuals with the relevant expertise to each group, only one or the other would represent both interests within a merged group. The range of expertise contributing to ICES advice would therefore be reduced. Opportunities for networking within disciplines (one of the reasons which keeps institutes funding attendance at WG meetings – WG members must get something back as well as contributing to ICES aims in order for the whole system to keep functioning) would also be reduced. In order to improve the way in which the groups work together, improvements in the communications and connectivity could be sought instead. Meetings between WG chairs would help to meet this requirement, but may be difficult to arrange and fund. Where the two groups (and WGS/AEM) have had a common task in 2005, in the design of one-off surveys for OSPAR, there has been no duplication of effort and the work in the three groups has been complementary, contributing equally to the development of ACME advice. As long as the two WGs together serve the Advisory Committees well, then we can see no good arguments for a merger. It should also be borne in mind that, in today's science institute funding climates, such a merger would not be reversible if unsuccessful.

### **8.22 Respond to requests from the ICES Data Centre**

Three requests were received in all. Initially, it was hoped that an ICES representative would be able to attend the meeting in order to expedite these requests, but unfortunately this proved not to be possible. A telephone conference with Marilyn Sørensen was planned as an alternative, and this took place at 11 am on Thursday, 10 March.

The requests related to the following topics:

1. Parameter group reorganization;
2. Organotin parameters;
3. Environment salinity codes.

ICES had asked MCWG about the form in which organotin data should be stored on the database – as Sn, and the cation or as a compound (e.g., tributyltin oxide or chloride)? MCWG would prefer the concentrations to be expressed as the cation. MCWG also confirmed that all the salinity codes currently within the ICES environmental database are necessary.

Having clarified the issues, and particularly those relating to database design, MCWG made a suggestion to ICES. MCWG members felt very strongly that the question regarding database design was being handled in an ineffective manner. The collation of answers on a single discipline (single WG) basis and a subsequent web-based discussion, as described, was thought unlikely to yield the multidisciplinary approach being sought. As an alternative, MCWG rec-

ommended that ICES create a multidisciplinary group to be chaired by someone very familiar with assessments (Ian Davies as an example) with representation from the relevant environmental WGs to meet with the database experts and work on the overall architecture, consulting WGs (through their chairs) as needed with specific questions.

On the specific questions from the ICES Data Centre, the following general approach was decided:

Foppe Smedes will make four excel files available on his website (<http://home.tiscali.nl/fsmedes/mcwg/mcwg>).

- 8122\_5 Pargroup.xls (containing 4 fields: ParGroup, Description of group, Param code and Description of parameter), more than 600 Param codes are included;
- File containing all field codes;
- File containing cofactors for CS (contaminants in sediment);
- File containing cofactors for CF (contaminants in biota);
- File containing cofactors for CW (contaminants in seawater).

Each MCWG member can make proposals for changes, additional groups (in a new field) or additional groupings, removal of groups,... in the Pargroup file and the field codes file. For the latter 3 files, cofactors for the given matrices can be suggested for inclusion.

All proposals for changes should be formulated as text (e-mail, Word, ...); don't send an Excel file with changes. Proposals should be sent to Patrick Roose before 15 April. He will collate all suggestions and forward them to Marilyn Sørensen, and also ask Bo Jansson if he wishes to be involved as he was at an earlier stage.

Answer to question 5) Specifically, the PAH metabolites are currently included in B-MBA. Should they be included in O-PAH? Should they be included in both groups or in just one?

There was a consensus to categorise all PAH-metabolites under both groups O-PAH and B-MBA.

Answer to question 6) What parameter group(s) should include coloured dissolved organic material and phytoplankton absorption coefficients?

“Coloured dissolved organic material” should be probably categorised as a physical method (P-PHY). There was some uncertainty in regard to the second parameter. Phytoplankton absorption coefficient seems to indicate light absorption which is proportional to the amount of chlorophyll *a* present. If it is a real coefficient, it is a fixed value and should not be held in the database. If it is not, it can be in a group on its own (param code?).

### **8.23 Review the draft MON assessment report, particularly the way in which Background Concentrations and Environmentally Acceptable Concentrations have been used**

Note: Agenda Item 8.23 was added to the terms of reference on 7 March 2005.

MCWG received a request during the meeting for a general review of the draft MON assessment report (ca. 170 pages plus many appendices). Our review is therefore not detailed as the time available at the meeting was insufficient. A tremendous amount of work has obviously been involved in the assessment process, and it represents good progress in the development of these assessments. Patrick Roose presented the main points in relation to background concentrations and environmentally acceptable concentrations in biota, and this presentation is summarised in Annex 10. Many data have been presented in the report (including those for time trends in sediments in biota) but the dataset will benefit from further study and synthesis over time. In particular, statistical significance in time trends is not sufficient of itself, and



these trends also need to be examined for chemical and biological relevance. Trends for sediments and biota can differ at the same site, also many chemicals which share similar sources (e.g., combustion-derived PAH) show different behaviours. This may reflect differences in the length of time-trends available for different compounds, but merits further study. Trends in different matrices from areas with defined inputs (catchments to estuaries to coastal waters) could also be usefully studied. As noted by OSPAR MON, the BC, BAC, and EAC values need to be considered further in some cases. EACs can be lower than BCs, and BCs for metals need to recognise local conditions (e.g., geology, upwelling) which cause natural elevations of concentrations at some locations. BCs have currently been drawn from pre-existing data (essentially lowest concentrations generally equal background) but it may be desirable to fill data gaps in remote areas so as to yield better estimates. Regarding BCs for metals in sediments; these seem to be more successful than the previous BRCs, and BCs also need to be developed for biota in advance of the next assessment. Also, EACs for PAHs in sediments are currently given on a “ring number” basis, whilst BCs and BACs are cited for individual compounds.

## **9 Plenary discussion of draft report**

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This took place on Friday 11 March.

## **10 Any other business**

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For the next meeting of four environmental working groups together in Copenhagen in 2006, the co-Chairs of MCWG will help to develop the detailed work programme to involve representatives of all WGs. Relevant topics of interest could include availability of contaminants, integrated chemical and biological effects monitoring guidelines, and the preparations for the REGNS integrated assessment for ASC2006.

## **11 Recommendations and Action List**

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These are given as Annexes 3 and 4.

## **12 Date and venue of the next meeting**

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As requested by ACME, MCWG will meet during 27–31 March 2006 at ICES Headquarters in Copenhagen.

## **13 Closure of the meeting**

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At 12 pm on Friday 11 March a five minute silence was observed along with the whole IEO staff on the first anniversary of the Madrid train bombings. Thanks were then given and presentations made to those who had helped to organise and run the meeting; Victoria Besada, Miguel Crujeiras, Matilde Ferrer, Dámaso Hernandez, Teresa Nunes, and Marta Pena. The co-Chairs closed the meeting at 12.55 pm on 11 March.

## Annex 1: MCWG List of Participants

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## **Annex 2: Agenda**

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1. **OPENING OF THE MEETING**
2. **ADOPTION OF THE AGENDA**
3. **REPORT OF THE 92<sup>nd</sup> 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 The work of the AMPS group in implementation of the EU Water Framework Directive.
5. **REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES**
6. **REQUESTS FROM ACE, ACME AND REGULATORY AGENCIES**

Requests from ACE and ACME which arose prior to the preparation of the agenda were included.
7. **PLENARY PRESENTATIONS**
  - 7.1 **Lucía Viñas (IEO, Vigo)**

Monitoring and assessment of the pollution caused by the *Prestige* oil spill on the Spanish coast.
  - 7.2 **Ricardo Beiras (University of Vigo)**

Integrative assessment of marine pollution on the Galician coast using sediment chemistry, bioaccumulation in mussels and embryolarval bioassays.
  - 7.3 **Jarle Klungsøyr**

The analysis of alkylphenols in produced water and their biological effects on fish.
8. **MAIN AGENDA**
  - 8.1 continue to provide guidance and assistance relating to the development of a series of data products to illustrate eutrophication status within the ICES area;
  - 8.2 examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft

advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];

- 8.3 continue to report on new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish;
- 8.4 continue to report on new information on the use of membrane systems for sampling;
- 8.5 with WGMS and WGSAEM, develop draft advice on appropriate strategies for undertaking one-off surveys to provide new information about the following chemicals identified by OSPAR for Priority Action: 2,4,6-tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define “hot-spots” of the substance, in sediments of the OSPAR area), and short-chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy) according to specific OSPAR requests; taking into account sources and modes of dispersion/transport. The specific questions to be addressed for each substance (or groups of substances) under consideration are:
  - i) indicate whether there is any new information available on presence in the marine environment that has not already been taken into account in the relevant OSPAR background document as updated by the OSPAR lead country,
  - ii) indicate whether the matrix (sediment, biota, water) proposed to be sampled is appropriate or whether an additional or more appropriate matrix should be included in the survey,
  - iii) identify whether analytical techniques are available for the relevant matrices,
  - iv) identify achievable detection limits, and reference materials, and
  - v) determine how many stations/samples from each part of the OSPAR Convention area are necessary to address the objectives of the one-off surveys proposed, taking into account that more than one one-off survey may be required [OSPAR 2005/1];
- 8.6 continue to report on the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website;
- 8.7 report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;

(there are 3 of these; a technical note on quality assurance of the determination and documentation of co-factors; Guideline chapter 5 on routine quality control (within-laboratory quality control), and Guideline chapter 4.2.3 on limit of detection, limit of determination and limit of application. Annexes 4–6 in the draft SGQAC 2005 report MCWG 2005 8.1.7/1).
- 8.8 continue to determine priorities for assistance from the Working Group on the Statistical Aspects of Environmental Monitoring (WGSAEM) with statistical analyses and develop with WGSAEM a plan for the necessary collaboration;
- 8.9 compile data (notably winter nutrients) for the North Sea (in Excel spreadsheet format) for marine chemistry, taking account of the work already being undertaken by WGMS in response to the OSPAR MON request/meeting in December 2004. The data should be compiled (averaged) for ICES rectangles where possible, for the pe-

riod 1984 to 2004 and submitted to the secure REGNS website in preparation for the REGNS Integrated Assessment Workshop to be held from 9–11 May 2005;

- 8.10 continue to report on new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants;
- 8.11 continue to report on new information concerning the analysis of dioxins and the preparation of reference materials for these compounds;
- 8.12 continue to report on new information on the monitoring and analysis of toxaphene;
- 8.13 continue to report on developments within the UNEP Global POPs Monitoring Network;
- 8.14 continue to report on new information on the impact of alkylphenols from produced water;
- 8.15 report on new information on contaminant concentrations in marine fish and other marine food products;
- 8.16 report on new information regarding perfluorinated compounds;
- 8.17 in relation to guidelines on frequency and spatial coverage of monitoring for nutrients and eutrophication parameters (phytoplankton, zoobenthos, phytobenthos), together with WGSAAEM examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];
- 8.18 with WGBEC, consider the current developments within OECD/EU regarding endocrine disruptors and whether this is adequate for the marine environment, and draft advice on any further work considered necessary to address issues specific to the marine environment [OSPAR 2005/8];
- 8.19 with BEWG and WGBEC, contribute to an assessment of the long-term impact of oil spills on marine and coastal life, based on a list of issues from OSPAR [OSPAR 2005/7];
- 8.20 review the outcome of the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-Sea Areas (WKIMON) to resolve any outstanding issues and, together with WGBEC and WGSAAEM, finalise a draft set of guidelines for integrated monitoring for OSPAR [OSPAR 2005/6];
- 8.21 report on the feasibility of merging WGMS and MCWG;
- 8.22 respond to requests from the ICES data centre.
- 8.23 review the draft MON assessment report, particularly the way in which Background Concentrations and Environmentally Acceptable Concentrations have been used.

## **9. PLENARY DISCUSSION OF DRAFT REPORT**

## **10. ANY OTHER BUSINESS**

## **11. RECOMMENDATIONS AND ACTION LIST**

## **12. DATE AND VENUE OF THE NEXT MEETING**

ACME suggested at their 2004 meeting that in 2006 MCWG should meet alongside WGMS, WGBEC and WGSAAEM at ICES Headquarters to facilitate collaboration

among the groups and also to facilitate communication with the ICES Data Centre. The dates suggested are 27–31 March 2006.

**13. CLOSURE OF THE MEETING**



### Annex 3: 2004 Terms of Reference

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- 2E03 The **Working Group on Marine Chemistry** [MCWG] (Co-Chairs: Robin Law, UK, and Jacek Tronczynski\*, France) will meet in Vigo, Spain, from 7–11 March 2005 to:
- a) continue to provide guidance and assistance relating to the development of a series of data products to illustrate eutrophication status within the ICES area;
  - b) examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];
  - c) continue to report on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe) in flatfish;
  - d) continue to report on new information on the use of membrane systems for sampling;
  - e) with WGMS and WGS AEM, develop draft advice on appropriate strategies for undertaking one-off surveys to provide new information about the following chemicals identified by OSPAR for Priority Action: 2,4,6 tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define “hot-spots” of the substance, in sediments of the OSPAR area), and short-chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy) according to specific OSPAR requests; taking into account sources and modes of dispersion/transport. The specific questions to be addressed for each substance (or groups of substances) under consideration are:
    - 1.1. indicate whether there is any new information available on presence in the marine environment that has not already been taken into account in the relevant OSPAR background document as updated by the OSPAR lead country,
    - 1.2. indicate whether the matrix (sediment, biota, water) proposed to be sampled is appropriate or whether an additional or more appropriate matrix should be included in the survey,
    - 1.3. identify whether analytical techniques are available for the relevant matrices,
    - 1.4. identify achievable detection limits, and reference materials, and
    - 1.5. determine how many stations/samples from each part of the OSPAR Convention area are necessary to address the objectives of the one-off surveys proposed, taking into account that more than one one-off survey may be required [OSPAR 2005/1];
  - f) continue to report on the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website;
  - g) report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;
  - h) continue to determine priorities for assistance from the Working Group on the Statistical Aspects of Environmental Monitoring (WGS AEM) with statistical analyses and develop with WGS AEM a plan for the necessary collaboration;

- i) compile data (notably winter nutrients) for the North Sea (in Excel spreadsheet format) for marine chemistry, taking account of the work already being undertaken by WGMS in response to the OSPAR MON request/meeting in December 2004. The data should be compiled (averaged) for ICES rectangles where possible, for the period 1984 to 2004 and submitted to the secure REGNS website in preparation for the REGNS Integrated Assessment Workshop to be held from 9–11 May 2005;
- j) continue to report on new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants;
- k) continue to report on new information concerning the analysis of dioxins and the preparation of reference materials for these compounds;
- l) continue to report on new information on the monitoring and analysis of toxaphene;
- m) continue to report on developments within the UNEP Global POPs Monitoring Network;
- n) continue to report on new information on the impact of alkylphenols from produced water;
- o) report on new information on contaminant concentrations in marine fish and other marine food products;
- p) report on new information regarding perfluorinated compounds;
- q) in relation to guidelines on frequency and spatial coverage of monitoring for nutrients and eutrophication parameters (phytoplankton, zoobenthos, phytobenthos), together with WGS AEM examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];
- r) with WGBEC, consider the current developments within OECD/EU regarding endocrine disruptors and whether this is adequate for the marine environment, and draft advice on any further work considered necessary to address issues specific to the marine environment [OSPAR 2005/8];
- s) with BEWG and WGBEC, contribute to an assessment of the long-term impact of oil spills on marine and coastal life, based on a list of issues from OSPAR [OSPAR 2005/7];
- t) review the outcome of the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-Sea Areas (WKIMON) to resolve any outstanding issues and, together with WGBEC and WGS AEM, finalise a draft set of guidelines for integrated monitoring for OSPAR [OSPAR 2005/6];
- u) report on the feasibility of merging WGMS and MCWG.

MCWG will report by 11 March 2005 on item e) for ACME and generally on 1 April 2005 for the attention of the Marine Habitat and Oceanography Committees and ACME.

### Supporting Information

Priority:	This Group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. These activities are considered to have a high priority.
Scientific Justification and relation to Action Plan:	Action Plan Nos: 2.2.2: (ToR a, and b). 2.2.3: (ToR i) 2.8: (ToR c, d, e, h, j, k, l, m, n, o, and p)

	<p>4.12: (ToR f and g)</p> <ul style="list-style-type: none"> <li>a) Data available in the ICES databank will be used to prepare illustrative data products under the OSPAR Common Procedure.</li> <li>b) This is in response to an OSPAR request.</li> <li>c) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment.</li> <li>d) These systems are being reviewed for application to monitoring of contaminants in the marine environment.</li> <li>e) This is in response to an OSPAR request.</li> <li>f) This is intended as an aid to laboratories participating in collaborative international marine monitoring programmes.</li> <li>g) This is in response to a standing request from HELCOM.</li> <li>h) This is in response to a request from ICES. This task will support long-term planning for WGSAM.</li> <li>i) This is response to a request from the REGNS group.</li> <li>j) Owing to continuing concerns about the distribution and effects of poly-brominated diphenylethers and other flame retardants in the marine environment, it is relevant to consider the results of recent research on this topic.</li> <li>k) Owing to continuing concerns about the distribution and potential health effects of dioxins and other planar compounds in the marine environment, it is relevant to consider the results of recent research on this topic.</li> <li>l) Owing to continuing concerns about the distribution and effects of toxaphene in the marine environment, it is relevant to consider the results of recent research on this topic.</li> <li>m) The development of the UNEP monitoring programme is relevant to other collaborative international monitoring programmes, and a watching brief will be maintained.</li> <li>n) Owing to continuing concerns about the possible endocrine-disrupting effects of alkylphenols derived from produced water in the marine environment, it is relevant to consider the results of recent research on this topic.</li> <li>o) Owing to continuing concerns about contaminants in marine fish and other marine food products, it is relevant to consider the results of recent research on this topic.</li> <li>p) These compounds are widespread contaminants in the marine environment, and it is relevant to consider the results of recent research on this topic.</li> <li>q) This is in response to an OSPAR request.</li> <li>r) This is in response to an OSPAR request.</li> <li>s) This is in response to an OSPAR request.</li> <li>t) This is in response to an OSPAR request.</li> <li>u) There is a considerable overlap between the ToRs for MCWG and WGMS. These Expert Groups will report to MHC on feasibility of merging for a recommendation by MHC by ASC 2005.</li> </ul> <p>MCWG provides input across the field of marine chemistry which underpins the advice given by ACME, and also supports the work of national and international collaborative monitoring programmes, e.g., within OSPAR.</p>
Resource Requirements:	The resource required to undertake activities within the framework of this group is negligible.
Participants:	The Group is normally attended by some 20–35 members.

Secretariat Facilities:	None.
Financial:	No financial implications.
Linkages to Advisory Committees:	There is a close and direct linkage with ACME.
Linkages To other Committees or Groups:	There is a close working relationship with WGMS, WGBEC, and WGS AEM.
Linkages to other Organisations:	The work of this Group is closely aligned with work being undertaken within EU/AMPS on the requirements and implementation of the Water Framework Directive. This Group provides the basis for some advice to OSPAR.
Secretariat Marginal Cost Share:	40% OSPAR, 60 % ICES.

## **Annex 4: Recommendations**

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MCWG recommended that ICES create a multidisciplinary group to be chaired by someone very familiar with assessments (Ian Davies as an example) with representation from the relevant environmental WGs to meet with the database experts and work on the overall architecture, consulting WGs (through their chairs) as needed with specific questions.

## Annex 5: Action List

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- T. Nunes (Spain) to send the collected flatfish samples and M. Haarich (Germany), and other members of MCWG, to provide new data on TCPM/Me and DDTs in flatfish (liver) samples to M. Lebeuf (Canada) by September 2005. M. Lebeuf (Canada) to analyse samples from Belgium and Spain and to prepare a report on TCPM/Me in flatfish from the data produced by the MCWG members and to present the results at the next MCWG meeting.
- Katrin Vorkamp to present details of two current studies on perfluorinated compounds to MCWG2006. The first study is a preliminary screening study of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, bird and marine mammals from Greenland and the Faroe Islands, a paper on which has been accepted for publication in Environmental Pollution. The second is a retrospective time trend study (1986-2005) on PFCs in ringed seal from East Greenland which is ongoing at NERI.
- Robin Law, Lucia Viñas, Lynda Webster, Jacek Tronczynski and Patrick Roose to prepare a paper on the assessment of the long-term impact of recent oil spills for ASC2005 theme session S.
- Katrin Vorkamp to present new data on toxaphene to MCWG 2006.
- In view of the coming changes in the management of QUASIMEME activities the MCWG Chairs will contact Wim Cofino and Jacob de Boer to arrange an update for MCWG2006.
- Jarle Klungsøyr to make a presentation on the subject of drill cuttings from offshore installations in the North Sea, and their impact.
- Patrick Roose to report on current passive sampling projects within Belgium. Jacek Tronczynski to report on current work on membrane models at the sediment-water interface.
- Robin Law to report on the small-scale UK survey for 2,4,6-tri-*tert*-butylphenol in estuaries.
- Evin McGovern to report on a current Irish survey on dioxins, CBs and other compounds.
- Patrick Roose and Robin Law to report on current studies on brominated flame retardants.
- Katrin Vorkamp to report on current studies on toxaphene.
- Marc Raemaekers to report on the findings of the current marine fish/food programme.
- Peter Lepom to report on the project PBDEs in fish liver from the North and Baltic Seas.
- All MCWG members to send comments on the ICES database questions to Patrick Roose by 15 April 2005.

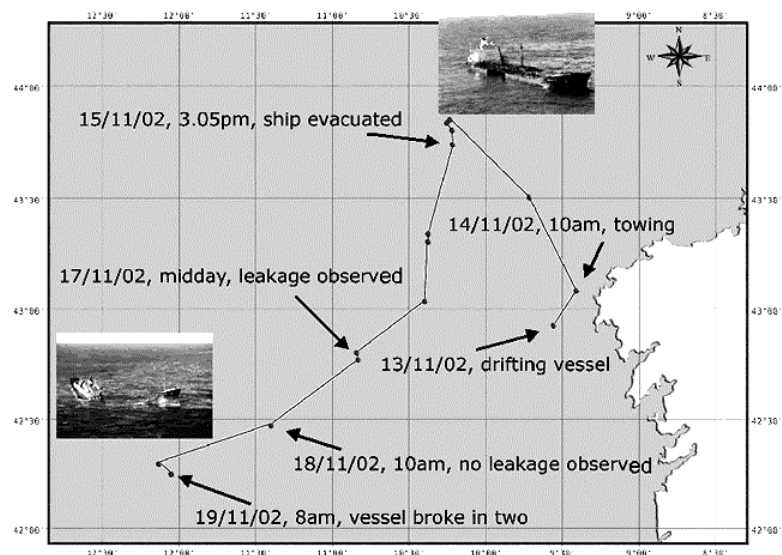
## Annex 6: Monitoring and assessment of the pollution caused by the Prestige oil spill in the Spanish coast

Viñas, L.; Franco, M.A.; Soriano, J.A; González, J.J.

### 1 Programa de Contaminación Marina. I. E. O. Centro Oceanográfico de Vigo. Cabo Estay-Canido. Vigo 36200. Spain

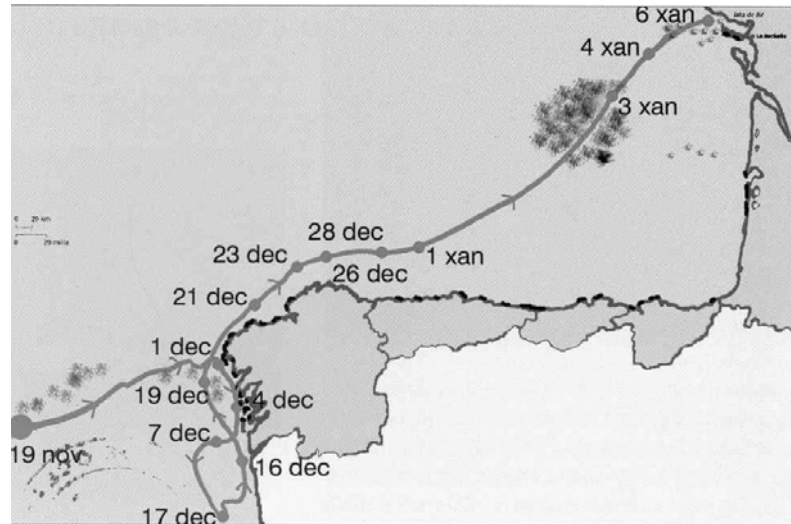
On 13 November 2002, the single-hulled, 26 year old tanker **Prestige** started leaking part of the 77 000 tonnes of heavy fuel oil that was carrying. The ship got near to the coast being as close as 4 miles from Muxía (NW Spain).

The Spanish maritime authorities ordered that the vessel should be towed off the coast out to sea. First it sailed North-west, then on 15 November its towing was turned initially south and then southwest, sailing all along the coast until the vessel broke in two and sank at about 140 nautical miles off the Spanish coast. The stern part of the Prestige sank into 3,500 metres of water. The bow part followed at about 4 p.m. Both parts are 3 km away one from another on the sea bottom.



The Prestige was leaking an estimated 125 tonnes of fuel a day for some weeks until the submarine “Nautilé” could seal the main cracks.

The fuel spilled by the tanker during her path and from the wreck was reaching the coast, with different intensities, during a wide period of time. It affected the entire Galician coast (except the inside of the Rías Bajas), the Spanish part of the Gulf of Biscay and even part of the French coast.



The Instituto Español de Oceanografía (IEO) was one of the Spanish Institutions involved in the assessment of this impact. In order to divide the work that should be done, the IEO was entrusted with the assessment of the platform and the Universities did their work in the coastal area.

There were different groups involved in this assessment: Hydrography, Fisheries, Marine Environment and Chemistry.

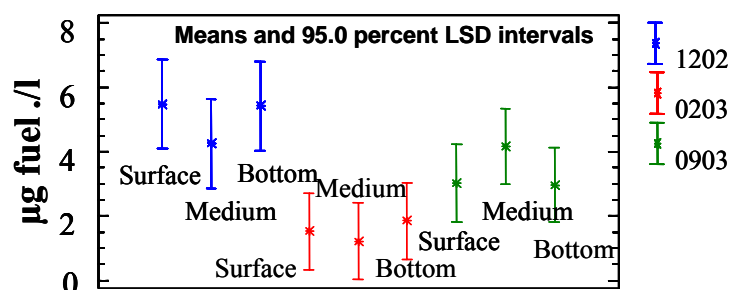
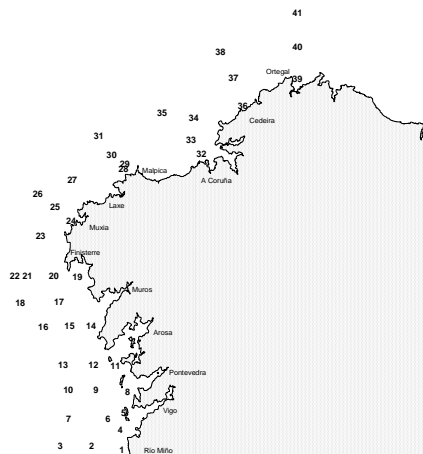
From December 2002, just 15 days after the sinking, six sampling surveys have been developed in the area affected by the fuel in order to take water and sediment samples. The data available at present date cover the period from December 2002 to September 2004.

Besides, different species of molluscs, crustaceans and echinoderms were also analysed for PAHs. The samples were taken monthly for the commercial species and every three months for the wild mussel.

## 2 Water

### 2.1 Galicia

The water samples were collected in the stations marked in the map at three different depths: subsurface (1 m below the water surface), medium and bottom (1–2 m above the sediment). The samples were taken with a Go-Flo bottle in order to avoid the contamination of the surface layer, except for the subsurface water that was collected using a stainless steel cage with the bottle inside. Mercuric chloride was added as a preservative.



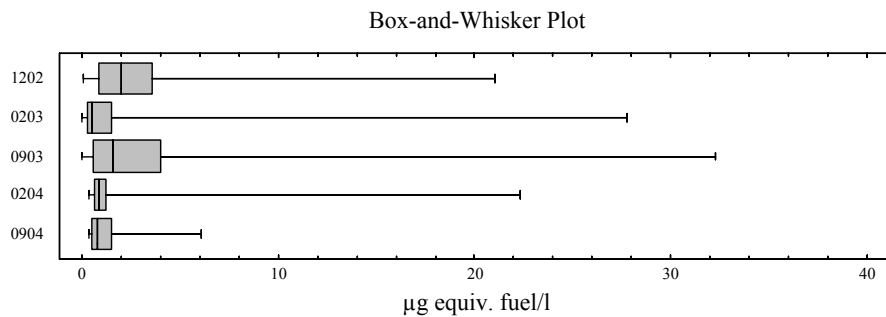


This water was extracted three times with hexane and then the total dissolved/dispersed aromatic hydrocarbons measured by spectrofluorimetry. The results were both given in chrysene equivalents and Prestige fuel equivalents.

The result of the Fisher’s test for the first three surveys is also represented in the figure above. This test has been applied to determine whether the differences in concentrations are significant or not. They are considered significant when the intervals around the media are not overlapped.

According to this, there are significant differences between the samples collected in December 2002 and February 2003, but there are no significant differences between those from February 2003 to September 2003.

Within the same sampling survey and with regard to depth, there are no significant differences among the values at the three depths studied.



The box-and-whisker plot above shows the results of the five surveys. The rectangular part of the plot extends from the lower quartile to the upper quartile, covering the central half of each distribution. The centre lines within each box show the location of the sample medians. The whiskers extend from the box to the minimum and maximum values in the sample.

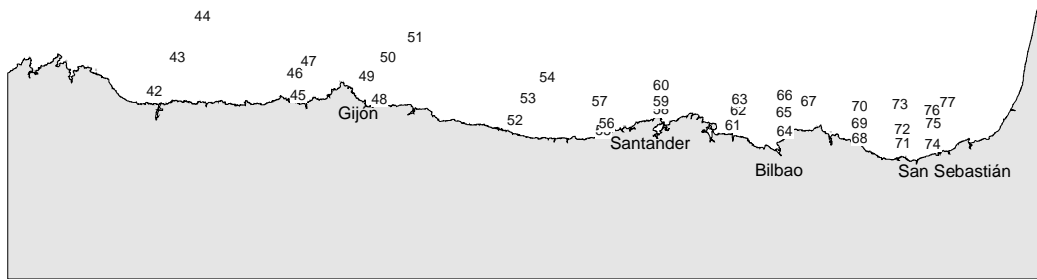
So again, a decrease in total dissolved/dispersed aromatic hydrocarbons can be seen from December 2002 to February 2003, and then in September 2003 the concentrations seem again to go up. This behaviour of higher values in September than in February can also be guessed in 2004, but considering the whole period, it can also be observed that the concentrations are decreasing as the time goes on.

It is important, however to emphasize that the concentrations were never too high, due to the nature of the fuel spilt.

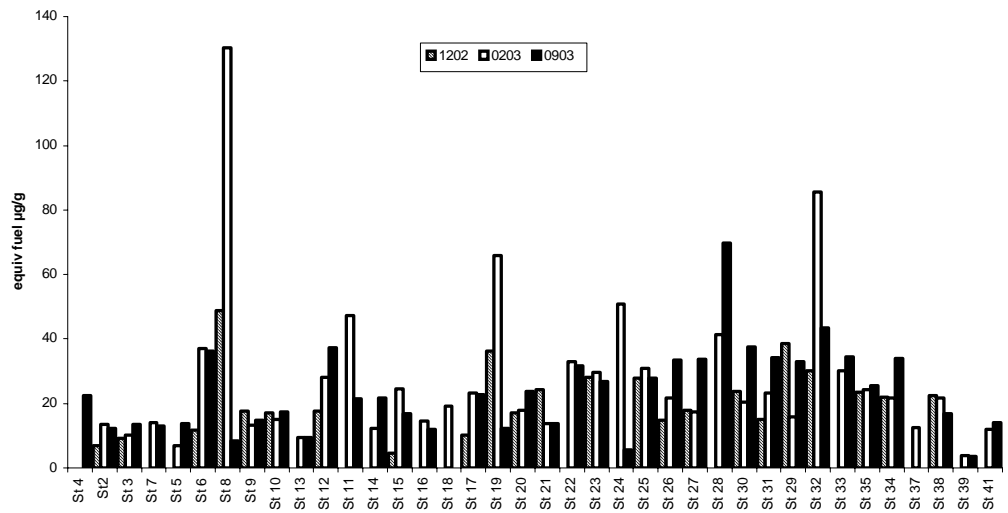
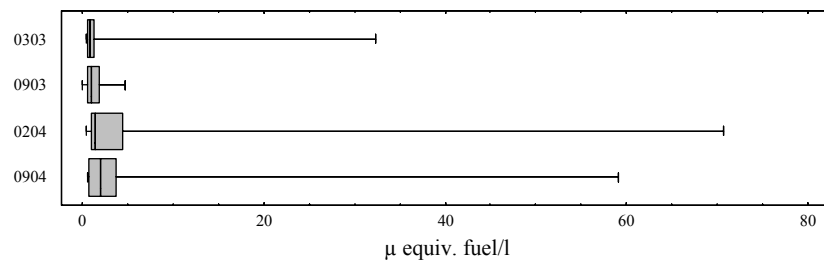
## 2.2 Gulf of Biscay

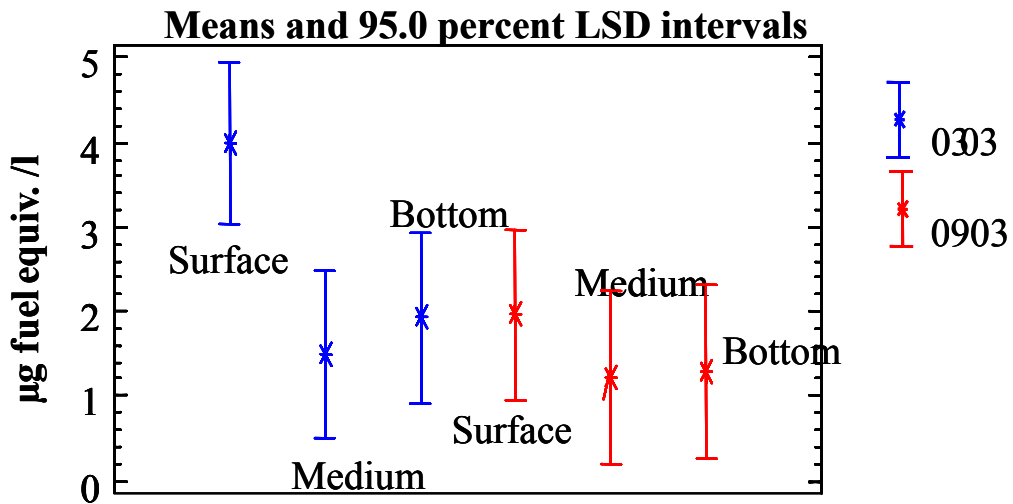
The sampling stations in this area are represented in the map shown below, and here again three depths were sampled: surface, medium and bottom

If the same type of graphs is prepared for the data obtained in this case, it is clear in the first survey that the only significant observable difference occurs in the surface concentration in March 2003, when the first slicks arrived at this area.



Box-and-Whisker Plot





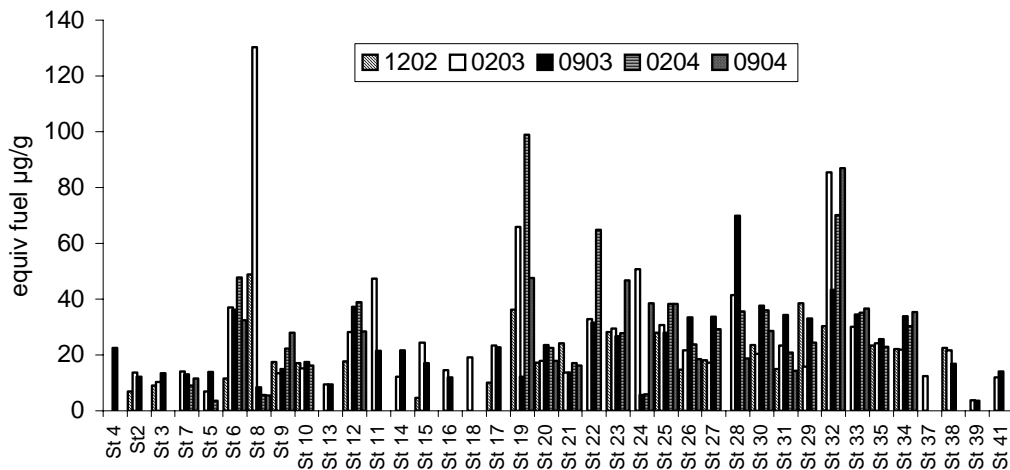
Then, if we compare the four surveys it can be seen that the values have increased for the first three surveys and then seem to be falling. In this area two effects overlap, on the one hand that of the Prestige oil spill, and on the other hand the possible effect of the heavy industrialisation in this area; therefore, the high values found is not immediately correlated with the spill.

### 3 Sediment

#### 3.1 Galicia

The sediments were sampled in the same stations as the water, and the total aromatic hydrocarbons and the individual PAH were measured in all of them. In the graph above, the fuel equivalents in  $\mu\text{g g}^{-1}$  are presented for the first three surveys. The values that are noticeable here are for station 8, situated in the mouth of the Ria de Pontevedra, where a group of islands acted as a natural barrier so preventing the entrance of the fuel oil into the Rías.

Other important points are station 19 and 28, both situated in the most affected area known as “Costa da Morte”, as well as the station situated in the mouth of Ría da Coruña.

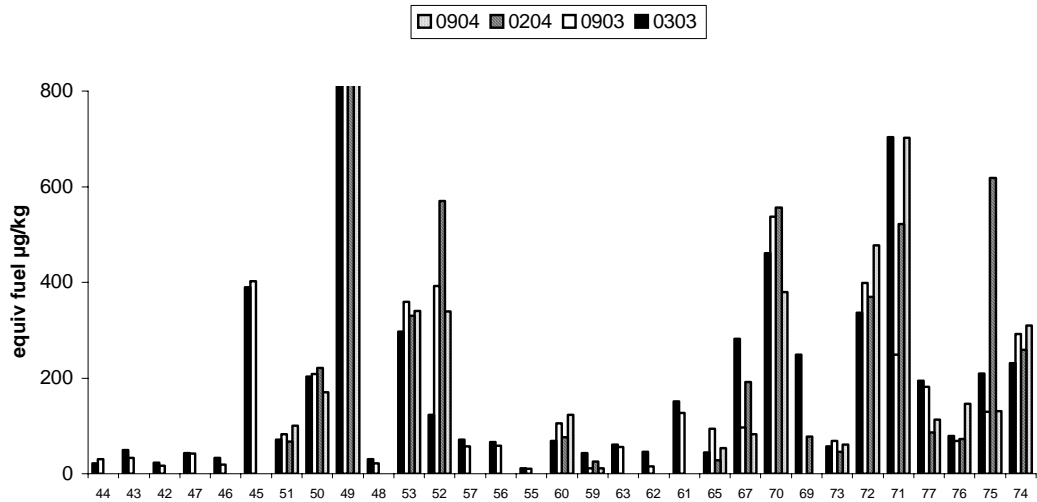


In the following surveys (4 March and 4 September), the stations that still have medium values are 19 (Finisterre) and 32 (A Coruña).

### 3.2 Gulf of Biscay

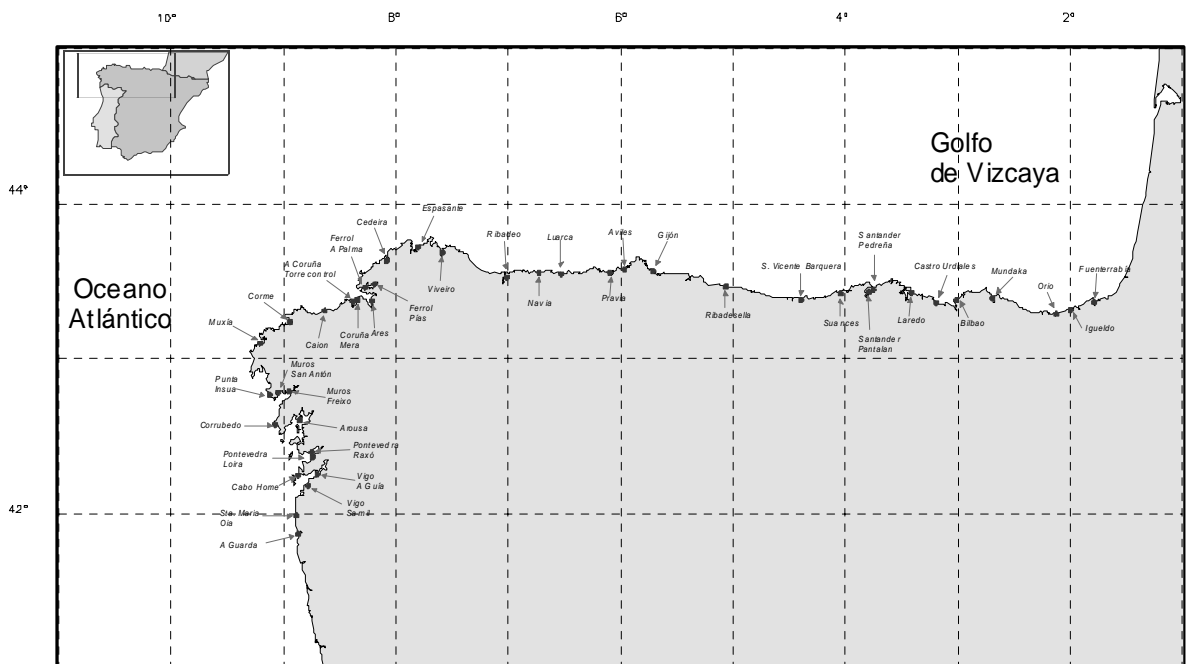
In the Gulf of Biscay the values are higher than those found in Galicia.

Here the Prestige influence is not so clear, as this area is usually more affected by other impacts (i.e., chronic impacts and very small accidental spills) than is Galicia. In fact, some of these higher values can be attributed to the different oil slicks that were reaching this coast during 2003, but some others represent a normal, chronic level of contamination in the area. Besides, the area immediately offshore of the País Vasco is a sedimentation area where the contaminants are usually accumulated



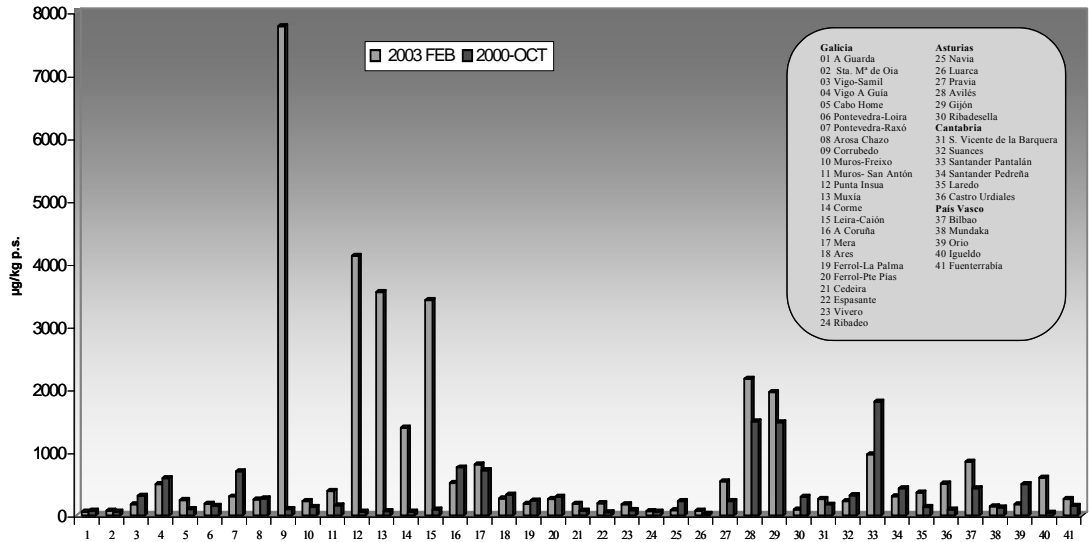
## 4 Biota

### 4.1 Blue mussel



The monitoring that is carried out by the Instituto Español de Oceanografía on a regular basis in this area, includes the forty points represented in the map above.

As these previous data were available, the same sampling points were established for this study and wild mussels were collected there in February and November 2003, April, July and November 2004



The samples are collected and transported to the lab where the shells of the mussels are taken off, and then the soft tissue is pooled. This pool is then analysed by HPLC-FL for determining the concentrations of 13 individual PAHs.

If we compare the data from February 2003 with those obtained in 2000, the values in the area in the Gulf of Biscay are similar to those measured in the previous samplings.

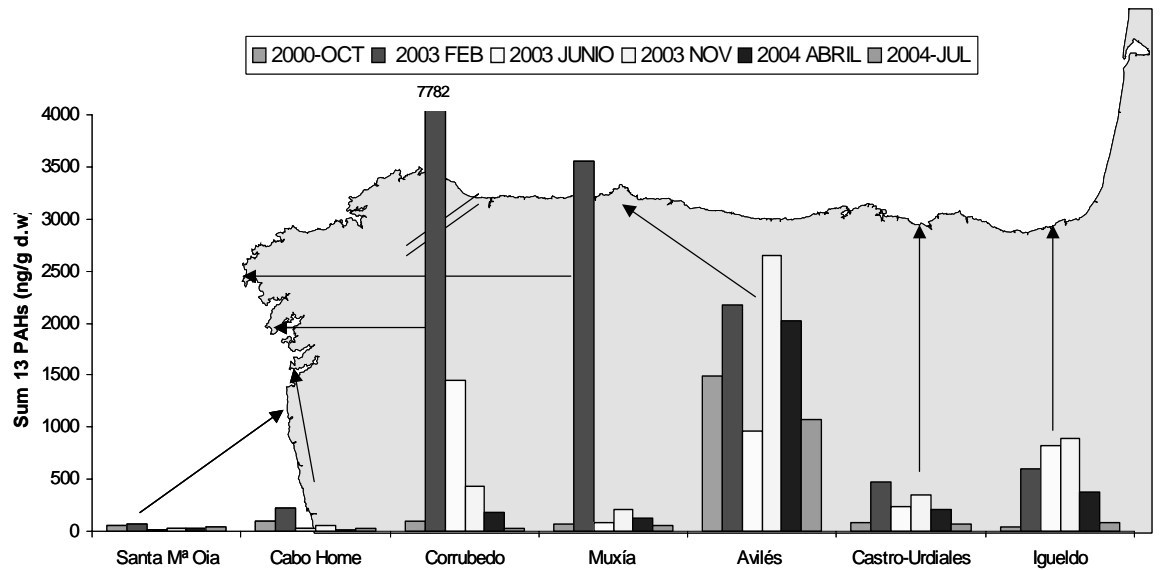
However, the Costa da Morte (stations 12–15), which was the cleanest area in the 2000 sampling, in February showed the highest concentrations, being clearly affected by the fuel spill.

In the figure below, it is possible to see the different behaviours for the PAHs evolution.

In this graph six samplings are represented: the first one is from 2000, before the Prestige oil spill, and is representative of the “normal” situation of the area.

For the first point (Sta M<sup>a</sup> de Oia) it can be seen that it has not been affected and the concentrations are maintained through the years. In Cabo Home, that was slightly affected, an increase can be observed for the sampling in February 2003 that quickly reached the normal concentrations with time. Then we have two points in the most affected areas, Corrubedo and Muxía that before the Prestige accident had very low values: these increased to a maximum in February 2003, and then were falling to a normal value during the following year.

A different situation is found in Avilés, whose values do not seem to be affected by the Prestige spill, but by other circumstances. Finally, Castro Urdiales and Igueldo apparently received the Prestige influence during 2003. In fact, some fuel was entering this area during the summer of 2003.



## 4.2 Fish

Fish were also analysed because of the social and political pressure, although they are known to quickly metabolise PAHs.

Therefore, fish (monkfish, hake, blue whiting, megrim, mackerel, horse mackerel and sardine) were sampled and the edible parts were analysed for individual PAHs.

The Fishing authorities had established some rules to determine whether the fish or shellfish could be either extracted or commercialised. These rules fixed 6 individual PAHs (BaA, BbF, BkF, BaP, dBahA, IP) to be analysed, and the sum of the six should not exceed the value of  $20 \mu\text{g kg}^{-1}$  (dry weight) for fish and  $200 \mu\text{g kg}^{-1}$  (d w) for shellfish.

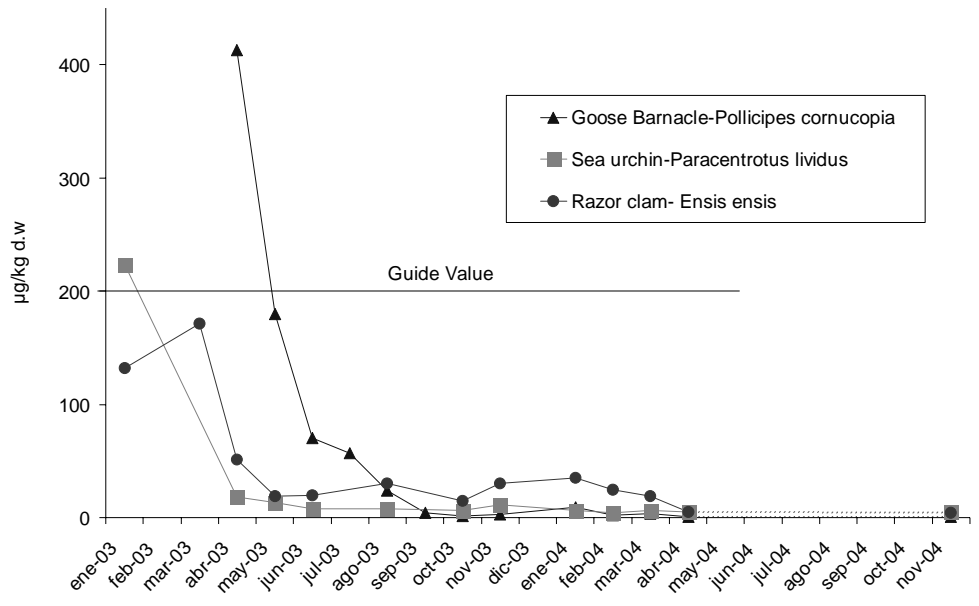
The PAHs concentrations in the fish samples not only were always below the guideline value, but were always below the detection limit for the analytical method used to quantify these 6 PAHs.

Other commercial species

In addition, some shellfish species were studied monthly from January 2003: razor clam, purple sea urchin and goose barnacle.

In the graph below, the values for the sum of the 6 PAHs are represented and compared with the guideline value.

It can be seen that in the initial stages following the spill the concentrations exceeded this guideline value, but in a few months they reached what can be considered a “normal” situation.



## **Annex 7: Review note on 2,4,6-tri-tert-butylphenol.**

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MCWG 2005 8.1.5/6

### **Review note on 2,4,6-tri-tert-butylphenol**

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#### **Introduction**

2,4,6-Tri-*tert*-butylphenol is a chemical which is included on the OSPAR list of chemicals for priority action. The UK is acting as lead country, and has produced a draft background document for OSPAR (SIME 02/2/15-E). This noted that there are currently no measured data available for the marine environment, and no information on inputs. Predicted Environmental Concentrations (PECs) of tens of nanograms per litre in water, and tens to hundreds of micrograms per kilogram in sediments were cited. In addition, appreciable bioaccumulation is expected for this compound (estimated bioconcentration factor 3,280). According to the OSPAR background document, 2,4,6-Tri-*tert*-butylphenol (CAS registry number 732-26-3) is produced in relatively small quantities in the EU (10 tonnes per annum or less) and is used as a chemical intermediate for the production of antioxidants used in rubber and plastics. A spokesman for the European Association of the Rubber Industry has informed us that there is only one UK producer of 2,4,6-tri-*tert*-butylphenol, a petroleum additives manufacturer located in Bracknell, Berkshire. His view was that this compound is not used by the rubber industry. One outstanding question within the OSPAR document was the possible use of 2,4,6-tri-*tert*-butylphenol by the offshore oil and gas industry. A search of the Offshore Chemicals Notification Scheme database made on 23 February 2005 has confirmed that this compound is not present in any products currently licensed for use on the UK Continental Shelf.

#### **Initial UK Survey**

As the UK is the lead country for this compound within OSPAR, CEFAS has been asked to conduct some method development and a small-scale initial survey during January–March 2005. Our plan initially was to identify sites of production and use and to target sampling around these as a “worst-case” scenario, through contact with the UK Chemical Industries Association and the rubber and plastics manufacturers’ trade associations. Unfortunately they were unable to help on this occasion, but for future planning purposes the European Chemical Industry Council (CEFIC) may be worth contacting. As an alternative, we plan to analyse surface sediments (ca. 25 samples) from a range of major UK industrial estuaries (Belfast Lough, the Burbo Bight (inner Liverpool Bay), and the Rivers Tees, Tyne, Wear, Mersey, Humber, Thames and Dee).

The analytical method being used is a modification of an established alkylphenols method targeted mainly at octyl- and nonylphenols and their ethoxylates. 5 to 10 g of dried sediment is extracted on a wrist-action shaker for 10 minutes with 10 % acetic acid in ethyl acetate, the mixture centrifuged and the supernatant decanted. The extraction is repeated twice more and the extracts combined. The solvent is evaporated using a rotary-film evaporator, and water added to the acid remaining. The samples are then cleaned up using StrataX solid-phase extraction cartridges, with a 30 % methanol in water wash before elution with methanol and dichloromethane. The sample extracts are then evaporated to dryness and made up to the required volume (1 ml) with dichloromethane and transferred to GC injection vials. The samples are analysed by GC/MS operated in full scan electron-impact ionisation mode, scanning



from 50–350 Daltons. Sample injection is via a cold on-column injector system at 35 °C. This temperature is held for 2 minutes and the oven temperature programmed first to rise to 100 °C at 10 degrees per minute, then to 170 °C at 2 degrees per minute, and finally at 10 degrees per minute to 300 °C. Average recoveries were 105% for octylphenol, 101% for nonylphenol, and 60 % for 2,4,6-tri-*tert*-butylphenol. Whilst less than ideal, this level of recovery was felt to be adequate for the purposes of the initial survey, which is primarily aimed at presence/absence.

### **Proposed OSPAR One-off Survey**

Within the background document choices for actions and/or measures are given. The key for these is to identify sites within OSPAR countries at which 2,4,6-tri-*tert*-butylphenol is being used, so that samples can be taken adjacent to these facilities. Sediment samples have been chosen as the appropriate matrix, and this choice is endorsed. Sediments will to a large degree integrate inputs over time, and the concentrations of 2,4,6-tri-*tert*-butylphenol should be higher than in water and so easier to measure. Concentrations in water are also likely to be highly variable due to variations in use and discharge, tidal state, amount of recent rainfall, and other factors. If significant concentrations are found at these sites, or within the initial, broader-scale, UK survey, then a more widespread survey will need to be devised. For a compound with such a small level of production and use, however, it seems wasteful of resource which could be deployed in other studies to begin with a large-scale survey across the whole OSPAR area.

## **Annex 8: Review note on short chain chlorinated paraffins.**

### **Short Chain Chlorinated Paraffins (SCCPs) – Analysis and Occurrence in the Marine Environment**

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#### **1 Introduction**

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Risk assessment for short-chain chlorinated paraffins has been completed under Regulation 793/1993/EEC<sup>1</sup> in 1999. SCCPs were classified as dangerous to the environment, being very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. The Commission has adopted a recommendation to take measures to restrict the use of SCCPs, in particular in metal working fluids and leather finishing products in order to protect the aquatic environment<sup>2</sup>. Moreover, SCCPs have been added to the list of priority substances of the European Water Framework Directive<sup>3,4</sup> and categorised as priority hazard substance for which specific measures have to be taken.

This review focuses on information about the occurrence of SCCPs in the marine environment, which has been published upon completion of the European Risk Assessment Report and methods for their analysis. With regard to general information, physico-chemical properties as well as production and use figures a summary was given. As regards exposure assessment and toxicological data we refer to the European Risk Assessment Report<sup>1</sup> and previous reviews<sup>5-7</sup>. The intention was to summarise the current knowledge of the occurrence of SCCPs in marine waters and sediments including data from estuaries and harbour areas as well as in marine fish species, mammals, invertebrates, and seabirds. Data were critically evaluated with regard to their quality and comparability. Moreover, an overview on analytical methods for detection and quantification of SCCPs in water, sediment and biota samples was presented.

## 2 Substance information and physico-chemical properties

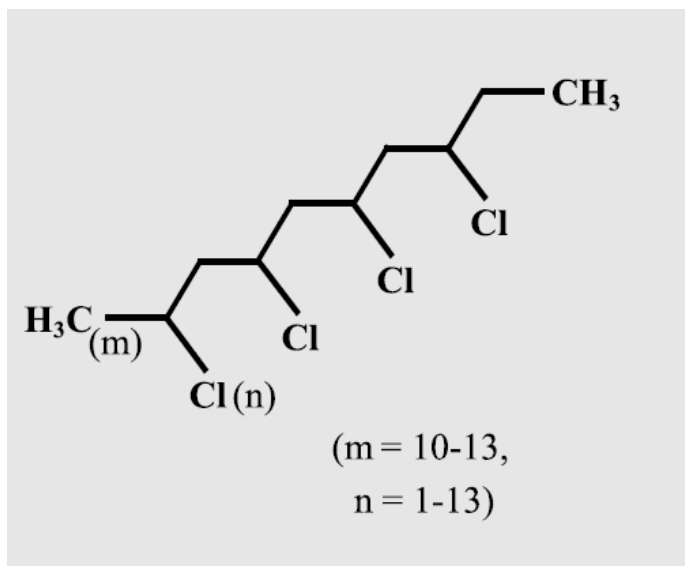


Figure 2.1. Structural formula of C<sub>10-13</sub> chlorinated paraffins

The following substance information has been given in the European Union Risk Assessment Report for SCCPs<sup>1</sup>

CAS No:	85535-84-8
EINECS No:	287-476-5
IUPAC Name:	Alkanes, C <sub>10-13</sub> , chloro
Molecular formula:	C <sub>m</sub> H <sub>(2m-n+2)</sub> Cl <sub>n</sub> , where m=10-13 and n=1-13
Molecular weight:	320-500
Synonyms:	alkanes, chlorinated; alkanes (C <sub>10-13</sub> ), chloro-(50–70%); alkanes (C <sub>10-12</sub> ), chloro-(60%);

chlorinated alkanes, chlorinated paraffins; chloroalkanes;

chlorocarbons; polychlorinated alkanes; paraffins-chlorinated.

There is a range of commercially available C<sub>10-13</sub> chlorinated paraffins, commonly referred to as short chain chlorinated paraffins (SCCPs). They are usually mixtures of different carbon chain lengths and different degrees of chlorination, although all have a common structure in that no secondary carbon atom carries more than one chlorine. The physical and chemical properties of the SCCPs (Table 2.1) are determined by the chlorine content (typically 49-70% for commercial substances). There are a wide number of possible chlorinated paraffins (of different chain length, degrees of chlorination and position of the chlorine atoms along the carbon chain) present in any given commercial product.

**Table 2.1: Physico-chemical properties of some SCCPs taken from<sup>1</sup>.**

PROPERTY	CHLORINE CONTENT (% WT)	VALUE	REMARKS
Physical state (at npt)	49–70	-	clear to yellowish liquid
Pour point	49 70	-30.5 °C +20.5 °C	
Boiling Point (at npt)		> 200 °C	decomposition with release of hydrogen chloride
Density (at 25 °C)	49–70 52–70	1.2–1.6 g/cm <sup>3</sup> 1.3–1.6 g/cm <sup>3</sup>	
Vapour pressure (at 40 °C)	50	0.021 MPa	
Water solubility (at 20 °C)	59	0.15–0.47 mg l <sup>-1</sup>	with partial hydrolysis
Log K <sub>ow</sub>	49 60 63 70 71	4.39–6.93 4.48–7.38 5.85–7.14 5.47–7.30 5.68–8.69 5.37–8.01	measured by HPTLC method except which was measured by slow stirring method
Flash point	50 56	166 °C 202 °C	closed cup
Autoflammability		not stated	decomposes with release of hydrogen chloride above 200 °C
Explosivity		not explosive	
Oxidising properties		none	

### 3 Production and use in the European Community

Production figures for SCCPs are hardly to find in the literature. Based on EURO-Chlor information, the total EU production volume was 15,000 t or less in 1994 and about 4,000 t in 1998<sup>8</sup>. It is thought that the current level is probably lower than this, particularly due to reduction in uses of SCCPs, especially in the metalworking industry. SCCPs are currently manufactured by two companies in the EU (INEOS CHLOR and CAFFARO) under a variety of trade names. The major use of SCCPs is as an extreme pressure additive in metal working fluids. These fluids are used in a variety of engineering and metal working operations such as drilling, machining/cutting, drawing and stamping. Other important uses were as plasticiser in paints, coatings and sealants, as flame retardant in rubbers and textiles, and in leather processing (fat liquoring).

### 4 Levels of SCCPs in the marine environment

Data already discussed in the European Union Risk Assessment Report for SCCPs<sup>1</sup> published 2000 was summarised in Tables 4.21-4.2.3.

#### 4.1 Sea Water

No SCCPs were detected in two sea water samples from the North Sea (LOQ <0.2 ng l<sup>-1</sup>) by Oehme *et al.* (unpublished data).

#### 4.2 Marine Sediments

Surface sediment samples collected in 1997 and 1998 in the Canadian Arctic were analysed for SCCPs<sup>7</sup>. Sediment concentrations ranged from 5 to 77 µg kg<sup>-1</sup>. A clear decreasing trend

was observed from south (Barrow Strait) to north (Peary Channel) and western Arctic sediment (M'Clure Strait/Viscount Melville) concentrations were lower than those in the eastern Arctic (Nanisivik/Lancaster Sound). Lower chlorinated C<sub>10</sub> and C<sub>11</sub> formula groups predominated in the sediment relative to that of water from the same region and air from high Arctic suggesting that these two groups may be less susceptible to microbial degradation.<sup>7</sup>

In a recent study Hüttig *et al.*<sup>9</sup> reported SCCP concentrations in marine sediments collected at ten locations in the Baltic and North Sea in 2001 and 2002. Total SCCP concentrations found in samples from the North Sea were in the range 5 to 27 µg kg<sup>-1</sup> dry weight, except one sample collected in the German Bight near to the River Elbe estuary, in which 112 µg kg<sup>-1</sup> dry weight were measured. Concentrations in samples from the Baltic Sea ranged from 108 to 377 µg kg<sup>-1</sup> dry weight. When normalizing the results to organic carbon content total SCCP concentrations were 3.7–9.1 mg kg<sup>-1</sup> organic carbon in sediments from the North Sea and 2.1–8.4 mg kg<sup>-1</sup> organic carbon for samples from the Baltic Sea. This indicates a diffuse input of SCCPs to the marine environment and that differences seen in dry weight concentrations were mainly due to variation in organic carbon content of the sediments. SCCP levels in sediment samples taken in the same area in 2003 (n=8) were 15 to 34 µg kg<sup>-1</sup> dry weight and 3.4 to 47.1 mg kg<sup>-1</sup> organic carbon, respectively (Hüttig *et al.*, unpublished results). For the purpose of comparison, the authors analysed also a few sediment samples from the River Seine estuary, France (n=3), the Hamburg harbour area, Germany (n=3), Tromsø, Norway (n=3) and SPM from the North Sea (n=3). SCCPs were found in all samples and total concentrations ranged from 71 to 293 µg kg<sup>-1</sup> dry weight and 2.7 to 10.9 mg kg<sup>-1</sup> organic carbon, respectively (Hüttig *et al.*, unpublished results), except one sample from the River Seine estuary, in which the concentration was 120 mg kg<sup>-1</sup> organic carbon. This result is questionable due to the very low organic carbon content of the sediment (0.07 %).

Sediment samples (0–2 cm) were collected at four locations in the Drammensfjord, Norway, one in the main basin and three close to industrial sites and analysed for short and medium chain chlorinated paraffins<sup>10</sup>. Total SCCP concentrations were in the range 94 to 1,300 µg kg<sup>-1</sup> dry weight with the highest levels close to a wharf. Very high MCCP levels (7,500 µg kg<sup>-1</sup> dry weight) were seen in a sediment sample close to a floating dock.

**Table 4.2.1: Polychlorinated paraffins in the marine environment - Levels in marine waters including estuaries and harbour areas.**

LOCATION	NUMBER OF SAMPLING SITES	NUMBER OF SAMPLES	CONCENTRATION* [µg L <sup>-1</sup> ]	REFERENCE
Remote from Industry				
Irish Sea	7	not specified	<0.5–1.0	Campbell and McConnell 1980 <sup>11</sup>
Barmouth Harbour	1	not specified	0.5	
Menai Straights	1	not specified	0.5	
Tremadoc Bay	1	not specified	<0.5	
North Minch	3	not specified	<0.5–0.5	
Goile Chroic	1	not specified	0.5	
Sound of Taransay	1	not specified	4.0	
Sound of Arisaig	1	not specified	1.0	
North Sea	3	not specified	<0.5	
Firth of Lorne	1	not specified	0.5	
Firth of Clyde	2	not specified	<0.5–0.5	
Close to Industry				
Humber estuary	3	not specified	1.0–3.0	Campbell and McConnell 1980 <sup>11</sup>
Mersey estuary	3	not specified	3.0–4.0	
Wyre estuary	12	not specified	<0.5–1.5	
Humber Estuary (Hull Docks)		not specified	0.12–1.45 SCCP 0.62–3.75 MCCP	ICI 1992 cited in <sup>1</sup>

\*Intermediate chain length chlorinated paraffins (C10-C20)

**Table 4.2.2: Polychlorinated paraffins in the marine environment - levels in marine sediments including estuaries and harbour areas.**

LOCATION	NUMBER OF SAMPLING SITES	NUMBER OF SAMPLES	CONCENTRATION* [ $\mu\text{G KG}^{-1}$ WET WEIGHT]	REFERENCE
Remote from Industry				
Irish Sea	7	not specified	<0.50–100	Campbell and McConnell 1980 <sup>11</sup>
Barmouth Harbour	1	not specified	500	
Menai Straights	1	not specified	<0.50	
Tremadoc Bay	1	not specified	<0.50	
North Minch	3	not specified	<0.50	
Goile Chroic	1	not specified	<0.50	
Sound of Taransay	1	not specified	<0.50	
Sound of Arisaig	1	not specified	<0.50	
North Sea	3	not specified	<0.50–50	
Close to Industry				
Humber Estuary	3	not specified	2,000	Campbell and McConnell 1980 <sup>11</sup>
Mersey Estuary	4	14	<0.50–8,000	
Wyre Estuary	12	not specified	<0.50–1,600	
Hamburg Harbour		not specified	17 <sup>a)</sup>	Ballschmiter <i>et al.</i> 1994 cited in <sup>1</sup>
Hamburg Harbour		not specified	25,000–125,000 <sup>a)</sup>	Krautter, 1996 cited in Lahaniatis 2001 <sup>12</sup>
Rotterdam Harbour		not specified	37,000–49,000 <sup>a)</sup>	

\* Intermediate chain length chlorinated paraffins (C<sub>10</sub>-C<sub>20</sub>)

<sup>a)</sup> Total content of SCCPs in  $\mu\text{g kg}^{-1}$  dry weight

**Table 4.2.3: Polychlorinated paraffins in the marine environment - levels in marine organisms.**

LOCATION	NUMBER OF SAMPLES	SPECIES	TISSUE	CONCENTRATION [µG KG <sup>-1</sup> WET WEIGHT]		REFERENCE
				Mean	Range	
United Kingdom	6	Plaice ( <i>Pleuronectes platessa</i> )	not specified	30	<50–200	Campbell and McConnell 1980 <sup>11</sup>
(no exact location)	4	Pouting ( <i>Trisopterus luscus</i> )	not specified	100	<50–200	
	9	Mussel, ( <i>Mytilus edulis</i> )	not specified	3,250	100–12,000	
	4	Grey seal ( <i>Halichoerus grypus</i> )	blubber, liver	75	40–100	
	not specified	Guillemot ( <i>Uria aalge</i> )	liver		100–1,100	
	not specified	Herring gull ( <i>Larus argentatus</i> )	liver		200–900	
	23	<b>Seabird Eggs*</b>			<50–2,000	
Bothnian Sea	100	Herring ( <i>Clupea harengus</i> )	muscle	1,400**		Jansson <i>et al.</i> 1993 <sup>13</sup>
Baltic Proper	60		muscle	1,500**		
Skagerrak	100		muscle	1,600**		
Kongsfjorden, Svalbard	7	Ringed Seal ( <i>Pusa hispida</i> )	blubber	130**		
Baltic Sea	8	Grey Seal ( <i>Halichoerus grypus</i> )	blubber	280**		

\* Species : Cormorant (*Phalacrocorax carbo*), Gannet (*Morus bassanus*), Great Skua (*Stercorarius skua*), Guillemot (*Uria aalge*), Kittiwake (*Rissa tridactyla*), Puffin (*Fratercula arctica*), Manx Shearwater (*Puffinus puffinus*), Razorbill (*Alca torda*), Shag (*Phalacrocorax aristotelis*)

\*\* Concentrations in µg kg<sup>-1</sup> lipid weight



### 4.3 Marine Fish and mussels

Whole fish samples (herring, bluefish, sardine, silverside) or fish fillets (cod, shark, angler, sole) of various origins obtained from the market were analysed for SCCPs by Coelhan<sup>14</sup>. SCCPs were detected in about one third of the fish samples and total concentrations ranged from 326 to 1217 ng g<sup>-1</sup> lipid weight (Table 4.3.1). Polychlorinated decanes predominated in five out of eight samples, while in the others, polychlorinated undecanes or polychlorinated dodecanes had the highest proportion.

**Table 4.3.1: Concentrations (ng g<sup>-1</sup> lipid weight) of short chain chlorinated paraffins in market fish (Coelhan<sup>14</sup>).**

SPECIES	ORIGIN	YEAR	CP 10	CP11	CP12	CP13	Σ SCCPs
Bluefish	Maramara Sea	1996	426	156	82	61	725
Silverside	Maramara Sea	1996	43	40	169	74	326
Sardine	Mediterranean Sea	1997	411	486	180	140	1217
Angler	Atlantic	1997	192	75	44	n.d. <sup>a)</sup>	311
Herring	North Sea	1996	132	52	55	11	250
Cod	Atlantic	1997	538	64	95	30	727
Shark	Atlantic	1997	325	175	166	19	685
Sole	Atlantic	1997	244	228	310	136	918

a) not determined

In a further study Lahaniatis *et al.*<sup>15</sup> analysed market fish of various origins for short and medium chain chlorinated paraffins (Table 4.3.2). Concentrations of SCCPs and MCCPs were 88–237 and 39–85 ng g<sup>-1</sup> lipid weight, respectively. Total SCCP levels seen in this study were much lower than those reported by Coelhan<sup>14</sup>.

**Table 4.3.2 Concentrations (ng g<sup>-1</sup> lipid weight) of short chain chlorinated paraffins in market fish (Lahaniatis *et al.*<sup>15</sup>)**

SPECIES	ORIGIN	YEAR	LIPID (%)	CP 10	CP11	CP12	CP13	Σ SCCPs
Sprat	England	1993	5.8	23	41	27	91	182
Redfish	Norway	1994	5.4	13	34	35	33	115
Salmon	Chile	1994	15.4	26	30	24	8	88
Herring	Norway	1994	14.5	18	51	22	44	135
Mackerel	North Sea	1996	13.2	16	33	50	7	106
Halibut	Norway	1994	12.7	32	135	39	31	237
Sardine	Greece	1999	14.4	15	73	30	47	165

Reth *et al.*<sup>16</sup> examined pooled livers samples (n=1-5) from three different fish species, North Sea dab (*Limanda limanda*), cod (*Gadus morhua*) and flounder (*Platichthys flesus*) collected at seven locations in the Baltic and five locations in the North Sea for short and medium chain chlorinated paraffins. SCCPs were found in all fish liver samples. MCCPs were also present except in the sample collected at Outer Firth of F ourth, Scotland (NS4).

The calculated average chlorine contents of SCCPs in the fish liver samples ranged from 59 to 62 % and were close to that of the standard used for calibration (60±1%, n=7). Total SCCP and MCCP concentrations are summarised in Table 4.2.1. The total SCCP concentrations varied between 19 and 286 ng g<sup>-1</sup> wet weight, MCCP levels (25–260 ng g<sup>-1</sup> wet weight) were in the same range. Within-species variation in concentrations of samples collected at various locations was one order of magnitude for cod and North Sea dab, whilst SCCP levels in flounders sampled at three locations in the Baltic Sea were fairly similar.

**Table 4.3.3:  $\Sigma$  SCCP and  $\Sigma$  MCCP concentrations (ng g<sup>-1</sup> wet weight), lipid content (%) in liver samples collected in the Baltic and North Sea (Reth *et al.*<sup>16</sup>).**

SAMPLING LOCATION	SPECIES	NUMBER OF POOLED LIVERS	LIPID CONTENT (%)	$\Sigma$ SCCP (NG G <sup>-1</sup> W.W.)	$\Sigma$ MCCP (NG G <sup>-1</sup> W.W.)
	<b>Cod</b>				
Baltic OS1		5	49	143	106
Baltic OS6		1	49	19	25
Baltic OS7		1	52	42	
North Sea NS3		5	44	90	75
	<b>Flounder</b>				
Baltic OS2		1	33	127	206
Baltic OS3		2	34	99	31
Baltic OS4		2	33	221	115
	<b>North Sea Dab</b>				
Baltic OS5		5	41	48	130
North Sea NS1		5	50	169	123
North Sea NS2		5	52	286	260
North Sea NS4		5	54	26	<10
North Sea NS5		5	32	37	221

The reported formula group abundance profiles of SCCPs in fish livers differed from sample to sample, but usually resembled that of technical mixtures with highest abundances of C<sub>11</sub> and C<sub>12</sub> formula groups. Samples collected in the German Bight (NS1) influenced by discharges from the River Elbe showed a shift to C<sub>13</sub> formula group. Samples collected at the Dogger bank (NS2 and NS3) showed a predominance of the shorter carbon chain length congeners, i.e., the C<sub>10</sub> and C<sub>11</sub> formula groups. The authors suggested that contamination of these congeners to the North Sea might be caused by long range atmospheric transport.

Reth *et al.* (unpublished data) screened cod samples from the European Arctic for total CPs (sum of short and medium chain chlorinated paraffins) by GC-MS/MS. A few samples were separately analysed by GC-ECNI-MS to quantify SCCPs and MCCPs. Cod samples were taken at Akureyri (northern coast of Iceland, n=2), at Vestammaeyar (southern coast of Iceland, n=2) and at the Lofoten Islands, Norway (n=2), Total SCCP concentrations in cod livers were in the range 11 to 70 ng g<sup>-1</sup> wet weight (n=6, median=53 ng g<sup>-1</sup> wet weight) and 28 to 143 ng g<sup>-1</sup> lipid weight, respectively. Due to the limited number of samples assessment of the results is difficult, but total SCCP levels in cod liver from the European Arctic seem to be in the same range as those in cod from North and Baltic Sea (range 19–90 ng g<sup>-1</sup> wet weight, median= 63 ng g<sup>-1</sup> wet weight)<sup>16</sup>.

Borgen *et al.*<sup>17</sup> analysed cod liver (n=4) and blue mussel (n=3) samples from three different parts of the Oslofjord by GC-ECNI-HRMS to indicate a spatial distribution of SCCP accumulation in these species. The concentrations of SCCPs found in cod as well as mussels indicate a higher contamination level in samples from the inner part of the Oslofjord (350-750 ng g<sup>-1</sup> wet weight in cod liver and 130 ng g<sup>-1</sup> wet weight in mussel) than in those from the outer part (23-25 ng g<sup>-1</sup> wet weight in cod and 14 ng g<sup>-1</sup> wet weight in mussel). Although the number of samples was very limited, the results were inline with previous studies on PCBs and brominated flame retardants in cod liver from the Oslofjord.

Schlabach *et al.*<sup>10</sup> examined fish samples from the Drammensfjord, Norway, including marine species such as cod (*Gadus morhua*) and flounder (*Platichthys flesus*) for their contents of chlorinated paraffins. The total SCCP concentrations in livers of cod and flounder were 30 ng g<sup>-1</sup> wet weight and 41 ng g<sup>-1</sup> wet weigh, respectively. Cod liver concentrations were in the same range as those found by Reth *et al.*<sup>16</sup> in cod liver from the Arctic and the North and

Baltic Sea, whilst SCCP concentrations in flounders from Norway were two to five times lower than those measured in samples from the Baltic Sea<sup>16</sup>.

#### 4.4 Seabirds

A very limited number of seabird samples, little auk (*Alle alle*, n=2), kittiwake (*Rissa tridactyla*, n=2) and glaucous gull (*Larus hyperboreus*, n=2) collected at Bear Island, Norway, were analysed for total CPs (sum of short and medium chain chlorinated paraffins), by GC-MS/MS and partly for SCCP using GC-ECNI-MS (Reth *et al.*, unpublished data). Total SCCP concentrations in liver and muscle tissue of little auk and kittiwake varied considerably and were lower in muscle (5–16 ng g<sup>-1</sup> wet weight) than in liver (6–88 ng g<sup>-1</sup> wet weight). For glaucous gull samples only sum of SCCP and MCCP concentrations (36–123 ng g<sup>-1</sup> wet weight) were reported.

#### 4.5 Marine Mammals

Marine mammals from various regions of the Arctic and the St. Lawrence River estuary were examined for levels of SCCPs by Tomy *et al.*<sup>18</sup>. Respective mean wet weight total SCCP concentrations in the blubber of beluga whales (*Delphinapterus leucas*) from Saqqaq and Nuusuaq, western Greenland, were 0.23±0.02 (n=2) and 0.164±0.06 µg g<sup>-1</sup> wet weight (n=2), similar to that in beluga from the Mackenzie Delta in the western Canadian Arctic 0.21±0.08 µg g<sup>-1</sup> wet weight (n=3). SCCP levels were higher in beluga blubber from the St. Lawrence River (0.37 to 1.4 µg g<sup>-1</sup>). Mean SCCP concentrations in blubber samples from walrus (*Odobenus rosmarus*) (Thule, northwest Greenland) and ringed seals (*Phoca hispida*) (Eureka, southwest Ellesmere Island) were 0.43 ± 0.06 (n=2) and 0.53 ± 0.2 µg g<sup>-1</sup> wet weight (n=6), respectively. Relative to commercial SCCP formulations, samples from Arctic marine mammals showed a predominance of the shorter chain length lower percent chlorinated SCCP congeners, the more volatile components of industrial formulations. This observation indicates long-range atmospheric transport of SCCPs to this region. The formula group abundance profiles of the belugas from the St. Lawrence River estuary, however, had higher proportions of the less volatile SCCP congeners, implying that contamination to this region is probably from local sources. Concentrations of SCCPs in the St. Lawrence beluga were higher than in any of the Arctic mammals. Mean wet weight SCCP levels in St. Lawrence belugas were four times higher than in Greenland and Mackenzie Delta belugas, but only 1.5 times higher than in ringed seals from Ellesmere Island. Walrus from northwest Greenland also had lower levels, ca. two times, of SCCPs than St. Lawrence belugas. The elevated levels of SCCPs in belugas from the St. Lawrence River were consistent with the findings of elevated levels of other organochlorines<sup>19</sup>.

SCCP levels in belugas from the St Lawrence River estuary were lower than mean wet weight concentrations of ΣPCB and ΣDDT by almost one order of magnitude. Tomy *et al.*<sup>18</sup> also reported that measured SCCP concentrations in beluga whale blubber from northwestern Greenland and the Mackenzie Delta were found to be significantly lower than those of ΣCHB (toxaphene), ΣPCB and ΣDDT. In ringed seal from southwest Ellesmere Island, Eureka, the mean SCCP concentration of 520 ± 170 ng g<sup>-1</sup> wet weight exceeded that of toxaphene and was slightly higher than that of ΣDDT<sup>18</sup>. ΣPCB levels were twofold higher. In walrus blubber from animals collected in northwestern Greenland concentrations of ΣPCB, ΣDDT and ΣCHB were significantly lower than those of SCCPs<sup>18</sup>.

Stern and Tomy<sup>7</sup> reported mean wet weight SCCP concentrations of 0.63, 0.20, 0.32 and 0.46 ng g<sup>-1</sup> in blubber from Beluga whales collected in Hendrickson Island (Southern Beaufort Sea near Mackenzie Delta) Arivat (western Hudson Bay), Sanikiluaq (Belcher Island area in southern Hudson Bay) and Pagnirtung (southeastern Buffin Island), respectively. Mean SCCP concentrations in samples from Hendrickson Island and Pagnirtung were significantly higher (t-test, p<0.05) than those from Hudson Bay. The authors also noted that formula group pro-

files in Arctic animals showed higher proportions of the lower chlorinated congeners (Cl<sub>5</sub> to Cl<sub>7</sub>), suggesting that the major source of contamination to the Arctic is via long range atmospheric transport.

Bennie *et al.*<sup>20</sup> analysed short and medium chain chlorinated paraffins in blubber and liver samples of 25 dead beluga whales (*Delphinapterus leucas*) from the St. Lawrence River estuary. SCCPs and MCCPs were detected in all samples (levels > 240 ng g<sup>-1</sup> wet weight). In blubber, SCCP concentrations ranged from 4.6 to 60.7 µg g<sup>-1</sup> wet weight (median 19 µg g<sup>-1</sup> wet weight, n=15) in females and 27.6 to 85.6 (median 38.2 µg g<sup>-1</sup>, n=10) in males. Concentrations seen in the liver samples (n=6) ranged from 0.54 to 8.5 ng g<sup>-1</sup> wet weight with one extremely high result of 38.2 ng g<sup>-1</sup> wet weight from a 4–6 week old young whale.

The mean SCCP concentrations reported in this study were one to two orders of magnitude higher than those reported by Tomy *et al.*<sup>18</sup> for beluga whale blubber from the St. Lawrence estuary. These authors applied gas chromatography – high-resolution electron capture negative ion mass spectrometry (GC-HR-ECNI-MS) to analyse the extracts, which has higher mass resolving power than low resolution mass spectrometry employed by Bennie *et al.*<sup>20</sup> and is therefore more selective. Differences in concentrations may be explained by the impact of co-eluting interfering compounds when using the less selective low resolution technique.

## 5 Methods for the analysis of SCCPs in environmental samples

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### 5.1 Standards for calibration and certified reference materials

Until recently, technical mixtures with known chlorine content have been used for calibration purposes. An international interlaboratory study<sup>21</sup> indicated that some of the observed variability in the analytical results may be introduced when different commercial formulations are used as external standards. These results were confirmed by Coelhan *et al.*<sup>22</sup> who investigated the influence of carbon chain length and chlorine content of the external standard used for quantification on the analytical results. In this study, SCCP concentrations of fish samples were quantified using several individual polychlorinated alkane standards and a commercial formulation. Results varied widely (by a factor of ten) depending on chlorine content of the standard used. These findings emphasise the importance of the choice of suitable standards for quantitative analysis. The authors showed that technical SCCP mixtures should not be used as standards in many cases because the SCCP carbon chain pattern in various fish species varied considerably and did not resemble that of the technical formulation.

A new quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionisation mass spectrometry, which is independent of the chlorine content of the reference standard used for calibration was proposed by Reth *et al.*<sup>23</sup>. The authors calculated the total response factors for seven standard CP mixtures of various chlorine contents (51–70%) from the relative total CP areas and found a linear correlation between the total response factors of CP mixtures and their chlorine contents ( $R^2 = 0.9494$ ). Variations in slope and intercept calculated from analysis of five replicates analysed on various days were less than 13% and the correlation coefficients  $R^2$  were constantly >0.90. Using this correlation, total response factors according to the chlorine content of the SCCPs present in the sample can be calculated and used for quantification. A final recommendation what standard to be used for quantification of SCCPs in environmental samples cannot be given at the moment. For the time being, there are neither standard reference materials for calibration purposes nor isotopically labelled reference standards. No reference materials have yet been certified for SCCP content. However, SCCPs were found in two SRMs from the National Institute for Standards and Technology (NIST). SRM 1588, a cod liver oil extract and SRM 1945 a whale blubber extract contained 49 and 172 ng g<sup>-1</sup> of SCCPs, respectively<sup>24</sup>. These SRMs are, therefore, possible candidates for future certification.

## 5.2 Analytical methods

Extraction and clean-up techniques for the analysis of SCCPs in biological samples and sediments are quite similar to those developed for the analysis of other halogenated compounds such as PCBs and chlorinated pesticides. Most procedures are based on batch or Soxhlet extraction with organic solvents, clean-up of the extracts by adsorption and gel permeation chromatography and determination by gas chromatography electron capture<sup>25-27</sup> or mass spectrometric detection<sup>13,14,28-31</sup>. Another approach is carbon skeleton analysis by gas chromatography with flame ionisation detection after simultaneous dechlorination and hydrogenation<sup>32,33</sup>.

An accurate chemical analysis of SCCPs in environmental samples is difficult to achieve due to the highly complex nature of commercial formulations, the impact of numerous physical, chemical and biological processes after use, and the lack of certified chemical standards. SCCPs are very complex mixtures containing many congener groups chlorinated to various degrees and at different positions on the carbon backbone. The theoretical maximum number of positional isomers calculated for  $n\text{-C}_n\text{H}_{2n+2-z}\text{Cl}_z$ , assuming no more than one bound chlorine atom on a carbon atom, for SCCPs is 7820<sup>24</sup>. However, the complexity of SCCP mixture is further enhanced because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers will be generated. Furthermore, although the hydrocarbon feedstocks used to prepare SCCPs are primarily n-alkanes, they do contain branched alkanes and probably other hydrocarbons, which would also add to the complexity of the mixtures. Even if only a small percentage of the theoretically possible number of chloroalkanes is readily formed, it can be assumed that commercial SCCP formulations contain many thousand compounds.

There are four different approaches to analyse SCCPs in environmental samples. These are:

Carbon skeleton analysis after simultaneous catalytic dechlorination and hydrogenation by gas chromatography with flame ionisation or mass spectrometric detection<sup>32-34</sup>, gas chromatography with electron capture detection<sup>25,26</sup>, gas chromatography-mass spectrometry in the negative chemical ionisation mode (see e.g.<sup>13,14,28-30,35-37</sup>) and gas chromatography in combination with electron ionisation mass spectrometry/mass spectrometry<sup>38</sup>.

Due to the lack in sensitivity and selectivity – no information on the degree of chlorination of the SCCPs can be achieved – the first approach was not widely used. GC-ECD analysis of SCCPs is quite unspecific. Since the compounds of interest elute over a wide retention time range, an unequivocal identification is not possible due to interferences from other halogenated compounds, even when applying lengthy and expansive clean-up procedures and using several stationary phases of different polarity. Therefore, electron capture negative ionisation mass spectrometry (ECNI-MS) at low or high resolution was generally favoured.

To obtain reliable results, the variability of the mass spectra of SCCPs in dependence on degree of chlorination and ion source temperature and to a lesser extent on chain length of the carbon skeleton has to be taken into consideration<sup>39,40</sup>. At 250 °C, mass spectra of higher chlorinated SCCPs are characterised by a peak cluster representing the  $[\text{M}-\text{Cl}]^-$  fragment ion for all chlorination degrees with a relative intensity ranging from some 50 to 65%. The relative intensities of the  $[\text{M}]^-$ ,  $[\text{M}-\text{HCl}]^-$ ,  $[\text{M}-2\text{HCl}]^-$  and  $[\text{M}-\text{HCl}_2]^-$ , are around or below 10%. At low ion source temperature (100 °C),  $[\text{M}-\text{Cl}]^-$  and  $[\text{M}-\text{HCl}]^-$  are most prominent ion clusters with higher intensity of the latter for lower chlorinated SCCPs. Fragmentation is shifted to  $[\text{M}-\text{Cl}]^-$  with increasing degree of chlorination. The relative response factors of SCCP mixtures vary by one order of magnitude depending on the degree of chlorination with lowest response factors for the low chlorinated mixtures (chlorine content 45 to 50%). Compared to the influence of chlorination degree on the fragmentation, that of carbon skeleton chain length is less important<sup>39</sup>.  $[\text{M}+\text{Cl}]^-$  as well as  $[\text{M}-\text{Cl}]^-$  ions were reported in the ECNI mass spectra of synthesised

lower chlorinated SCCPs<sup>40</sup>. Their abundances decreased with increasing ion source temperature, while the abundances of the structurally non-characteristic ions,  $[\text{Cl}_2]^-$  and  $[\text{HCl}_2]^-$ , increased.

Jansson *et al.*<sup>13,28</sup> analysed environmental samples using GC-ECNI-MS in the selected ion monitoring mode after selective clean-up. Structurally non-characteristic  $[\text{Cl}_2]^-$  and  $[\text{HCl}_2]^-$  ions at  $m/z=70$  to 73 that predominate in the mass spectra of SCCPs at high ion source temperatures were recorded. A similar approach was used by Nicholls *et al.*<sup>30</sup>. They analysed SCCPs and MCCPs in water, sediment, sewage sludge and biota samples from selected industrial areas in England and Wales. SCCPs were determined in sample extracts using GC-ion trap mass spectrometry operated in the negative chemical ionisation mode. Three technical products were chosen for reference calibration purposes. The analysis and quantification of formulations identified in sample extracts was undertaken by a two-step GC-MS process:

- qualitative identification of formulation type;
- quantitative analysis based on the response characteristics summed across the mass region  $m/z=70$  to 75 corresponding to  $[\text{Cl}_2]^-$  (70, 72, 74) and  $[\text{HCl}_2]^-$  (71, 73, 75) for most appropriate calibration standard.

Average recoveries of SCCPs from spiked sediments ( $1-2 \text{ mg kg}^{-1}$ ,  $n=8$ ) were 84%. The limit of determination was equivalent to a SCCP formulation containing  $1 \text{ ng } \mu\text{l}^{-1}$  in solution. Within batch repeatability for the GC-MS measurement using the internal standard method was in the range 6–10% RSD ( $n=10$ ) for SCCP.

Procedures based on monitoring structurally non-characteristic fragment ions corresponding to  $[\text{Cl}_2]^-$  and  $[\text{HCl}_2]^-$  present the problem that many other halogenated compounds fragment to yield such ions, e.g. *p,p'*-DDT, *p,p'*-DDE, lindane, dieldrin, aldrin and endrin. Thus, if these contaminants are not completely removed from the sample matrix during extraction and clean-up, they ultimately contribute to the response of the quantification ions  $[\text{Cl}_2]^-$  ( $m/z=70, 72, 74$ ) and  $[\text{HCl}_2]^-$  ( $m/z=71, 73, 75$ ) and lead to an overestimation of SCCPs.

Recently, Tomy *et al.*<sup>29</sup> published a method for quantifying SCCPs in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry in the selected ion monitoring mode at an ion source temperature of  $120^\circ\text{C}$ . The molecular compositions of commercial SCCPs and of SCCP-containing extracts were determined by monitoring the two most intensive ions in the  $[\text{M-Cl}]^-$  cluster, one for quantification and the other for confirmation for the following formula groups:  $\text{C}_{10}$  ( $\text{Cl}_5$  to  $\text{Cl}_{10}$ ),  $\text{C}_{11}$  ( $\text{Cl}_5$  to  $\text{Cl}_{10}$ ),  $\text{C}_{12}$  ( $\text{Cl}_6$  to  $\text{Cl}_{10}$ ), and  $\text{C}_{13}$  ( $\text{Cl}_7$  to  $\text{Cl}_9$ ), and assuming that integrated signals are proportional to molar concentrations weighted by the number of chlorine atoms in the formula group. Quantification was achieved by selecting the biggest peak corresponding to  $[\text{M-Cl}]^-$  ion in the most abundant formula group present in the sample and correcting for variations in the formula group abundances between standard and sample. It has been shown that high-resolution mass spectrometry eliminates self-interferences between SCCPs and potential interferences from chlordanes, toxaphenes, PCBs and other organochlorine pesticides. Recoveries of SCCPs from fish averaged  $>80\%$ . The analytical detection limit was  $60 \text{ pg}$  of injected SCCP at a signal-to-noise ratio of 4:1, while method detection limit was  $23 \text{ ng g}^{-1}$ .

Although the proposed method seems to be a suitable approach to analyse SCCPs in environmental samples on the research level, its application for routine analysis is questionable due to the use of a high-resolution mass spectrometer for detection that is not available in most environmental laboratories responsible for routine monitoring, its complexity and the observed variability in results as shown in a recent interlaboratory study<sup>21</sup>.

Coelhan<sup>14</sup> proposed a short-column GC-ECNI-MS method for the determination of SCCPs in fish samples that dispenses with chromatographic separation. Only a short capillary column of 62 cm length (thereof 42 cm in the interface) is coupled to a low resolution mass spectrometer

operated in the negative ionisation mode at an ion source temperature of 100°C using methane as reagent gas. SCCPs in fish samples were identified by comparison of mass spectra of sample extracts with those of synthesised polychlorinated alkanes and of CERECOLOR 63L. The quantification was performed by reintegration of selected ions from full-scan spectra. Without chromatographic separation, all SCCPs elute from the column as only one peak. Consequently, this leads to an enormous increase in sensitivity and makes it more easy to survey the mass spectra. If the SIM mode is used, an additional enhancement in sensitivity is possible. Detection limits in the full scan mode ranged from 10 to 100 pg depending on carbon chain length of the n-alkane and on the degree of chlorination. Recoveries of SCCPs from spiked herring oil averaged to 112% for the low spiking level (200 ng g<sup>-1</sup>) and to 102% for the high dose (800 ng g<sup>-1</sup>). Since no chromatographic separation has to be achieved, time of analysis is only one minute. Due to dispensing with chromatographic separation complete removal of all other halogenated compounds, which might interfere with the determination of SCCPs, is a fundamental requirement.

A new method for quantifying short chain chlorinated paraffins (C<sub>10</sub>–C<sub>13</sub>) in environmental samples using metastable atom bombardment ionisation (MAB) and high resolution mass spectrometry was recently published by Moore *et al.*<sup>35</sup>. Contrary to electron capture negative ionisation (ECNI), MAB can produce spectra for molecules having a low number of chlorine atoms. These molecules are present in commercial SCCPs and are responsible for a large fraction of the total SCCP concentration in water samples analysed by the authors. Using ECNI or MAB, no molecular ion can be seen in the spectra. ECNI spectra contain important peaks corresponding to [M-Cl]<sup>-</sup> and [M-HCl]<sup>-</sup> while the base peak in MAB spectra is [M-HCl]<sup>+</sup> with no [M-Cl]<sup>+</sup> present. The mass range for C<sub>10</sub>–C<sub>13</sub> CPs is very large and scanning the masses for all the compounds involved would lead to a loss of sensitivity. Two chromatographic analyses were thus performed using high resolution selective ion monitoring with only a limited number of masses recorded per run. To reduce analysis time, a short capillary column was used. The analytical detection limits were estimated to be between 10 and 100 pg l<sup>-1</sup> for MAB and 1–100 pg l<sup>-1</sup> for ECNI, depending on the formula group. The MAB method has been applied to the analysis of high-volume water samples (dissolved and particulates portions separately) from the St. Lawrence River near Quebec City.

Zencak *et al.*<sup>38,41</sup> applied gas chromatography in combination with electron ionisation (EI) tandem mass spectrometry (GC-MS/MS) to the fast determination of the sum of short and medium chain chlorinated paraffins in biota samples. Non-specific fragment ions (not containing chlorine) common to all CPs were identified and further fragmented by collision-induced dissociation (CID) using either ion trap or triple quadrupole instruments. Collision-induced reactions of m/z 91 → 53 (LOD = 0.15 ng μl<sup>-1</sup>), 102 → 65 (LOD = 0.2 ng μl<sup>-1</sup>), and 102 → 67 (LOD = 0.1 ng μl<sup>-1</sup>) were used to quantify the total short- and medium-chain PCA content of pooled fish liver samples. Accuracy was controlled with spiked samples and results deviated not more than 15% from expected values. The relative response factors of three technical SCCP and three technical MCCP mixtures with different degrees of chlorination showed other than in ECNI-MS similar response factors (standard deviation 14–21%), which facilitates quantification.

The use of dichloromethane/methane mixtures as reagent gas was proposed as an alternative to CH<sub>4</sub>/ECNI mass spectrometry for the determination of SCCPs<sup>37,42,43</sup>. [M+Cl]<sup>-</sup> adduct ions were formed nearly exclusively and other fragmentation pathways such as [M-Cl]<sup>-</sup> and [M-HCl]<sup>-</sup> usually seen under CH<sub>4</sub>/ECNI conditions were suppressed. Ionisation yields of other polychlorinated compounds present in environmental samples such as toxaphene or chlordanes, which might interfere with the determination of SCCPs, were strongly reduced. The resulting enhanced selectivity and sensitivity lowered limits of quantification to 3 ng for a technical PCA mixture and 10–13 pg for single congeners. Response factors for congeners of different degrees of chlorination varied only by factor of two, whilst when using methane as reagent gas

the relative response factors of SCCP mixtures vary by one order of magnitude depending on the degree of chlorination. The technique was applied to the determination of the composition of technical SCCP mixtures as well as to the analysis of SCCPs in fish liver. The introduction of dichloromethane into the ion source required only a very simple instrument modification resulting in a stable and reproducible reagent gas pressure and composition. Indeed, dichloromethane generates black deposits in the ion source after a few injections so that it has to be cleaned quite often (Zencak, personal communication).

Quantification can be disturbed by mass overlap of SCCP congeners with MCCP congeners of identical nominal mass; for example  $C_{11}H_{17}^{35}Cl_6^{37}Cl$  ( $m/z$  395.9) and  $C_{16}H_{17}^{35}Cl_5$  ( $m/z$  396.1), which differ in their composition by +5 carbon atoms and -2 chlorine atoms. This problem was studied by comparing chromatograms of pure SCCP and MCCP standards with those of a mixture of both formulations<sup>36</sup>. It was shown that the quantification of the most abundant carbon chain length groups ( $C_{11}$  to  $C_{13}$ ) present in typical SCCP mixtures is not affected by interferences from other CPs. However, the determination of  $C_{10}H_{14}Cl_8$  could be affected by  $C_{15}H_{26}Cl_6$  from MCCPs if both congeners were present in a sample. An evaluation of the isotope ratio, retention time ranges and peak shape allows detecting the problem and avoiding overestimation of the corresponding formula group. Despite the discussed possible interferences the authors conclude that LRMS is an appropriate technique for the quantification of SCCPs and in environmental samples.

The suitability of four mass spectrometric methods for the analysis of polychlorinated n-alkanes was evaluated and compared using spiked and natural contaminated fish samples<sup>44</sup>. Electron ionisation tandem mass spectrometry (EI-MS/MS) as well as electron capture negative ionisation (ECNI) combined with low and high resolution mass spectrometry and  $CH_4/CH_2Cl_2$ -negative ion chemical ionisation (NICI) low resolution mass spectrometry were investigated. LODs were determined by analysing a SCCP mixture with a chlorine content of 55.5% and were in the range of  $1 \text{ ng } \mu\text{l}^{-1}$  for the three ECNI methods and three to five times lower for EI-MS/MS procedure. For the spiked samples, all methods showed deviations from the spiked level of less than 21%. However, the analysis of real samples revealed a notably higher variability of the results obtained with the four mass spectrometric methods.

## 6 Conclusion

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To date, there is still very limited information regarding the levels of SCCP in the marine environment. The few data published in the last years indicate an ubiquitous distribution of these compound group in the environment including remote areas in the Arctic. SCCPs were found in mussels, various marine fish species, seabirds, and marine mammals. Highest levels of SCCPs were reported for Belugas from the St Lawrence River estuary (up to  $1.4 \text{ mg kg}^{-1}$  wet weight). Assessment of the data was difficult due to obvious problems with the analysis of SCCPs and the lack of proper quality assurance information.

Although some work has been conducted on development of selective and sensitive methods for SCCP analysis in recent years, for the time being, no fully validated procedure is available that could be recommended for routine monitoring of SCCPs in environmental samples. Taking into account all information available, GC-ECNI-MS seems to be the most appropriate technique for quantitative analysis of SCCPs at the required low concentration levels. GC-EI-MS/MS seems to be a promising option for screening total content of short and medium chain chlorinated paraffins.

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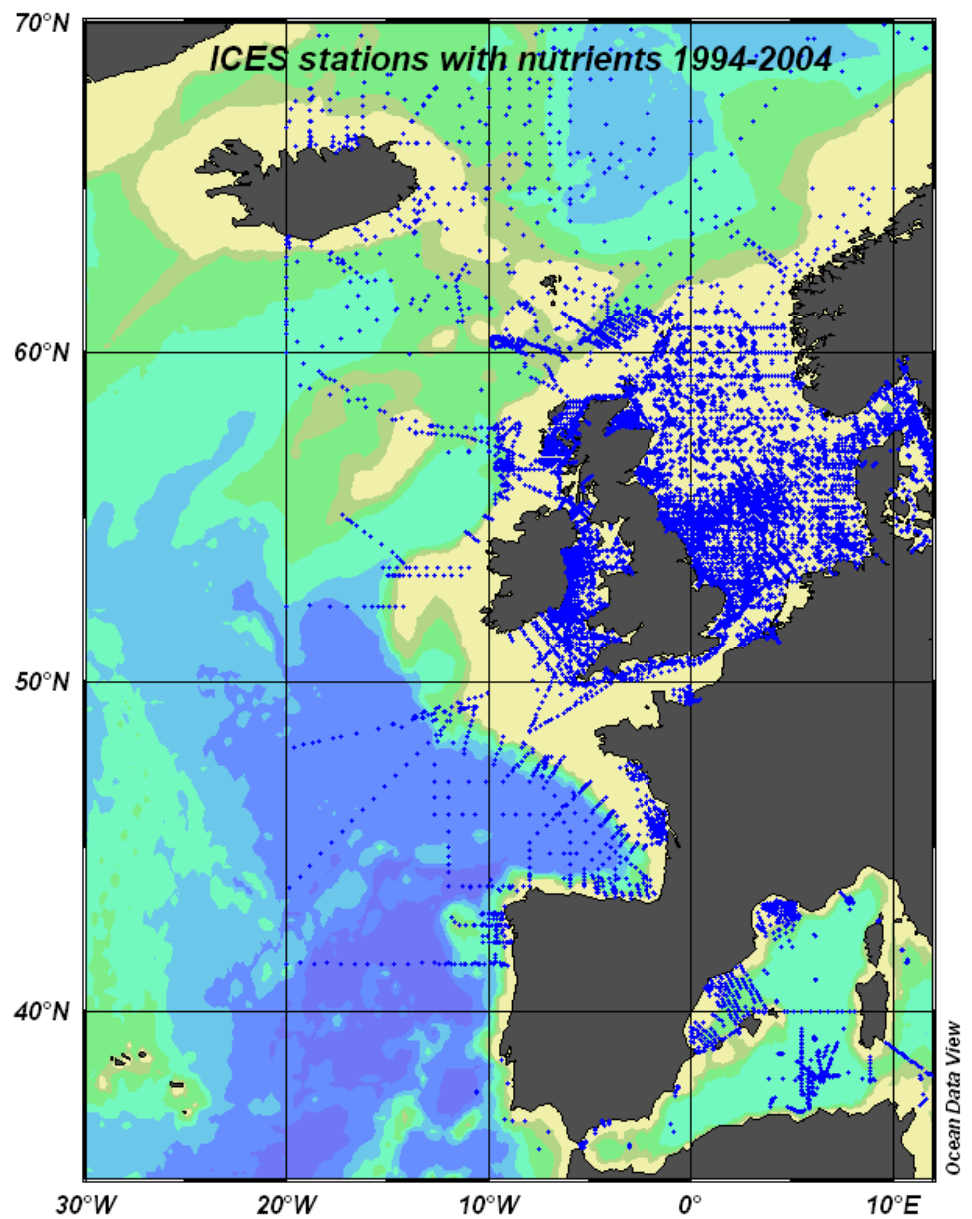
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## Annex 9: ICES data for nutrients in seawater

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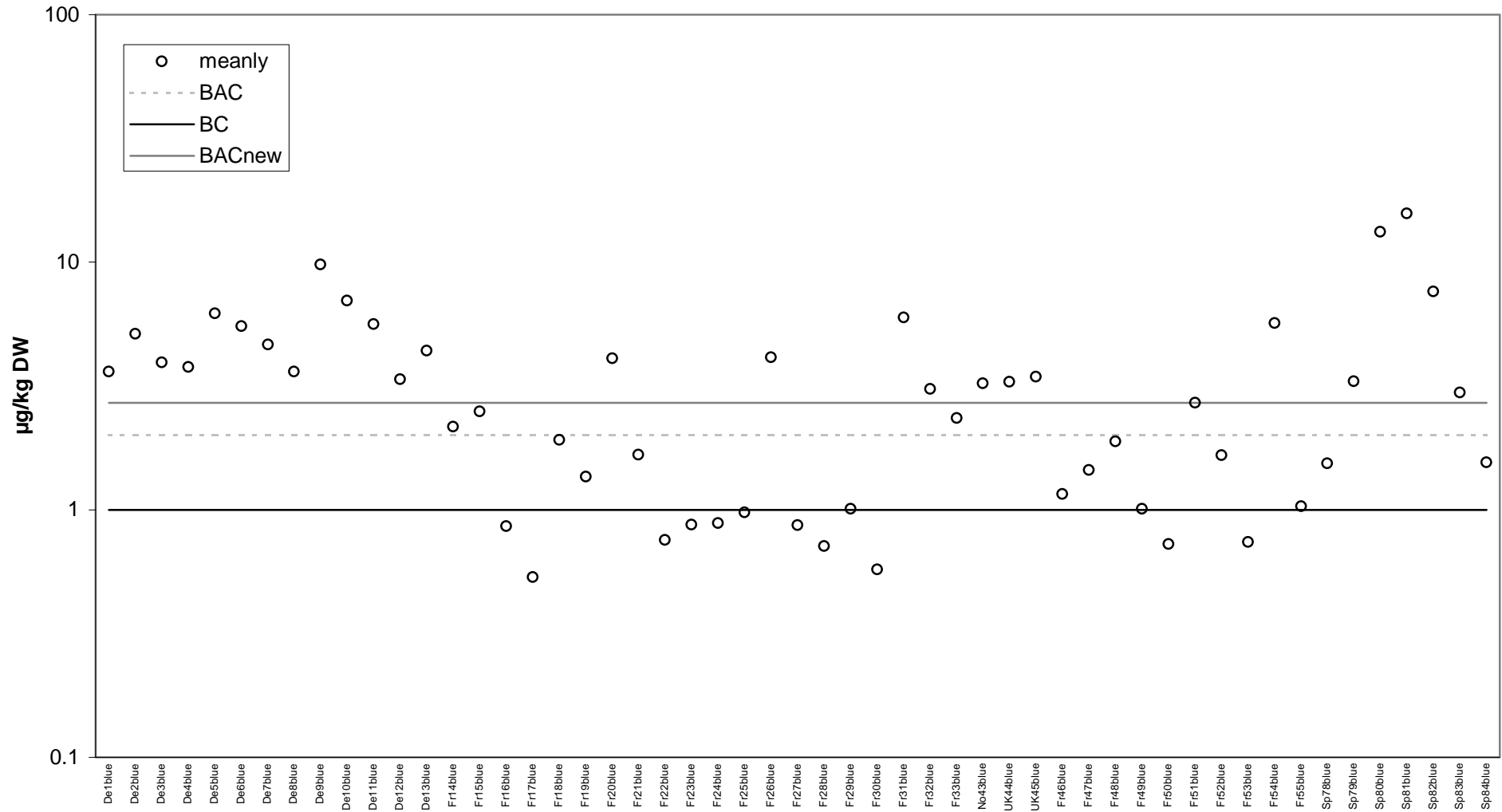


## **Annex 10: Material relating to the OSPAR MON assessment**

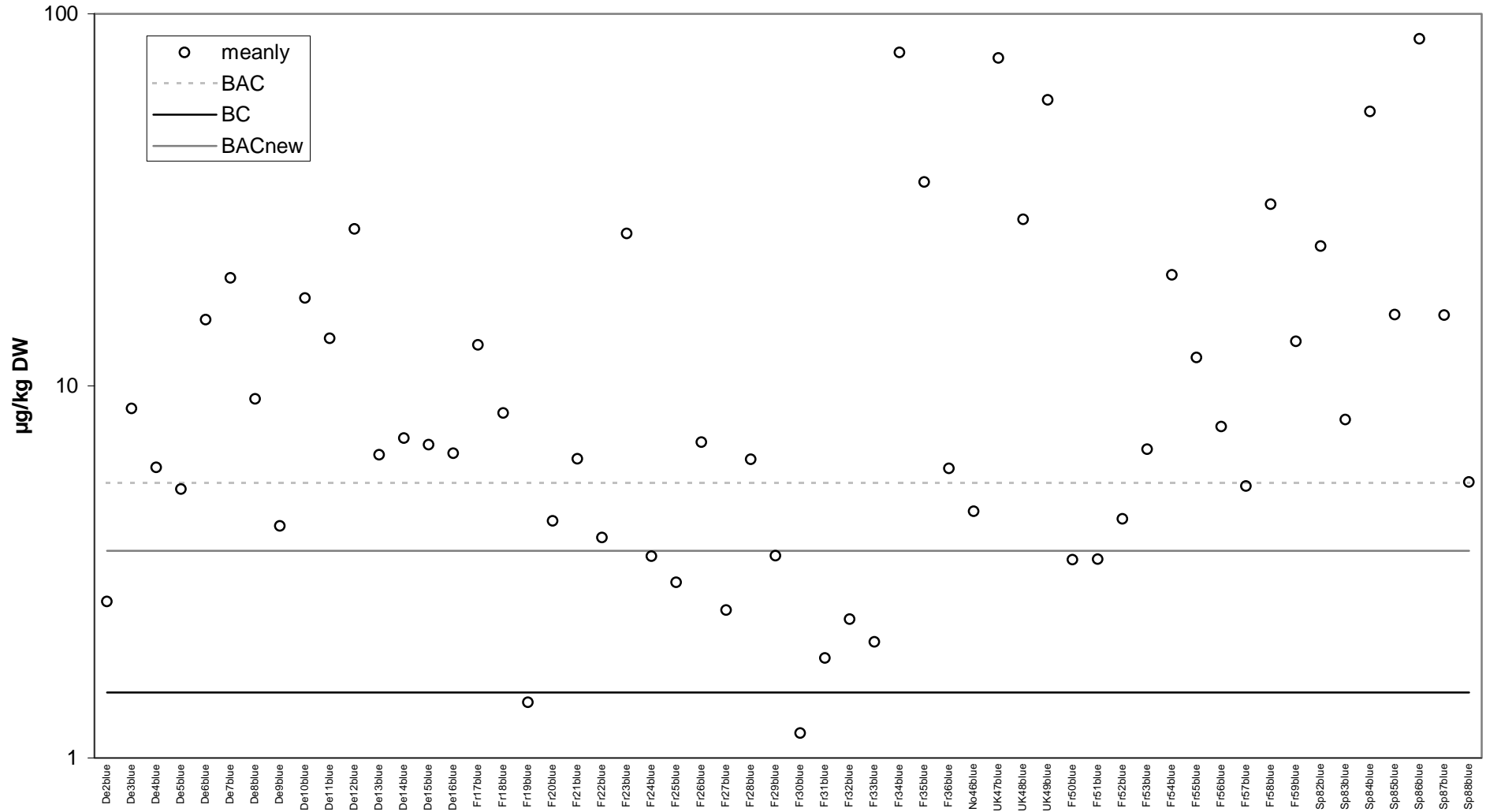
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The MON 2004 assessment made a trial application of proposals for updated assessment criteria – Background Concentrations (BCs) and associated Background Assessment Concentrations (BACs), and Environmental Assessment Criteria (EACs) – which were developed by OSPAR and ICES in 2004. In cases where a proposal for a BC/BAC or EAC has not been made, BRCs or EACs from the 1997 agreements have been used. The statistical analysis also provided a comparison of current concentrations against the BAC or EAC by calculating the ratio of the upper 95% confidence limit of the fitted estimate for the most recent sampled year to the BAC/EAC. The working group evaluated the used assessment criteria by plotting the fitted value of the last year of the trend assessment against these assessment criteria. The current evaluation was limited the data for blue mussel as this is the only dataset for which a sensible comparison can be made. The resulting graphs can be found in annex. In general, there is little difference between the BACs for PAHs proposed in 2004, calculated on the basis of UK data, and the new BACs calculated on the entire CEMP dataset. Nevertheless, only the BACs based on the entire CEMP dataset should be used for further assessments. A particular example is naphthalene, although this seems to involve a calculation or editorial error. For chrysene, benzo[ghi]perylene and indeno[123-ghi]pyrene approx. 50% of the data points are below the new BAC which seems somewhat high. This deserves further investigation. For CB153 and the sum of the ICES 7 CBs, most values seemed to be above the BACs and approx. 50% is above the EAC. For metals, the assessment tools could only be evaluated for Cd, Hg and Pb. In all cases, the metal concentrations are generally above the calculated BAC. However, for Cd and Pb all data points are above the EAC, which is even below the (old) BRC for Hg. It seems clear that this deserves particular attention.

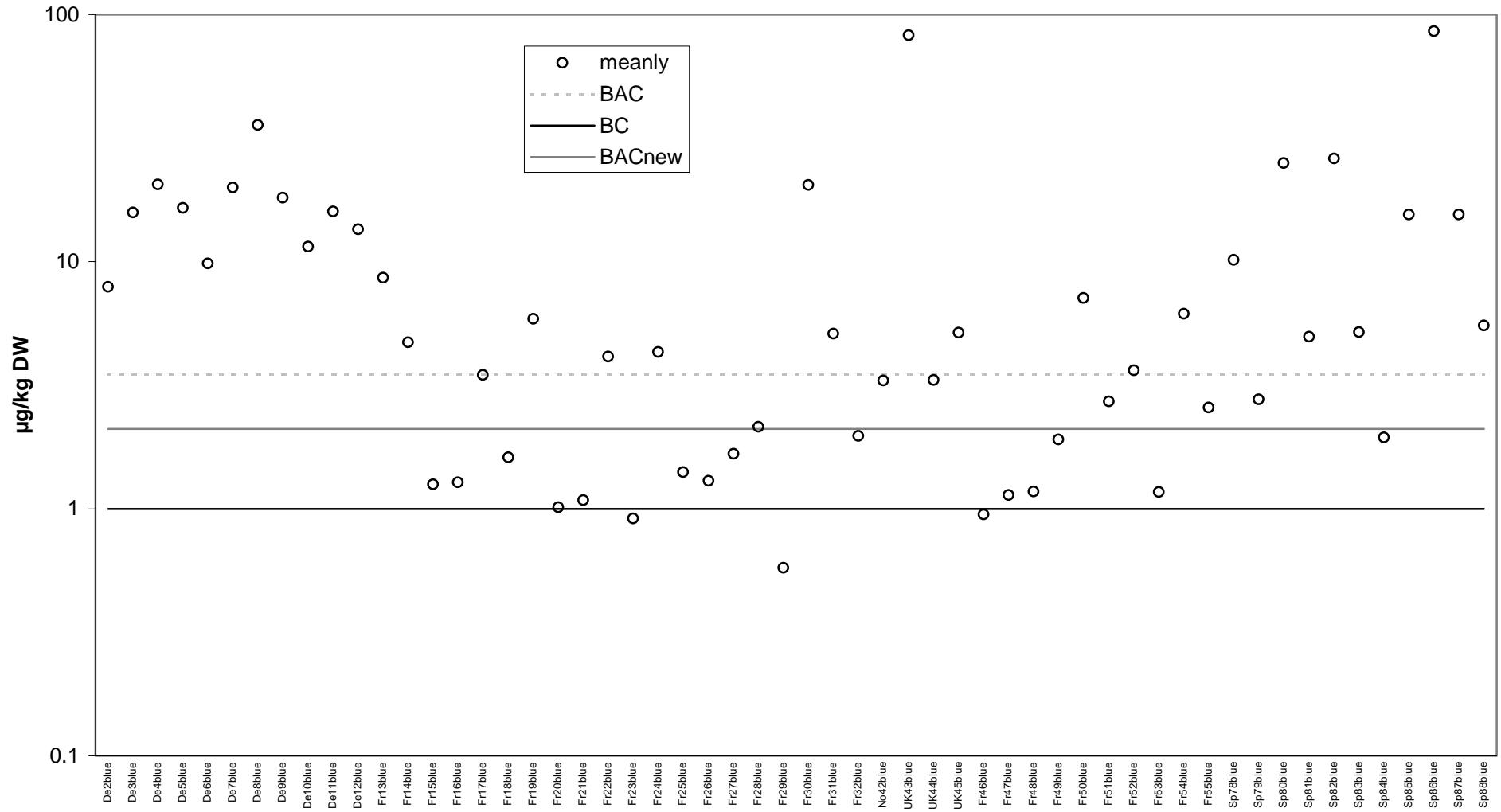
### Ant



### BaA

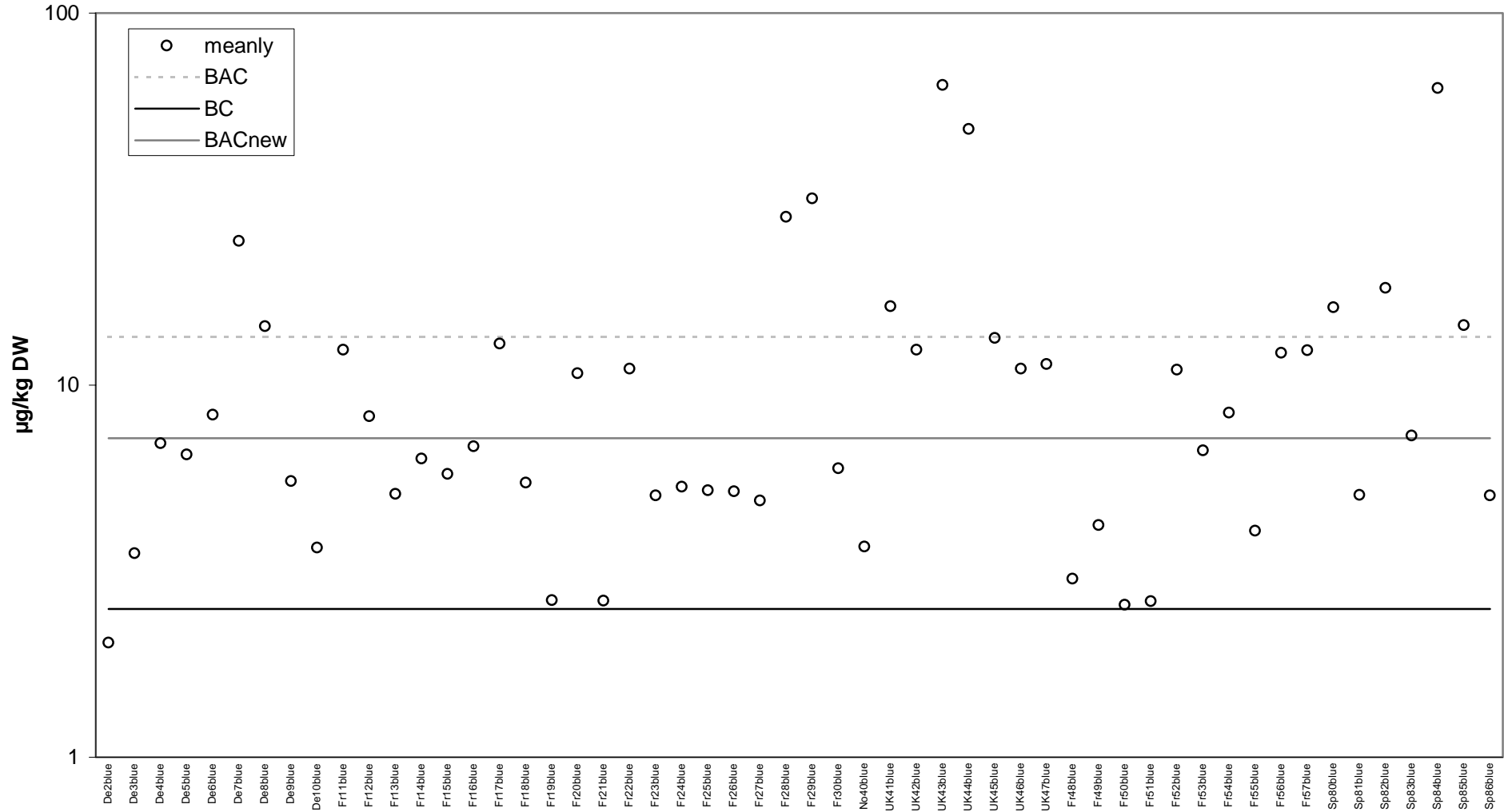


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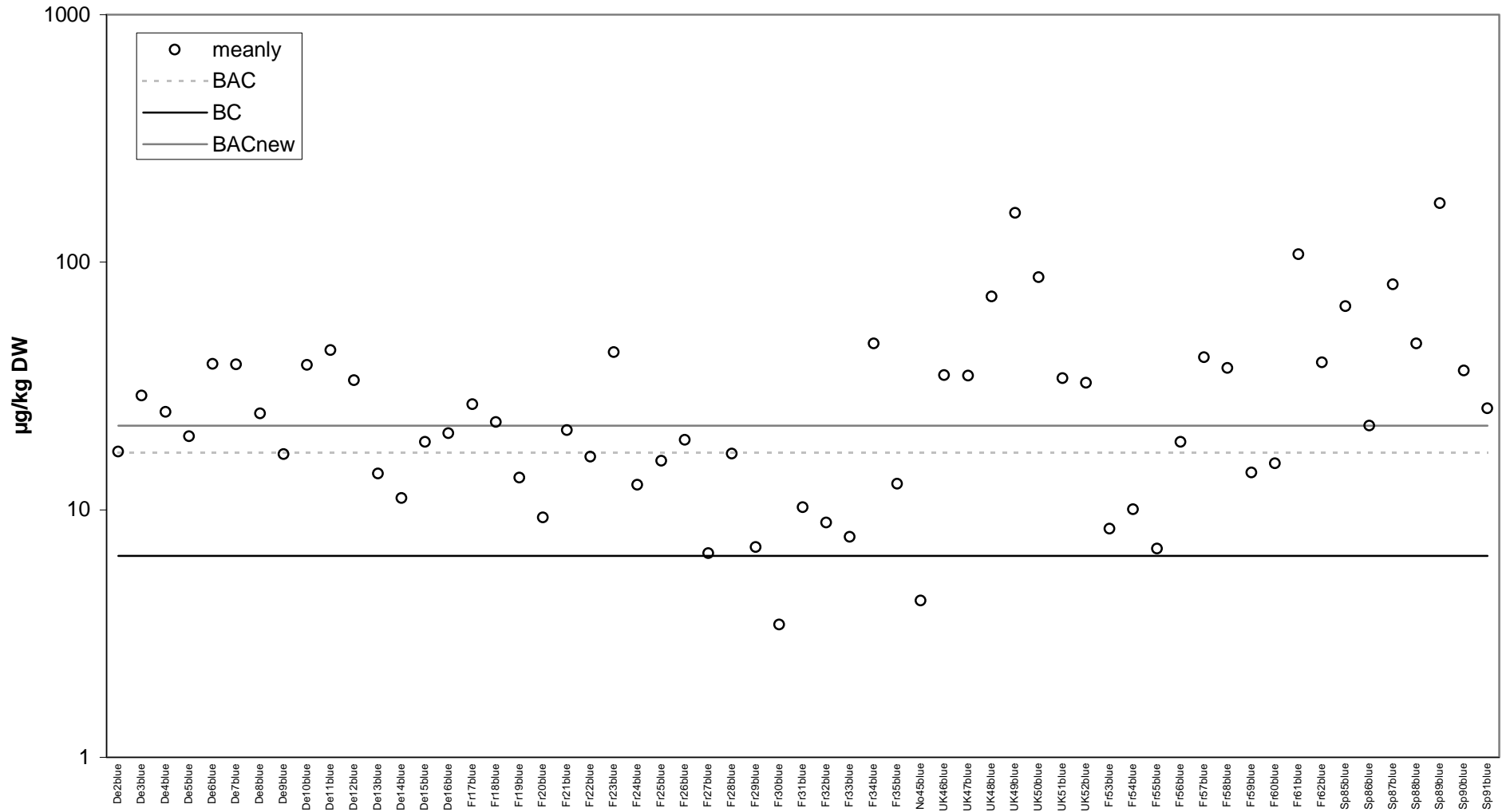




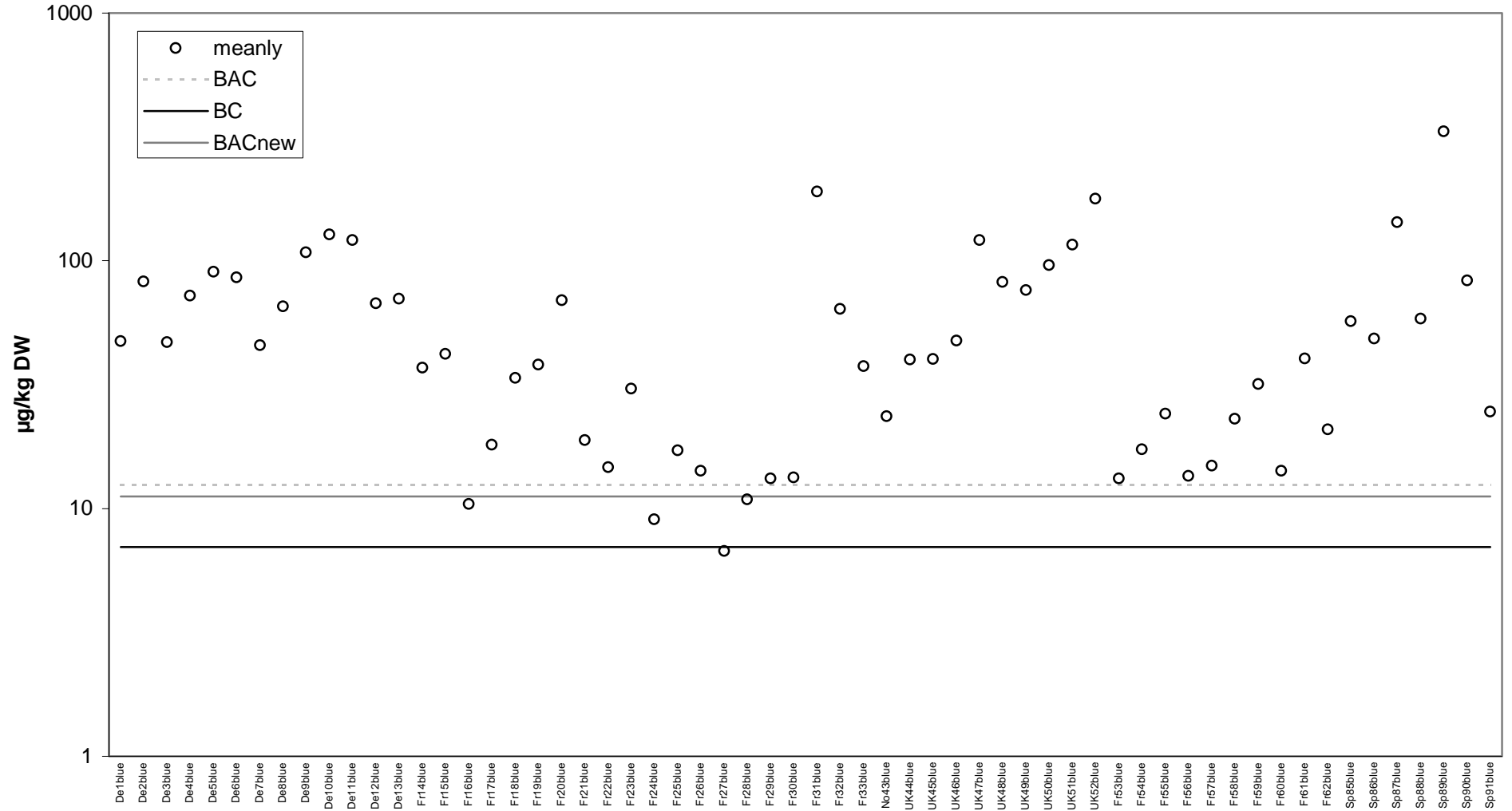
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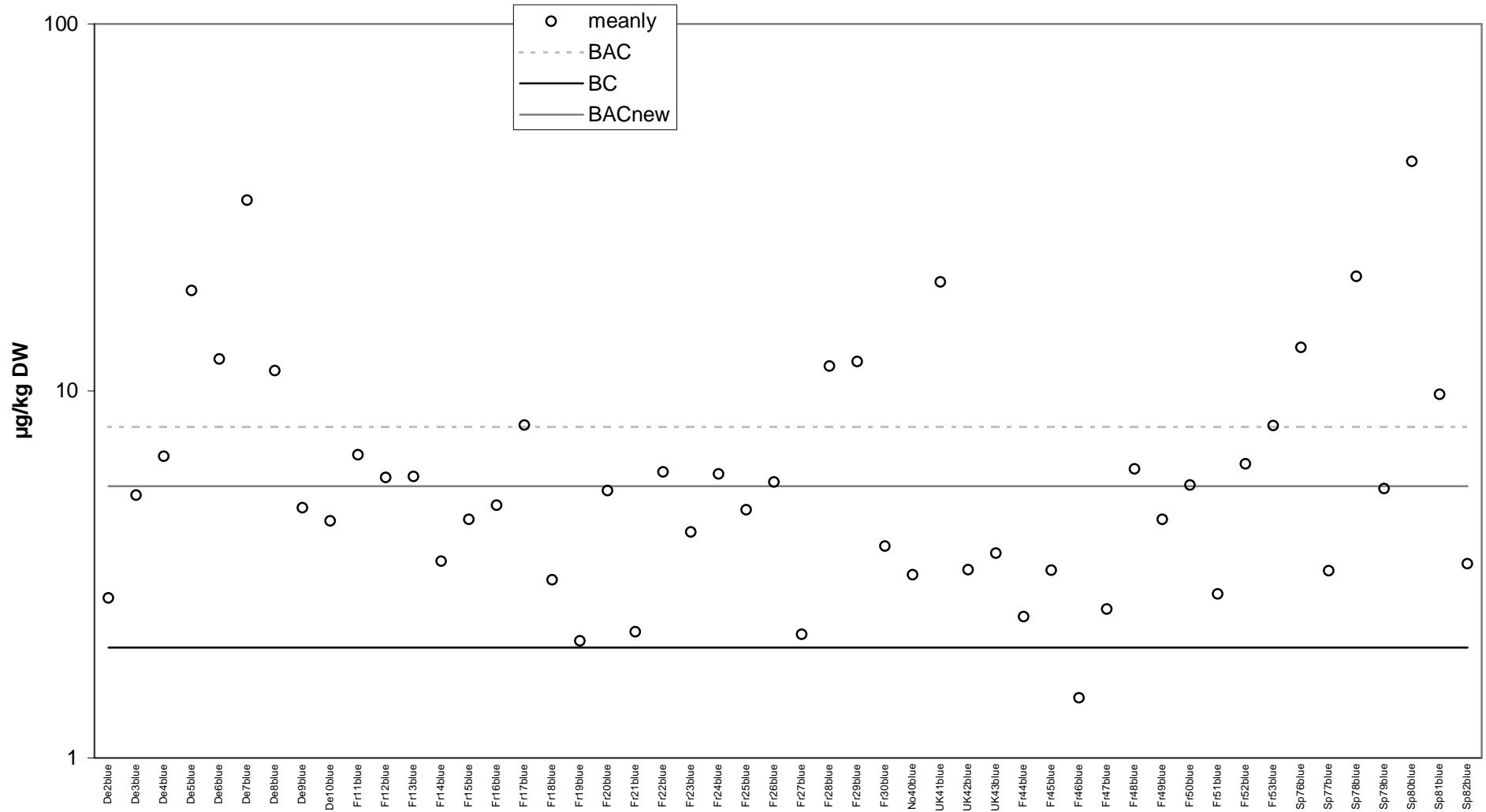
Chr

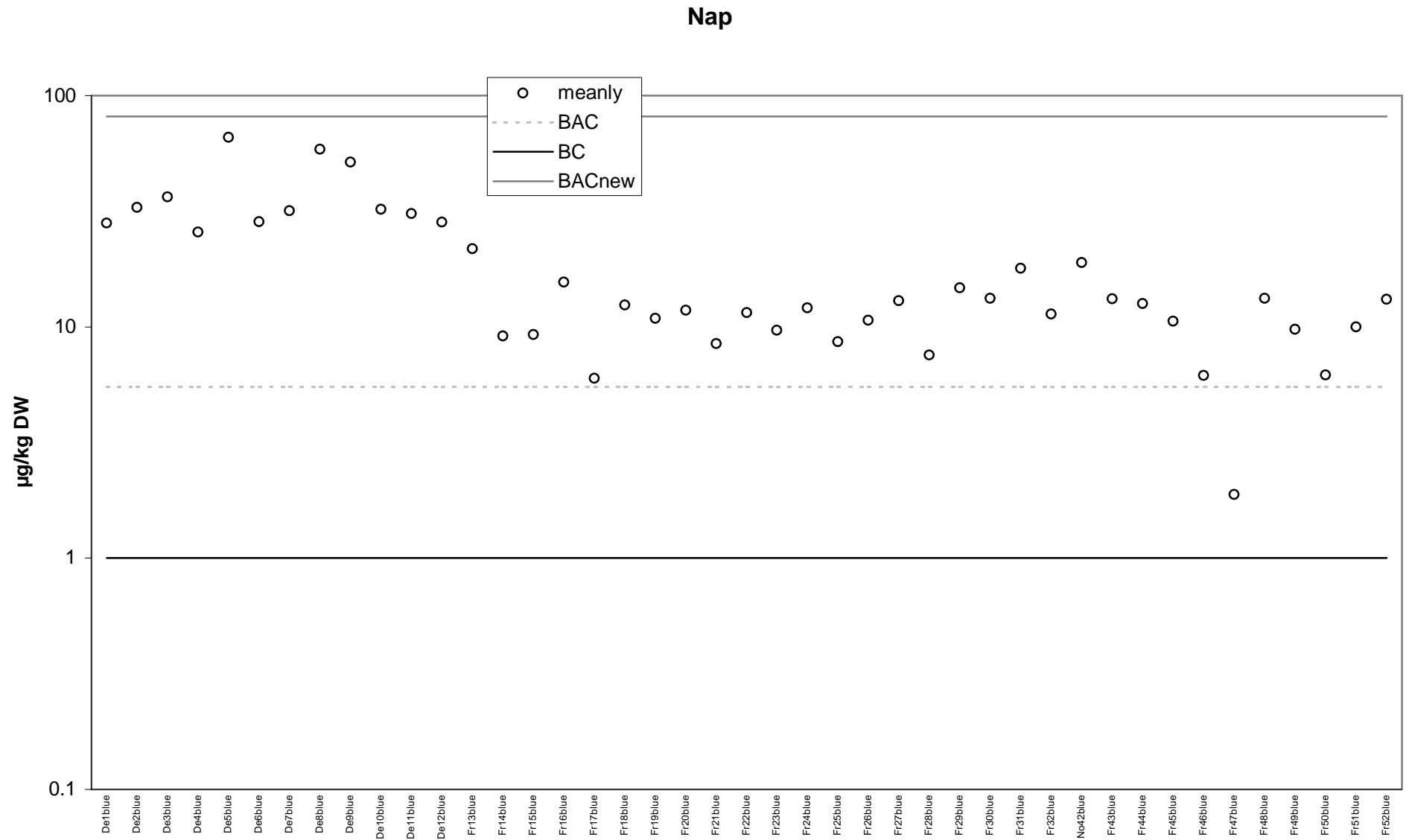


### Flu

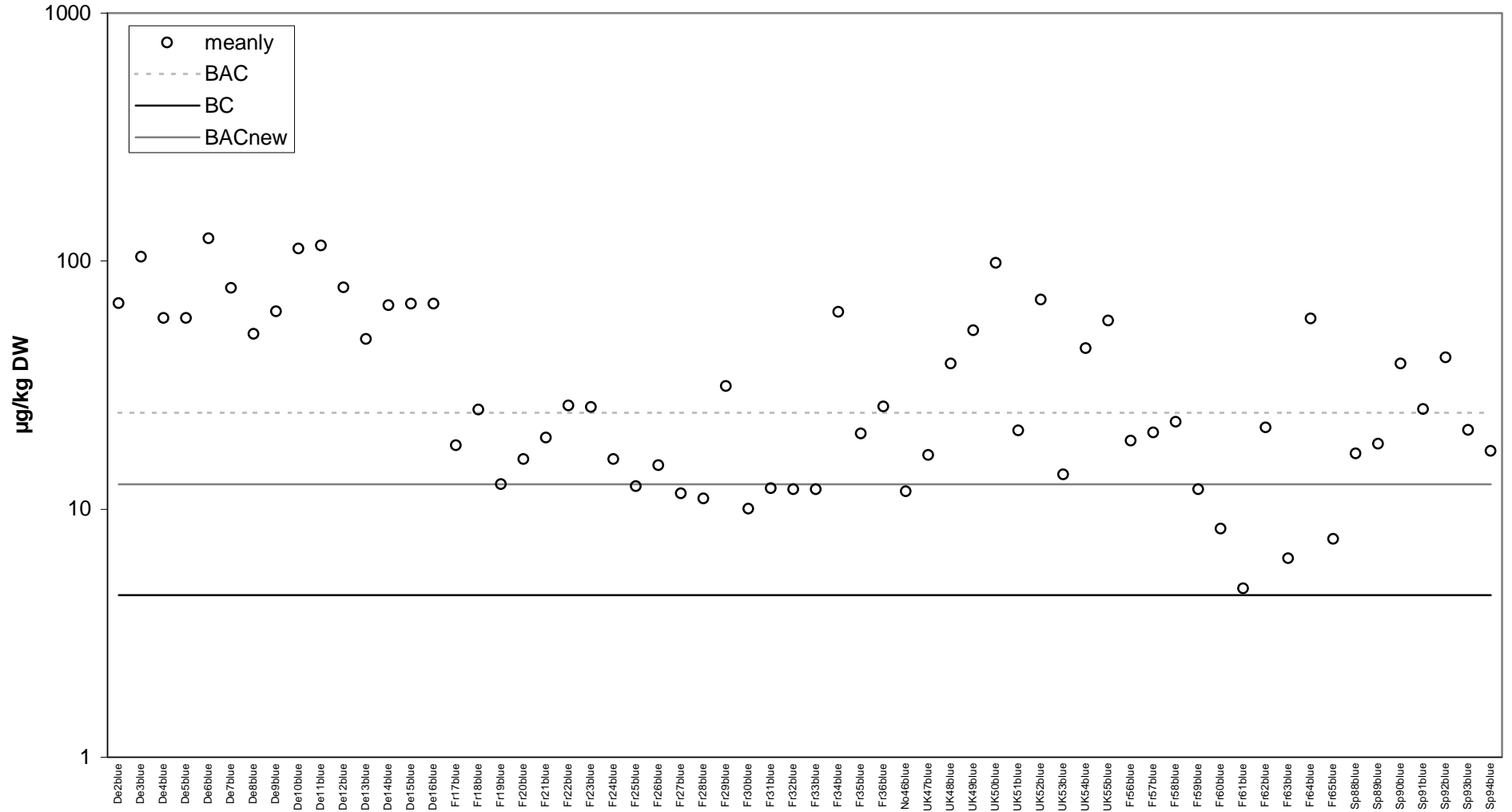


I123P

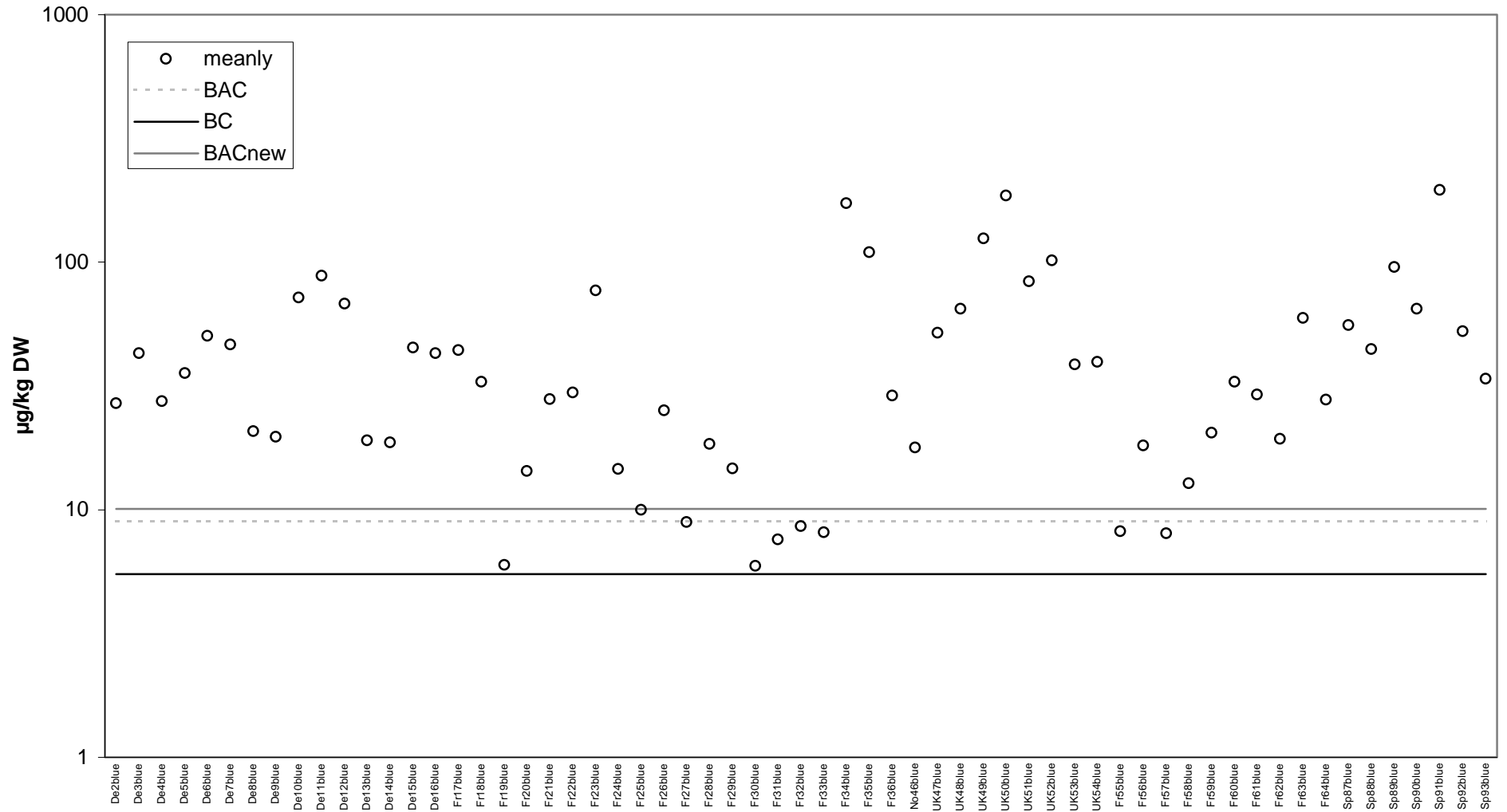




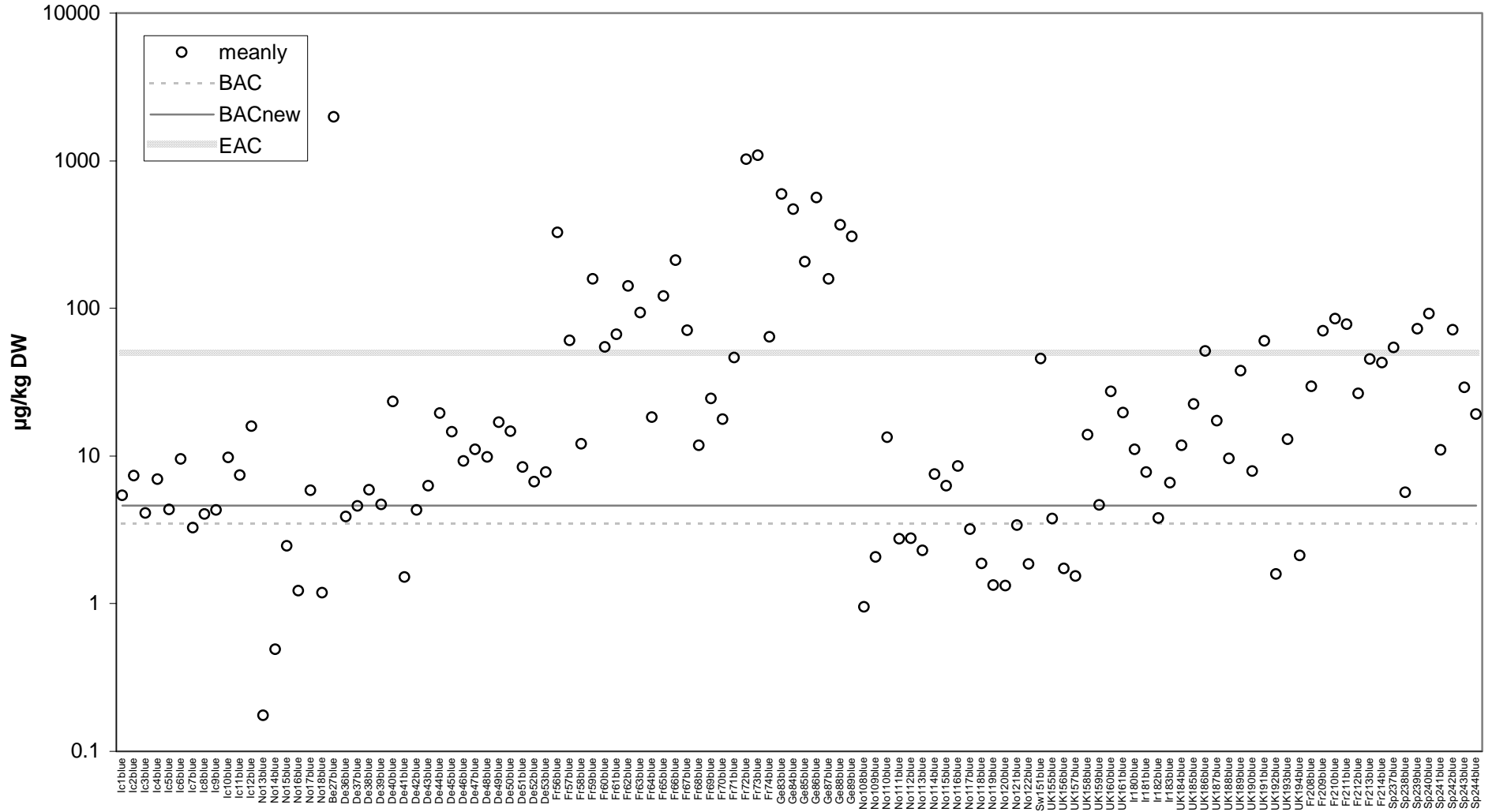
### Phe



### Pyr

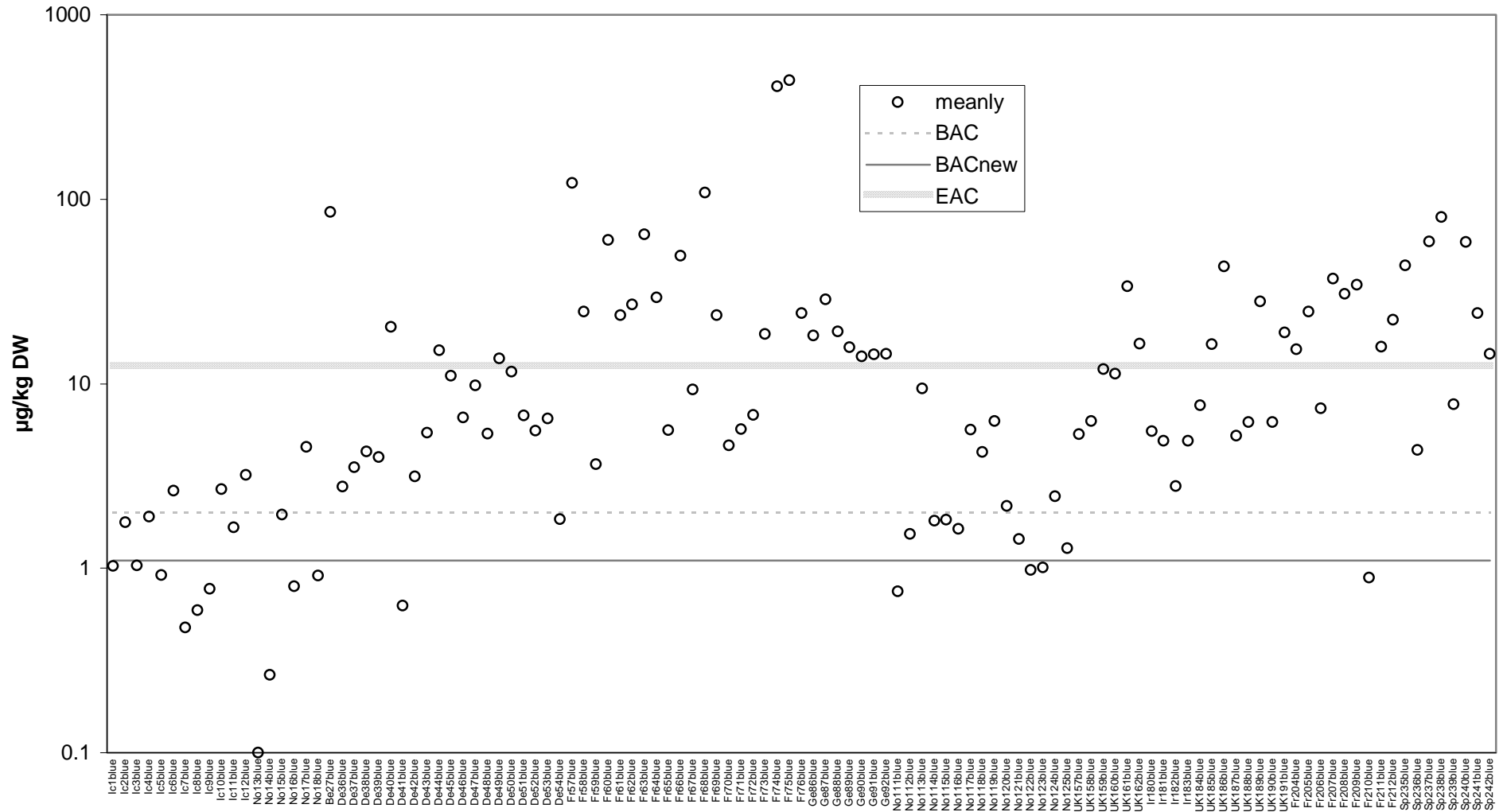


### SUM7CB

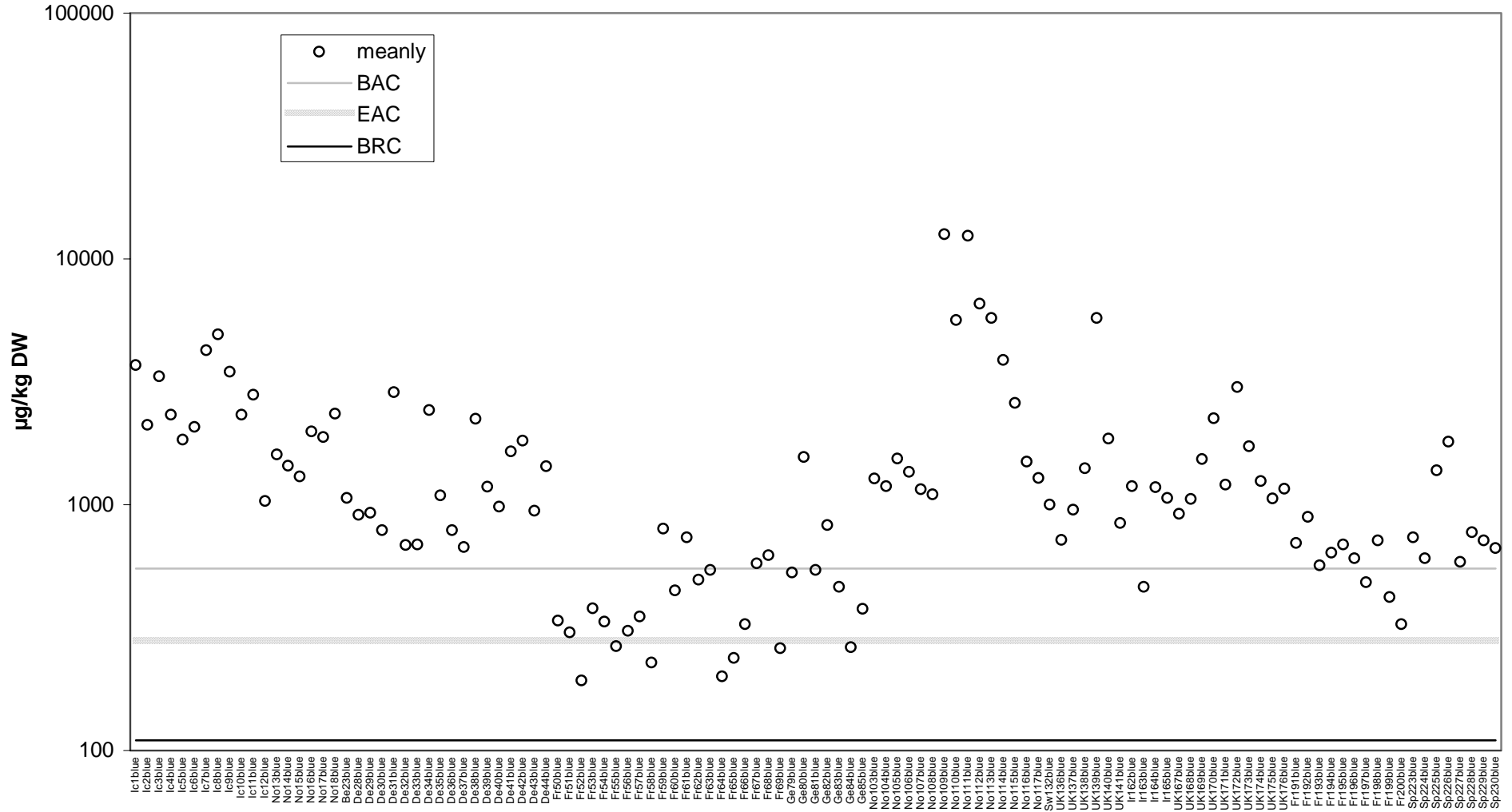




### CB153

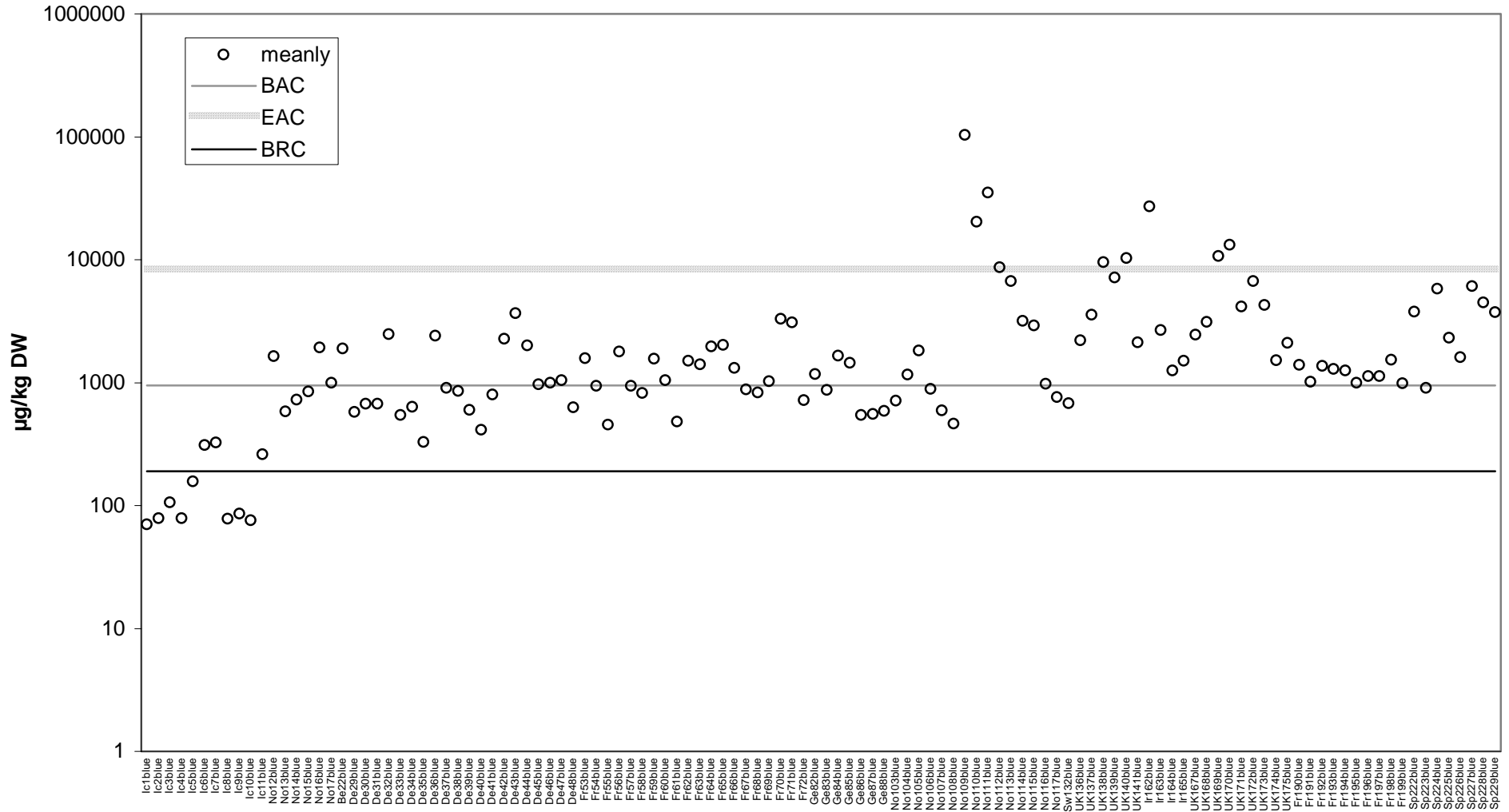


Cd





### Pb



## Annex 11: 2005 Draft Terms of Reference

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The **Working Group on Marine Chemistry** [MCWG] (Co-Chairs: R. Law, UK, and Jacek Tronczynski, France) will meet in Copenhagen, Denmark, from 27–31 March 2006 to:

- a) examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];
- b) continue to report on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe) in flatfish;
- c) continue to report on new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes;
- d) review the results of one-off surveys for the following chemicals identified by OSPAR for Priority Action: 2,4,6 tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define “hot-spots” of the substance, in sediments of the OSPAR area), and short chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy);
- e) report on new information on short-chain chlorinated paraffins;
- f) report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;
- g) continue to determine priorities for assistance from the Working Group on the Statistical Aspects of Environmental Monitoring (WGSAEM) with statistical analyses and develop with WGSAEM a plan for the necessary collaboration;
- h) prepare material as requested by REGNS for the integrated assessment to be held at ASC 2006;
- i) continue to report on new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants;
- j) continue to report on new information concerning the analysis and occurrence of dioxins;
- k) continue to report on new information on the monitoring and analysis of toxaphene;
- l) continue to report on developments within the UNEP Global POPs Monitoring Network;
- m) review the environmental impact of drill cuttings discharged from offshore installations;
- n) report on new information on contaminant concentrations in marine fish and other marine food products;
- o) report on new information regarding perfluorinated compounds;
- p) in relation to guidelines on frequency and spatial coverage of monitoring for nutrients and eutrophication parameters (phytoplankton, zoobenthos, phytobenthos), together with WGSAEM examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];
- q) with WGBEC, contribute to the development of detailed OSPAR guidelines deriving from the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-Sea Areas (WKIMON) [OSPAR 2005/6].

MCWG will report by 1 May 2006 for the attention of the Marine Habitat and Oceanography Committees and ACME.

### Supporting Information

Priority:	This Group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. These activities are considered to have a high priority.
Scientific Justification and relation to Action Plan:	<p>Action Plan Goals Nos:</p> <p>2.2.2: (tor a and p).</p> <p>2.2.3: (tor h)</p> <p>2.8: (tor b, c, d, e, g, i, j, k, l, m, n, o, and q)</p> <p>4.12: (tor f)</p> <p>a) This is in response to an OSPAR request.</p> <p>b) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment.</p> <p>c) These systems are being reviewed for application to monitoring of contaminants in the marine environment.</p> <p>d) This is in response to an OSPAR request.</p> <p>e) This is included as these compounds are of interest within e.g. the EU Water Framework Directive.</p> <p>f) This is in response to a standing request from HELCOM.</p> <p>g) This is in response to a request from ICES. This task will support long-term planning for WGSAAEM.</p> <p>h) This is response to a request from the REGNS group.</p> <p>i) Owing to continuing concerns about the distribution and effects of polybrominated diphenylethers and other flame retardants in the marine environment, it is relevant to consider the results of recent research on this topic.</p> <p>j) Owing to continuing concerns about the distribution and potential health effects of dioxins and other planar compounds in the marine environment, it is relevant to consider the results of recent research on this topic.</p> <p>k) Owing to continuing concerns about the distribution and effects of toxaphene in the marine environment, it is relevant to consider the results of recent research on this topic.</p> <p>l) The development of the UNEP monitoring programme is relevant to other collaborative international monitoring programmes, and a watching brief will be maintained.</p> <p>m) Discharges from offshore installations have the potential for environmental impacts in the marine environment, and it is relevant to consider the results of recent research on this topic.</p> <p>n) Owing to continuing concerns about contaminants in marine fish and other marine food products, it is relevant to consider the results of recent research on this topic.</p> <p>o) These compounds are widespread contaminants in the marine environment, and it is relevant to consider the results of recent research on this topic.</p> <p>p) This is in response to an OSPAR request.</p> <p>q) This is in response to an OSPAR request.</p> <p>MCWG provides input across the field of marine chemistry which underpins the advice given by ACME, and also supports the work of national and international collaborative monitoring programmes, e.g., within OSPAR.</p>
Resource Requirements:	The resource required to undertake activities within the framework of this group is negligible.
Participants:	The Group is normally attended by some 20–35 members.
Secretariat Facilities:	None.
Financial:	No financial implications.
Linkages to Advisory Committees:	There is a close and direct linkage with ACME.

Linkages To other Committees or Groups:	There is a close working relationship with WGMS, WGBEC, and WGS AEM.
Linkages to other Organisations:	The work of this group is closely aligned with work being undertaken within the EU Chemical Monitoring Group on the requirements and implementation of the Water Framework Directive. This group provides the basis for some advice to OSPAR.
Secretariat Marginal Cost Share:	40% OSPAR, 60 % ICES.

## Annex 12: Action Plan Progress Review 2005

Year	Committee Acronym	Committee name	Expert Group	Reference to other committees	Expert Group report (ICES Code)	Resolution No.		
2004/2005	MHC	Marine Habitat	MCWG		2005/E-03		MCWG 2005	
Action Plan	Action Required	ToR's	ToR	Satisfactory Progress	No Progress	Unsatisfactory Progress	Output (link to relevant report)	Comments (e.g., delays, problems, other types of progress, needs, etc.)
No.	Text	Text	Ref. (a, b, c)	S	0	U	Report code and section	Text
2.2.2	Assist in the development of spatial and temporal assessments of the indicators for those EcoQOs. [MHC/LRC/OCC/BCC/RMC/DFC]*	Continue to provide guidance and assistance relating to the development of a series of data products to illustrate eutrophication status within the ICES area	a)		X		8.1	insufficient expertise
2.2.2	Assist in the development of spatial and temporal assessments of the indicators for those EcoQOs. [MHC/LRC/OCC/BCC/RMC/DFC]*	Examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];	b)		X		8.2	no OSPAR draft on which to comment
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) in flatfish;	c)	X			8.3	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on new information on the use of membrane systems for sampling;	d)	X			8.4	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	With WGMS and WGS/EAEM, develop draft advice on appropriate strategies for undertaking one-off surveys to provide new information about the following chemicals identified by OSPAR for Priority Action: 2,4,6-tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define "hot-spots" of the substance, in sediments of the OSPAR area), and short-chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy) according to specific OSPAR requests; taking into account sources and modes of dispersion/transport. The specific questions to be addressed for each substance (or	e)	X			8.5	
		i) indicate whether there is any new information available on presence in the marine environment that has not already been taken into account in the relevant OSPAR background document as updated by the OSPAR lead country,	e)					
		ii) indicate whether the matrix (sediment, biota, water) proposed to be sampled is appropriate or whether an additional or more appropriate matrix should be included in the survey,	e)					
		iii) identify whether analytical techniques are available for the relevant matrices,	e)					
		iv) identify achievable detection limits, and reference materials, and	e)					
		v) determine how many stations/samples from each part of the OSPAR Convention area are necessary to address the objectives of the one-off surveys proposed, taking into account that more than one one-off survey may be required [OSPAR 2005/1];	e)					
4.12	Review and advise on procedures for quality assurance of biological, chemical and physical measurements. [OCC/MHC/ACME]	Continue to report on the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website;	f)	X			8.6	



4.12	Review and advise on procedures for quality assurance of biological, chemical and physical measurements. [OCC/MHC/ACME]	Report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;	g)	X			8.7	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to determine priorities for assistance from the Working Group on the Statistical Aspects of Environmental Monitoring (WGS/AEM) with statistical analyses and develop with WGS/AEM a plan for the necessary collaboration;	h)		X		8.8	included in tor e. The two groups will meet side-by-side in 2006.
2.2.3	Produce holistic assessments of spatial and temporal patterns of contaminants and their effects on marine ecosystems. [MHC/LRC/OCC/BCC/DFC]*	Compile data (notably winter nutrients) for the North Sea (in Excel spreadsheet format) for marine chemistry, taking account of the work already being undertaken by WGMS in response to the OSPAR MON request/meeting in December 2004. The data should be compiled (averaged) for ICES rectangles where possible, for the period 1984 to 2004 and submitted to the secure REGNS website in preparation for the REGNS Integrated Assessment Workshop to be held from 9–11 May 2005;	i)			X	8.9	No additional datasets could be identified
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on new information concerning polybrominated diphenylethers (PBDEs) and other brominated flame retardants;	j)	X			8.10	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on new information concerning the analysis of dioxins and the preparation of reference materials for these compounds;	k)	X			8.11	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on new information on the monitoring and analysis of toxaphene;	l)	X			8.12	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on developments within the UNEP Global POPs Monitoring Network;	m)	X			8.13	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Continue to report on new information on the impact of alkylphenols from produced water;	n)	X			8.14	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Report on new information on contaminant concentrations in marine fish and other marine food products;	o)	X			8.15	

2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Report on new information regarding perfluorinated compounds;	p)	X			8.16	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	In relation to guidelines on frequency and spatial coverage of monitoring for nutrients and eutrophication parameters (phytoplankton, zoobenthos, phytobenthos), together with WGS/AEM examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement [OSPAR 2005/2];	q)		X		8.17	no OSPAR draft on which to comment
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	With WGBEC, consider the current developments within OECD/EU regarding endocrine disruptors and whether this is adequate for the marine environment, and draft advice on any further work considered necessary to address issues specific to the marine environment [OSPAR 2005/8];	r)	X			8.18	could be the subject of an in-depth review by MCWG & WGBEC
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	With BEWG and WGBEC, contribute to an assessment of the long-term impact of oil spills on marine and coastal life, based on a list of issues from OSPAR [OSPAR 2005/7];	s)	X			8.19	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	Review the outcome of the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-Sea Areas (WKIMON) to resolve any outstanding issues and, together with WGBEC and WGS/AEM, finalise a draft set of guidelines for integrated monitoring for OSPAR [OSPAR 2005/6];	t)	X			8.20	
?	?	Report on the feasibility of merging WGS and MCWG.	u)	X			8.21	
?	?	respond to requests from the ICES data centre	v)	X			8.22	
2.8	Continue and further improve assessments of the transport, fate, and biological effect of contaminants on the marine ecosystem through sampling, analyses, data collection, and evaluation of sampling, analytical, and data processing techniques. [MHC/OCC/LRC/BCC]	review the draft MON assessment, particularly the way in which Background Concentrations and Environmentally Acceptable Concentrations have been used.	w)	X			8.23	