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Report of the Marine Chemistry Working Group (MCWG)

3–7 March 2014

ICES Headquarters, Copenhagen, Denmark

ICES International Council for the Exploration of the Sea

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Executive summary

The Marine Chemistry Working Group [MCWG] (Chair: Katrin Vorkamp, Denmark) met at ICES offices in Copenhagen, Denmark, 3–7 March 2014. The meeting was attended by 26 participants representing twelve countries. Guest speakers had been invited for plenary presentations and specific topics.

In response to requests by OSPAR, MCWG reviewed and updated technical annexes to the **JAMP Guidelines for Monitoring Contaminants** in Biota (metals) and Sediment (metals and organotin). The sediment-related technical annexes were revised in collaboration with WGMS. Experts of WGBEC assisted with the organotin revision.

In response to recommendations by SGOA, MCWG worked on reporting formats of **ocean acidification (OA)** data, in collaboration with the ICES Data Centre, and continued planning a workshop on OA methodology, in collaboration with QUASIMEME. The OA related topics were mainly addressed by MCWG's chemical oceanography subgroup (COSG).

Further subgroups worked on manuscripts on **perfluoroalkyl substances (PFAS)** and **environmental assessment criteria (EACs)**, on **passive sampling draft guidelines**, following up on WKPSPD and previous work by MCWG and WGMS, and on contaminant related issues of the **Marine Strategy Framework Directive (MSFD)**, with a view to providing comments to a newly established MSFD expert network.

Steven Tito of the **QUASIMEME project office** visited MCWG to present and discuss new developments at QUASIMEME and to report on a recent workshop on chlorophyll and nutrients. Furthermore, MCWG and QUASIMEME jointly plan a workshop on OA and a development exercise on passive sampling of hydrophobic organic contaminants.

As indicated by QUASIMEME's data analyses and MCWG members' own work, different methods of **chlorophyll *a*** determination might result in systematically different concentrations. MCWG welcomed using the QUASIMEME database for method assessments and decided to make OSPAR aware of this issue of potentially limited comparability. MCWG considers a publication on analytical methods of chlorophyll determination.

MCWG was informed about developments under the **Water Framework Directive (WFD),** in particular regarding Directive 2013/39/EU and links between WFD and MSFD. Following up on previous discussions of ways of highlighting MCWG's expertise with regard to contaminant monitoring in the marine environment, comments were provided to an MSFD network on contaminants and the decision of a publication on EACs (or environmental quality standards) was confirmed.

The issue of **marine litter** was addressed in a joint session with WGMS and WGBEC, with MCWG's focus being on litter-contaminant interactions. Initial scientific evidence suggests a minor role of marine litter as a vector of organic contaminants, but more knowledge is needed. As a number of research initiatives are ongoing, MCWG will follow up on new findings at its 2015 meeting.

Besides the subgroup work on passive sampling guidelines, **passive sampling** as a general topic was addressed in a joint session with WGMS and WGBEC, with a contribution by **Prof. Philipp Mayer** (Technical University of Denmark) as an invited speaker. The three groups discussed how to take WKPSPD's work forward and future steps were defined for intersessional work and the 2015 meeting cycle.

In a third joint session, invited guest speaker **senior scientist Hans Sanderson** (Aarhus University, Denmark) presented long-term work on risk assessments of chemical warfare agents dumped in the Bornholm Deep (Baltic Sea). Special attention was given to potentially enhanced risks in relation to the Nord-Stream pipeline in the same area.

Following up on previous work, MCWG reviewed the literature on **seabird eggs** as a monitoring matrix for organic contaminants and trace elements. For more background knowledge MCWG had invited senior scientist Anders Mosbech (Aarhus University, Denmark), an expert in seabird ecology. MCWG also reviewed OSPAR's activities in this field and generally suggested more interactions.

MCWG members Bavo de Witte, Caroline Kivimae, Foppe Smedes, Jacek Tronczynski, Lutz Ahrens, Michael Haarich, Michiel Kotterman, Naomi Greenwood and Philippe Bersuder presented **projects of relevance** to MCWG.

1 Opening of the meeting

The Marine Chemistry Working Group (MCWG), chaired by Katrin Vorkamp, Denmark, met at ICES offices in Copenhagen, Denmark, 3–7 March 2014. The chair opened the meeting on 3 March 2014 at 10 a.m. and welcomed the participants to the 36th meeting of MCWG.

The participants introduced themselves and their affiliations and described their interests within the field of marine chemistry. Katrin Vorkamp conveyed regards and messages from MCWG members who were not able to attend MCWG 2014. The meeting was attended by 26 participants from 12 countries. The list of participants is given in Annex 1. Four guests attended the meeting for plenary presentations or specific sessions.

2 Adoption of the agenda

The draft agenda was discussed and adopted as shown in Annex 2. The full text of the OSPAR requests (see section 5.13) is given in Annex 5.

The action list from MCWG 2013 was updated. The timetable for the meeting was presented and discussed.

The Working Group on Marine Sediments in relation to Pollution (WGMS) and the Working Group on Biological Effects of Contaminants (WGBEC) met concurrently. Joint sessions had been arranged on passive sampling (agenda item 5.11) and marine litter (agenda item 5.4). WGMS and WGBEC also attended the plenary presentations arranged by MCWG.

The following subgroups were formed to work on specific tasks and agenda points:

Subgroup	Names	Task	Agenda item
OSPAR request: Technical annex on metals in biota	Victoria Besada, Gert Asmund, Jens Søndergaard, Michael Haarich, Martin M. Larsen (WGMS)	Review and update technical annex of OSPAR JAMP guideline	5.13.1
OSPAR request: Technical annex on organotins in sediments	Koen Parmentier, Norbert Theobald, Jakob Strand (WGBEC), experts of WGMS	Review and update technical annex of OSPAR JAMP guideline	5.13.2
OSPAR request: Technical annex on metals in sediment	Victoria Besada, Gert Asmund, Jens Søndergaard, Michael Haarich, experts of WGMS	Review and update technical annex of OSPAR JAMP guideline	5.13.3
Chemical Oceanography Subgroup	Evin McGovern, Carlos Borges,	Recommendations from SGOA; updates	5.7; 5.8

	Caroline Kivimae, Kristin Andreasson, Pamela Walsham, David Pearce, Naomi Greenwood, Solveig Olafsdottir	within ocean acidification; method comparisons of chlorophyll determinations	
PFAS manuscript	Lutz Ahrens, Katrin Vorkamp, Norbert Theobald	Presentation of PFAS manuscript and updates according to MCWG comments	5.12.1
EAC manuscript	Katrin Vorkamp, Lynda Webster, Patrick Roose, Peter Lepom, Michiel Kotterman	Further work on the current draft.	5.12
Passive sampling	Kees Booij, Foppe Smedes, Jacek Tronczynski, Katrin Vorkamp, Kine Bæk, Lutz Ahrens, Lynda Webster, Norbert Theobald, experts of WGMS	Discuss guidelines on passive sampling in sediments and determinations of partition coefficients	5.12.2; 5.12.3

3 Report of ICES activities

3.1.1 MCWG 2013 recapitulation

Katrin Vorkamp presented a summary of the main work at MCWG 2013, to refresh participants' memory and to provide links to the tasks at MCWG 2014. Since MCWG 2013, two reports had been published by members of MCWG:

Hydes, D.J., McGovern, E., Walsham, P., Borges, A.V., Borges, C., Greenwood, N., Hartman, S.E., Kivimae, C., Nagel, K., Olafsdottir, S., Pearce, D., Sahlsten, E., Rodriguez, C., Webster, L. (2013). Chemical aspects of ocean acidification monitoring in the ICES marine area. ICES Cooperative Research Report no. 319.

Webster, L., Roose, P., Bersuder, P., Kotterman, M., Haarich, M., Vorkamp, K. (2013). Determination of polychlorinated biphenyls (PCBs) in sediment and biota. ICES Techniques in Marine Environmental Sciences no. 53.

3.1.2 Intersessional activities

Katrin Vorkamp informed MCWG about ICES activities in the intersessional period since MCWG 2013, which likely are interesting and relevant for MCWG.

- Multi-annual management of ICES SCICOM working groups

  The changes in relation to the 3-year-work periods decided for all SCICOM working groups had been presented at MCWG 2013. Previous discussions

were not resumed at MCWG 2014. However, Katrin Vorkamp pointed out that the 3-year-management would become effective for MCWG after the MCWG 2015 meeting, following her term as chair of MCWG. She suggested that draft Terms of References (ToRs) for the 3-year-work period should be discussed at MCWG 2015.

- SCICOM comments on draft ToRs for MCWG 2014

  The ToRs drafted by MCWG 2013 and submitted to ICES subsequently, were approved by SCICOM in October 2013. The following comment was returned to MCWG: "The MCWG ToRs were approved, but there was a comment regarding ToR A-3: *Demonstrate new software developed by the Finnish Environmental Institute for estimations of measurement uncertainty.* SCICOM noted that you should consider if the computer program is relevant to the wider ICES community and possibly report on this to WGDIM."
  Unfortunately, Mikael Krysell who was in charge of this demonstration was unable to attend MCWG 2014. For this reason, the ToR and the comment connected to it could not be addressed by MCWG 2014.

- Conference "Pollutant Responses in Marine Organisms (PRIMO)"

  The 17th PRIMO conference was held in Faro (Portugal) from 5-8 May 2013. Following a suggestion by Matt Gubbins, former chair of WGBEC, ICES sponsored this conference, including the participation of Matt Gubbins, Vivian Piil and Katrin Vorkamp as ICES conveners. Matt Gubbins and Katrin Vorkamp were members of the Scientific Committee of this conference, with the task to review abstracts for poster and oral presentations and to chair conference sessions. Katrin Vorkamp described the session topics several of which covered MCWG's work areas. The next PRIMO conference is going to take place in Trondheim (Norway) from 24–27 May 2015.

- ICES Science Plan (2014-2018)

  Katrin Vorkamp presented the new ICES Science Plan with its focus on Integrated Ecosystem Understanding and referred to the full document for details. Katrin Vorkamp described the main elements of the Science Plan, i.e. Ecosystem Processes and Dynamics (EPD) covering the internal processes that control the ecosystems, Ecosystem Pressures and Impacts (EPI) about external processes affecting the ecosystems, Integrated Ecosystem Assessments (IEA) and Integrated Ecosystem Observation and Monitoring (IEOM). Below each of these headings, the Science Plan lists a number of objectives. Katrin Vorkamp presented these objectives and highlighted those which will be directly supported by MCWG's work.

- Workshop on the Passive Sampling and Passive Dosing of Contaminants in Marine Media (WKPSPD)

  The outcome of this workshop had been presented and discussed at MCWG 2013. Since then, the workshop report has been published. It includes two draft resolutions which require input from MCWG:
  "i) Update and finalise an earlier drafted document on passive sampling of nonpolar contaminants in sediments, for publication in the TIMES series.
  ii) Produce a TIMES publication on the determination of sampler-water partition coefficients and sampler-sampler partition coefficients, including their uncertainties."

Both resolutions are directed at MCWG and WGMS. The deadline for these documents is April 2015.

- ICES Annual Science Conference 2013

  See section 3.1.3.

- Attempts to promote MCWG's expertise at EU level

  Discussions at MCWG 2013 about highlighting MCWG's expertise at EU level, in particular regarding descriptors 5, 7, 8, 9 of the Marine Strategy Framework Directive (MSFD), led to a recommendation to ICES ACOM by MCWG 2013.
  In addition, an action was defined for Jacek Tronczynski and Katrin Vorkamp at MCWG 2013 to contact Georg Hanke at the Joint Research Centre. Jacek Tronczynski contacted Georg Hanke who was interested in MCWG's expertise in relation to MSFD.
  In this context, Jacek Tronczynski made the chair aware of a meeting of the ICES Council Steering Group (CSG) of the MSFD in September 2013. Katrin Vorkamp wrote a letter to CSG MSFD, which repeated the recommendation to ICES ACOM originally placed in the MCWG 2013 report. Furthermore, the letter described the MCWG expertise with regard to several MSFD descriptors and highlighted the strong contaminant expertise available in ICES (MCWG, WGMS, WGBEC).
  No answer was received by CSG MSFD. The question of becoming visible at EU level was further discussed in relation to agenda point 5.2.

- New expert group on marine litter

  In October 2013, the chairs of MCWG, WGMS and WGBEC were contacted by Claus Hagebro (ACOM) with regard to a proposal which ICES had received to form a new working group on marine litter. Draft ToRs were sent to the chairs for comments.
  Katrin Vorkamp responded that the draft ToRs should focus on relevant questions at hand and anticipated requests (e.g. on sampling, QA/QC, data reporting), that the products of the 3-year-working period were not clear and that assistance to the ICES Data Centre should be a priority. Little overlap was anticipated with MCWG, however, contaminant-related questions should be addressed in collaboration with (or given to) MCWG.
  During the MCWG 2014 meeting, the question was repeated and posed to all members of MCWG, WGMS and WGBEC, see section 5.4.

- Publications

  See section 3.1.1 and section 5.12.

- Workshop on linking contaminant issues with integrated ecosystem assessment (WKLINCON)

  The chair had come across an announcement of this workshop, originally planned for 2013, but postponed to 2014. The chairs currently appointed are Matt Gubbins, Kari Lehtonen and Dick Vethaak.
  Katrin Vorkamp presented the ToRs of this workshop and commented that MCWG participation seemed highly relevant. Most members agreed and it was decided that Katrin Vorkamp would make further enquiries about location and date for this workshop.

3.1.3 2013 Annual Science Conference

Solveig Olafsdottir reported from the ICES Annual Science Conference (ASC) 2103 which had taken place in Reykjavik, Iceland, 23–27 September 2013.

MCWG had suggested a theme session for the ASC 2013 on physico–chemical aspects of ocean acidification in the ICES area (see also section 5.7.4). The theme session call was rather narrow in scope, initially planned for analytical techniques and quality control and for baseline studies on carbon cycle parameters and pH in the ICES area. Studies for determination of seasonal and interannual variability were also invited. There were only four presentations in the session. Two were about observations and their interpretation, one had the focus on observational methods and gave some basic results and the last one on modelling of ocean acidification processes in three different regions in the North-Atlantic. The session followed the invited plenary talk of Dr. Richard Feely of NOAA titled "Ocean acidification: significant predictions for marine life" which influenced discussions at the end of the session. Taking this lecture together with the theme session did a lot to highlight the fact that OA is likely to affect the ICES area in near future.

Three conveners, Jon Olafsson (Iceland), Alberto Borges (Belgium) and David Hydes (UK) had been suggested by MCWG. However, only Jon Olafsson was able to attend the meeting and Adi Kellerman (SCICOM, ICES) came in as the second convener. About 60 people attended the session.

MCWG discussed that given the ICES focus on topics related to fisheries, experts in marine chemistry are difficult to attract to the ASC. Jacek Tronczynski remarked that the new ICES Science Plan with its focus on ecosystem understanding (see section 3.1.2) might accommodate research into contaminants, for example their uptake and transfer in foodwebs.

The ASC 2014 is going to take place at A Coruña, Spain, from 15 to 19 September 2014. Of the MCWG members at MCWG 2014, Victoria Besada considered participating in the ASC 2014.

3.1.4 OSPAR/ICES Study Group on Ocean Acidification (SGOA)

Evin McGovern, co-chair of the OSPAR/ICES Study Group on Ocean Acidification (SGOA), provided an update of progress of SGOA in addressing its ToR as defined by OSPAR. SGOA has a three-meeting cycle and the conclusions and products of SGOA will be incorporated in a report by the final meeting in October 2014 (see also section 5.7.1).

SGOA is drafting an OA monitoring strategy which is well developed for physico-chemical monitoring of OA conditions although OA-specific biological impact indicators are less mature. Shell morphology of *Thecosomata* pteropods is a potentially sensitive indicator and SGOA suggests that a specimen repository would be a useful facility to enable retrospective monitoring for evidence of OA impacts once suitable indicator metrics are developed. SGOA 2013 discussed sensitivity of cold-water corals to perturbations in the carbon cycle and also new information on species responses and ecosystem interactions across CO_2 gradients at volcanic CO_2 vent sites as proxies of future OA conditions.

Guidelines for chemical monitoring have been submitted to OSPAR and data reporting formats and checks for OA-data from discrete samples to the ICES DOME database have been defined and tested by MCWG and SGOA. SGOA identified some tasks to be addressed by MCWG, specifically some outstanding reporting queries and

to progress a workshop on Quality Assurance of OA measurements to support monitoring. These items were included in MCWG 2014 agenda point 5.7. Other biological expert groups have a role in the ongoing development of appropriate impact metrics and in providing new information on ecosystem responses to OA. SGOA noted that WGBEC members had expressed an interest in contributing to this work and WGBEC members are invited to participate in SGOA.

References

ICES (2013). Report of the Joint OSPAR/ICES Ocean Acidification Study Group (SGOA), 7-10 October 2013, Copenhagen, Denmark. ICES CM 2013/ACOM:31.82 pp.

4 Plenary presentations

Two guests had been invited to present their research at MCWG 2014. The plenary presentations were attended by WGBEC and WGMS as well.

4.1 First plenary presentation

Hans Sanderson (Senior scientist at Aarhus University, Denmark)

Sea dumped chemical munition in the Baltic Sea – a review with regards to fish community risk

Hans Sanderson presented a summary of his work on the measured chemical warfare agent (CWA) concentrations found in the Bornholm Deep CWA dump site. Most of the work had been conducted in the FP6 project MERCW and in relation to the Nord-Stream pipeline work in Danish waters for the past 5 years.

Exposure assessment was presented: Sediment and biota sampling were performed along the pipeline route in four campaigns; prior to (in 2008 and 2010), during (in 2011) and after (in 2012) the construction work. No parent CWAs were detected in the sediments, patchy residues of CWA (degradation products of Adamsite, Clark I, phenyldichloroarsine, trichloroarsine and Lewisite II), were detected in a total of 29 of the 391 sediment samples collected and analyzed in the past 5 years. The cumulative fish community risk quotient for the different locations, calculated as a sum of background and added risk, ranged between 0 and 0.017 suggesting a negligible acute CWA risk towards the fish community. The added risk from sediment disturbance in relation to construction of the pipelines represented less than 2% of the total risk in the areas with the highest calculated risk. The analyses of benthic fauna corroborate the finding of CWA related low risk across the years. There was no significant difference in CWA risk before (2008) and after the pipeline construction (2012).

References:

Sanderson *et al.* (2012). Weight-of-evidence environmental risk assessment of dumped chemical weapons after WWII along the Nord-Stream gas pipeline in the Bornholm Deep. J. Haz. Mat. 215-216; 217-226.

Sanderson *et al.* (2010). Environmental hazards of sea-dumped chemical weapons. Feature. Environ. Sci. Technol. 44, 4389-4394.

Sanderson *et al.* (2009). Human health risk screening due to consumption of fish contaminated with chemical warfare agents in the Baltic Sea. J. Haz. Mat. 162; 416-422.

4.2 Second plenary presentation

Philipp Mayer (Professor at the Technical University of Denmark):

Equilibrium sampling and passive dosing of hydrophobic pollutants – approaches, applications and findings

Philipp Mayer presented research conducted by his group and others on equilibrium passive sampling of nonpolar contaminants, with a focus on sediments. This method allows to measure pore water concentrations of freely dissolved compounds (C_{free}) in the range $3 < \log K_{OW} < 8$ by incubating micrometer thin polymer coatings in sediments for periods of up to a few weeks. C_{free} is better related to sediment toxicity and bioaccumulation than total concentrations in the sediment phase, even if the latter are normalised to organic carbon. The concentration in the polymer phase ($C_{polymer}$) is also a good measure of the toxicity of these sediments. Using a polymer-lipid partition coefficient, $C_{polymer}$ can easily be converted to an equilibrium concentration that a nonpolar lipid phase would have (C_{lipid}). Finally, this lipid based concentration can be directly compared with lipid normalised contaminant concentrations in biota. The latter concentrations are typically smaller than the passive sampler derived lipid concentrations.

Philipp Mayer further showed that equilibrium passive sampling allowed for identifying pollution sources and assessing the degree of sediment-water equilibrium in the environment, and that these data were easier to interpret than biota-sediment accumulation factors.

Below, some references are given for further reading. For an extended list of references, see Annex 7.

References

Jahnke A., Mayer, P., McLachlan, M.S. (2012). Sensitive Equilibrium Sampling to Study Polychlorinated Biphenyl Disposition in Baltic Sea Sediment. Environmental Science and Technology 46, 10114−10122.

Jahnke, A., Mayer, P., McLachlan, M.S., Wickström, H., Gilbert, D., MacLeod, M. (2014). Silicone passive equilibrium samplers as 'chemometers' in eels and sediments of a Swedish lake. Environmental Science: Processes & Impacts 16, 464-472.

Mäenpää, K., Leppänen, M.T., Reichenberg, F., Figueiredo, K., Mayer, P. (2011). Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment: comparison of two approaches to determine equilibrium partitioning concentrations in lipids. Environ. Sci. Technol. 45, 1041-1047.

Mayer, P., Parkerton, T.F., Adams, R.G., Cargill, J.G., Gan, J., Gouin, T., Gschwend, P.M., Hawthorne, S.B., Helm, P., Witt, G., You, J. (2014). Passive sampling methods for contaminated sediments: scientific rationale supporting use of freely dissolved concentrations. Integrated Environmental Assessment and Management 10 (2), 197-209.

Rojo-Nieto, E., Smith, K.E.C., Perales-Vargas-Machuca, J.A., Mayer, P. (2012). Recreating the seawater mixture composition of HOCs in toxicity tests with Artemia franciscana by passive dosing. Aquatic Toxicology 120-121, 27-34.

Witt, G., Liehr, G.A., Borck, D., Mayer, P. (2009). Using solid phase microextraction to measure freely dissolved concentrations and chemical activities of PAHs in sediment cores of the western Baltic Sea. Chemosphere 74: 522-529.

Witt, G., Lang, S.C., Ullmann, D., Schaffrath, G., Schmidt, K., Schulz-Bull, D., Mayer, P. (2013). A passive sampler for in situ measurements of freely dissolved concentrations of hydro-

phobic organic chemicals in sediments. Environmental Science & Technology 47, 7830–7839.

5 Main agenda

5.1 Quality assurance of marine chemistry

5.1.1 Report and discuss new developments in QUASIMEME

Steven Tito (QUASIMEME project office) visited MCWG 2014 to present new developments at QUASIMEME and to discuss various issues with MCWG.

- Combined nutrients and chlorophyll workshop

MCWG 2013 had recommended a workshop on chlorophyll and nutrients under the auspices of QUASIMEME and had suggested topics and speakers for this workshop. The workshop was held in Ostend, Belgium, from 4 to 6 February 2014 and attended by nearly 50 participants (see also section 5.8.1).

Steven Tito reported on data presented by QUASIMEME at the chlorophyll and nutrient workshop, as described in detail in section 5.8.1. A review of chlorophyll *a* proficiency test performance by QUASIMEME indicated that little improvement in performance had been observed over the last 10 years. As a result, QUASIMEME investigated analytical methods in Round 72 by sending additional materials to scheme participants, mainly with the purpose of assessing extraction, storage, delivery time and methods of analysis. The use of methodology with HPLC resulted in lower z-scores. In addition, sonication did not seem to be the best method for quantitative chlorophyll *a* extraction. Issues with poor performance when nannochloropsis was used as a material were shown not to be caused by the analytical technique (i.e. HPLC or fluorometry), although the use of HPLC resulted in better relative standard deviations and lower z-scores. However, extraction technique and extraction solvents had a significant effect, ethanol seemingly being the better solvent to extract chlorophyll *a*. However, due to these issues, QUASIMEME decided not to use nannochloropsis as a material in the future. The workshop resulted in a list of actions for QUASIMEME to progress.

Also, as a result of the workshop and the meta-analysis of the data in the QUASIMEME database, results for HPLC and non-HPLC techniques will be reported separately for AQ-11 from Round 72.

MCWG 2014 commended the investigative work carried out by QUASIMEME and felt that the resulting information and recommendations were very valuable. MCWG encouraged QUASIMEME to publish the data and recommendations issued at the workshop. The evaluation of datasets for other parameters in various QUASIMEME materials might be similarly valuable, although MCWG 2014 understands that this is a timely and costly exercise.

- Points raised at MCWG 2013

Steven Tito subsequently provided a follow up on various points raised during MCWG 2013.

Forty new parameters were added to MS-1 starting from Round 71, but low numbers of participants made use of the new parameters, and ultimately statistical evaluation was only possible for ten parameters. An additional thirty eight parameters are available for BT-1 from Round 73, but few data have been submitted to date.

Steven Tito informed that there would be a possibility of restarting the BT-3 and BE-1 exercises if enough pre-applications were registered.

The new report format, as announced at MCWG 2013, has been delayed, but is expected to start with next rounds.

As requested at MCWG 2013, QUASIMEME also publishes fat values in biota materials if available, as part of the information given in the protocols.

- Workshop on ocean acidification parameters (see also section 5.7.3)

MCWG 2013 had suggested a workshop on determinations of total alkalinity, dissolved inorganic carbon and other parameters related to ocean acidification monitoring. The suggestion was supported by SGOA (see also section 3.1.4 and section 5.7.4).

QUASIMEME is willing to facilitate this workshop, but has no data to offer, and is looking for an institute to organise the workshop and set down some dates. The NOC in Southampton (UK) is willing to organise the workshop and there is wide interest from the group in terms of participation. Funding of the workshop needs to be discussed, with a view to attract keynote speakers, in particular Prof. Andrew Dickson of Scripps Institution of Oceanography (University of California, San Diego, USA). Participant numbers might be an issue, as a minimum of 20 participants will be needed. MCWG 2014 members were designated to contact keynote speakers to evaluate availability.

The Chemical Oceanography Subgroup further discussed the workshop in terms of aims, expected outcomes and actions for MCWG members. These deliberations are described in section 5.7.3.

- Proficiency testing scheme on passive sampling (see also section 5.11.1)

WKPSPD and MCWG 2013 had suggested a laboratory proficiency testing scheme for passive sampling, organised by QUASIMEME (see also section 5.11.1).

An exercise on passive sampling was discussed at the QUASIMEME Scientific Assessment Board (SAB), and was added to the 2014 programme as development exercise DE-13. However, there was only one subscription by the time of the MCWG 2014 meeting. MCWG 2014 suggested that the exercise should be promoted amongst the freshwater community via existing networks (e.g. NORMAN network, etc.) as well as participants of WKPSPD. MCWG 2014 members are involved in the design of the exercise, which will consist of exposed and non-exposed silicone rubber samplers, but also a check on calculations (as a major source of variability due to their complexity). There is a potential issue with performance reference compounds (PRCs) to be used, as these might interfere with analytical internal standards used by laboratories, and this should be part of the exercise announcement.

- Other new developments at QUASIMEME and other points of discussion

With regard to accreditation, QUASIMEME plans to extend the scope of accreditation to include the BT-11 and BT-12 exercises.

The development of a new website for QUASIMEME members has progressed albeit more slowly than planned. However, from round 74, the existing SharePoint site used by members will be replaced. An additional functionality includes viewing laboratory specific historical data.

In the background, the data management system is gradually being replaced with a new one, which will allow more automation (e.g. processing data and reporting). The administrative and financial management modules are now up and running.

Finally, participation costs to QUASIMEME will not increase for 2014.

Steven Tito solicited feedback from MCWG 2014 with regards to QUASIMEME using freeze-dried biota material, with an increase in participation costs to be expected. MCWG 2014 was generally not in favour of freeze-dried materials as the more volatile compounds (e.g. HCHs, lower molecular weight PCBs/PAHs) might be removed to non-detectable levels. Additionally, drying of biotic materials is an integral part of the analytical methods used by participating laboratories. This step might result in contamination or losses in individual laboratories, and the use of freeze-dried material as a proficiency test would circumvent this step.

MCWG 2014 raised the issue of high levels of BDE209 and γ-HBCD in a sediment material (from Goole, UK) provided in round 73. Levels for these compounds exceeded the concentration range provided in the QUASIMEME protocol, apparently by several orders of magnitude. Consequently, the effort required by participating laboratories was significantly increased in terms of repeated analyses, extract dilutions, but also increased instrument maintenance from contamination. In addition, situations like this can lead to issues with accreditation bodies (i.e. if results are not submitted).

The recommendation from MCWG 2014 is that the concentration of relevant indicator determinands of each compound group to be analysed in the QUASIMEME exercises should be determined by QUASIMEME before sending out new materials, and the range of concentrations provided in the material protocol should be representative of actual concentrations.

In terms of biota materials, MCWG 2014 remarked that samples from fresh water are being used, and it was agreed that this was not an issue providing the preparation of biota materials remains focused on marine species and the use of materials originating from fresh water is clearly indicated in the protocol.

Also, the lack of z-scores for brominated flame retardants in biota was questioned, although it was felt that levels should be detectable by competent laboratories.

The discussions under this agenda point resulted in two recommendations for QUASIMEME, which are summarised in Annex 4.

5.1.2 Provide information on other proficiency testing schemes with relevance to MCWG

Katrin Vorkamp presented information on the Northern Contaminants Interlaboratory Quality Assurance Programme. The programme is free of charge, with a frequency of one exercise annually and claims to tailor materials to match Arctic interests. Results were presented for all the compound groups for the latest round, along with details of the statistical analysis, and evaluation of laboratory performance for some compound groups. Test materials were mainly a combination of biota certified reference materials and standard solutions. Compounds and compound groups are very much relevant to marine chemistry, and include Hg/MeHg, trace metals, POPs (dioxins, PCBs, OCs, etc…) and emerging contaminants (such as BFRs, PFAS, PCNs, chlorinated paraffins).

Peter Lepom remarked that the WFD network (PT-WFD) for proficiency testing has dissolved, but participating PT scheme providers still provide relevant materials.

5.1.3 Demonstrate new software developed by the Finnish Environmental Institute for estimations of measurement uncertainty

This topic had been brought up by Mikael Krysell at MCWG 2013. As he was unable to attend MCWG 2014, this item was not discussed (see also section 3.1.2).

5.2 Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)

WFD and MSFD were addressed as a combined agenda point as there are several links between these directives. The following text under 5.2.1 therefore describes work and discussions on WFD and MSFD.

5.2.1 Review and discuss developments of WFD, in particular regarding new priority (hazardous) substances and associated EQS values

Peter Lepom gave a presentation on the new WFD Priority Substance Directive 2013/39/EU amending Directive 2008/105/EC. Key features include:

- 12 additional priority substances are identified. Environmental Quality Standards for biota (EQS_{biota}) are set for 5 of these substances.
- EQSs amended for 7 substances including 3 new $EQS_{biota.}$
- Establishment of a Watch List for additional substances.
- Separate maps of chemical status can be prepared for ubiquitous PBT substances, newly identified priority substances and priority substances for which new EQSs have been established.
- Supplementary provisions for treatment of values below limits of quantification (LOQs) if best available technique was applied.
- EQSs for lead and nickel refer to bioavailable fraction.
- Specific provisions for pharmaceutical substances.

In the ensuing discussion it was noted that the approach taken to establishing EQS_{biota} involved deriving EQS for secondary poisoning ($EQS_{biota\ sec\ pois}$) and for human health ($EQS_{biota\ hh}$) with the lower value adopted as the EQS, though the directive does not make clear which EQS "type" each value is. To find this information it is necessary to go to the EQS technical dossiers.

This approach of using $EQS_{biota\ hh}$ gives rise to some inconsistencies between EQSs and with other legislative approaches. Furthermore, some EQS_{biota} have become very low (most notably for polybrominated diphenyl ethers (PBDEs) and heptachlor/ heptachlor epoxide). The monitoring guidance (CIS Guidance document No. 25) indicates that biota monitoring requires testing whole fish for $EQS_{biota\ sec\ pois}$ and filets for $EQS_{biota\ hh}$. It was noted that the CIS Working Group on Chemicals is developing new EQS guidance, specifically on biota monitoring and also on applying a bioligand model for certain metals.

Two issues were discussed further:

- Are $EQS_{biota\ hh}$ of relevance for D8 monitoring in the MSFD given that they are not set for ecological protection?
- Member States may apply an EQS for an alternative taxon or matrix once the same level of protection is offered. Monitoring of bivalve molluscs is widespread and offers some advantages as a monitoring matrix. It was suggested that as a practical input to the process, MCWG could consider

providing advice on conversion of EQS_{biota} from fish to mussels, noting the different trophic levels. This would aid member states in using mussels in their WFD monitoring and would avoid member states taking independent approaches. There was some concern expressed as to how this would apply in MSFD monitoring especially for $EQS_{biota\ hh}$ and indeed whether a conversion would be relevant for $EQS_{biota\ hh}$.

Following up on discussions at MCWG 2013, it was further discussed how MCWG could input into developing MSFD guidance on D8 and D9 as well as the WFD, noting that MCWG comments of previous years has probably had limited impact on the process.

Evin McGovern drew MCWG's attention to a document submitted by Ireland to OSPAR MIME 2013 working group on D8 and D9 monitoring, indicating that given the different sampling strategies required for the different purposes of D8 and D9 as well as the variety of approaches by Member States for implementing D9 monitoring, typically built on current seafood monitoring programmes, there was very limited scope for linkages between the descriptors. MCWG agreed with this view noting earlier advice from MCWG on this issue.

Apart from CIS Working Group on Chemicals a new informal expert group on MSFD D8 and D9, convened by the JRC, has been established with a number of MCWG members participating in this expert group. It was agreed that MCWG would prepare comments on implementation of D8 and D9 monitoring to this group. A subgroup (Evin McGovern, Jacek Tronczynski, Koen Parmentier, Peter Lepom, Norbert Theobald, Victoria Besada) drafted some text which was discussed and finalized in plenary. The final text is given as Annex 8. Katrin Vorkamp agreed to forward the comments to Georg Hanke, chair of the MSFD expert group (see action list in Annex 6).

Jacek Tronczynski commented that an alternative/additional way of reaching a higher impact on discussions was to publish a review of the issues in the peer-reviewed literature. MCWG members agreed with this suggestion and were generally in favour of pursuing this plan. It was decided that the EAC manuscript (see section 2) should be finalized as a first step.

Reference

Technical Report - 2010.3991, Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Guidance Document No. 25. Guidance on Chemical Monitoring of Biota and Sediment under the Water Framework Directive. ISBN 978-92-79-16224-4, European Union, 2010.

5.2.2 Review and discuss developments in MSFD, in particular regarding the monitoring of descriptors 5, 7, 8 and 9

See sections 5.2.1 and general comments under 5.2.

5.3 Present projects of relevance to MCWG

For the next MCWG meeting, it was decided to merge this agenda point with point 5.9 on emerging contaminants in the marine environment.

Bavo de Witte: 4DEMON – 4 decades of marine monitoring: uplifting historical data to today's needs

The 4DEMON project brings together a multidisciplinary consortium of five Belgian partners which hold a large amount of historic information on the marine environment of the Belgian continental shelf stretching back over a period of 4 decades. This information will be used to complete and interpret existing data sets. Within Work Package (WP) 2, data managers will coordinate the whole data management process. WPs 3, 4 and 5 comprise data collection, quality control and intercalibration.

WP 3 on contamination will focus on historical data of organic pollutants and heavy metals, analysed in marine sediments and biota. Priority will be given to the longest time series, i.e. monitoring of heavy metals and polychlorinated biphenyls. The key indicators that will be collected within WP 4, eutrophication, are turbidity, dissolved nutrient concentrations and ratios, and phyto- and zooplankton biomass and species composition. In WP 5, ocean acidification, the goal is to intercalibrate and compile data on pH, partial pressure of CO_2, total alkalinity and dissolved inorganic carbon. In WP 6, the quality-checked and intercalibrated data sets will form the basis of statistical analyses to assess and interpret change in contamination, eutrophication and acidification indicators on the Belgian continental shelf during the last four decades. The results of the different fields will be combined for integrated statistical analyses. In the final task, the trends observed in the data sets compiled in the 4DEMON project will be compared with long-term data sets of the same parameters from adjoining areas.

Jacek Tronczynski: Transfer and bioaccumulation of contaminants at first trophic levels in short pelagic food webs

Methods and preliminary results were presented of a study on the accumulation and transfer of persistent organic contaminants and metals at the primary trophic levels (autotrophes and hetetrophes), and then within the short food web of small pelagic fish (anchovies and sardines) in the Gulf of Lion, Western Mediterranean (COSTAS ANR French national project 2010–13). The assimilation of contaminants and elements at primary trophic levels, in plankton, is not yet very well documented. However, planktonic populations play a key role in the trophic food webs in marine ecosystems by the mobilisation and transfer of organic matter towards higher trophic levels.

Three groups of compounds and elements were studied: persistent organic contaminants (PCBs, PBDEs), mercury (Hg), methyl mercury (MeHg) and other metals (Pb, Cd, Cu, Ag, Zn…). The plankton and water samples were collected in the Gulf of Lion during several research cruises in spring and winter of 2009 and 2011. The plankton samples were fractionated in four size classes (60–200, 200–500, 500–1000, 1000–2000 μm). Furthermore, the physical and chemical parameters of the water column, as well as a series of biological parameters (biomass and communities of planktonic components, stable isotopes of carbon and nitrogen, pigments and CHN elemental composition) were also determined to better describe the structure of the food web (plankton and small pelagic fish) and infer potential contaminant transfer pathways.

The first results show that the relationship between PCB concentrations, size of plankton and δ15N signatures is not straightforward. Generally the concentrations of PCB determined in the lowest 60–200 μm size class were not significantly lower than in higher size classes. The PCB concentrations in the lowest size class dominated by phytoplankton are related to the passive diffusive partition uptake of contaminants. Significant, linear regressions were found between bioaccumulation factors of CB

congeners and their Kow partition coefficients. However, no dilution effect was observed between PCB concentrations and plankton biomass. The constant biomagnification factor over a whole range of PCB Kow values also indicates that biomagnification could not be evidenced with this set of results.

Indeed, the prey-predator contaminant transfer appears to be difficult to clearly distinguish within planktonic food-webs, especially in field studies. The higher zooplankton size classes may be composed of organisms with different diets, including herbivores, carnivores and detritivores, susceptible in addition to adapt their diet to the quantity of available resources. Consequently, biomagnification of PCBs over the range of plankton size classes was frequently not observed in the field studies. Furthermore, size class and isotope signatures of plankton do not necessarily reflect trophic relationship and complex ecology in plankton communities. The full data and results of this study, including trophic transfer of contaminants to the small pelagic fish will be presented at MCWG 2015.

Jacek Tronczynski: Historical records of Hg, Pb and PAH in a dated sediment core from the Eastern Mediterranean

Depth-distribution profiles of mercury, lead and its stable isotopes, and polycyclic aromatic hydrocarbons were determined in a dated sediment core from the Levantine basin. Sedimentary records show an almost concurrent uniform increase of both metals and PAHs occurring around the time of the Industrial Revolution onset, whereas their levels remain generally constant before 1850. Pre-industrial levels in the region were: 0.013 ± 0.002 μg g^{-1}; 11.3 ± 0.74 μg g^{-1} (n = 39) and 16.1 ± 4.4 ng g^{-1}; (n = 23) for Hg, Pb and PAHs respectively. The temporal coherence of the initial increase in metals and PAH fluxes suggests coal combustion as a main source of these contaminants in the Levantine basin after the 1850s. However, none of the contaminant profiles indicates a decline in surface layers characteristic of coal use reduction. The modern fluxes of Hg and Pb reveal a three to five-fold increase over pre-industrial loads, in agreement with other findings. While the contemporaneous flux of PAHs rises only by four to seven times, that is a much lower enrichment than for other sites. On the whole, records in the Eastern Mediterranean Sea suggest atmospheric inputs from relatively distant sources, likely from Central and Eastern Europe.

Reference

Azourz, S., Tronczynski, J., Chiffoleau, J.F., Cossa, D., Nakhlé, K., Schmidt, S., Khalaf, G. (2013). Historical records of mercury, lead, and polycyclic aromatic hydrocarbons depositions in a dated sediment core from the Eastern Mediterranean. Environmental Science & Technology 47, 7101-7109.

Michael Haarich: Contaminants in fish – Monitoring in the North Sea and the Baltic Sea

An overview of contaminant monitoring in fish from the North and Baltic Sea performed in the German national marine monitoring programme was presented. Time series of trace metals and organic contaminants, the latter covering also some years of data on brominated diphenyl ethers, indicated for the last decade no continuation of the downwards trends observed in the nineties of the last century. Only for PBDEs in the outer German Bight concentrations have decreased since 2011, but the period is too short for any prognosis.

Lutz Ahrens: New information on per- and polyfluoroalkyl substances in the environment

Lutz Ahrens presented new results about poly- and perfluoroalkyl substances (PFASs) in the environment. PFASs are distributed ubiquitously in the aquatic environment which raises concern for the ecosystem. Fire training facilities and sewage treatment plants (STPs) are important sources of PFASs in the environment (Ahrens, 2011a; Ahrens *et al.*, submitted). PFAS precursors can be degraded to persistent degradation products, which are in particular, perfluoroalkane sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs). PFSAs and PFCAs are subjected to partitioning processes in the environment, whereby short-chain PFSAs and PFCAs are mainly distributed in the water phase, whereas long-chain PFSAs and PFCAs tend to bind to particles and have a substantial bioaccumulation potential (Ahrens *et al.*, 2011b). A temporal study in tawny owl *(Strix aluco)* eggs collected in Central Norway showed general decreasing concentrations of perfluorooctane sulfonate (PFOS), while, conversely, the C10-C13 PFCA concentrations increased between 1986 and 2009 (Ahrens *et al.*, 2011b).

References

Ahrens, L. (2011a). Polyfluoroalkyl compounds in the aquatic environment: A review of their occurrence and fate. J. Environ. Monitor. 13, 20–31.

Ahrens, L.; Norström, K.; Viktor, T.; Palm Cousins, A.; Josefsson, S. (subm.). Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish.

Ahrens, L.; Herzke, D.; Huber, S.; Bustnes, J. O.; Bangjord, G.; Ebinghaus, R. (2011b). Temporal trends and pattern of polyfluoroalkyl compounds in tawny owl *(Strix aluco)* eggs from Norway, 1986-2009. Environ. Sci. Technol. 45, 8090–8097.

Caroline Kivimae: Presentation of the Shelf Sea Biogeochemistry project

Caroline Kivimae presented an overview of the work which will happen in CANDYFLOSS which is work package 1 of the new NERC/Defra Shelf Sea Biogeochemistry programme in the UK (see also section 5.7.2). As part of this work package, there will be one year of sampling (recently commenced) across the NW European Shelf for TA/DIC, inorganic and organic nutrients and pCO_2 to make an estimate of the air-sea CO_2 flux across the shelf.

5.4 Marine litter and its role as a potential source of contaminants (joint session with WGBEC and WGMS)

This agenda point was addressed in a joint session with WGBEC and WGMS, see also http://www.ices.dk/news-and-events/news-archive/news/Pages/43-scientists,-three-expert-groups,-one-overriding-theme.aspx

The joint session was chaired by WGBEC who also provided the majority of presentations on marine litter and microplastics, see section 5.4.1. Furthermore, Marilynn Sørensen of the ICES Data Centre presented the Data Centre's work on a draft format for litter reporting, as further described in section 5.5.1.

5.4.1 Report on new information on marine litter and its role as a potential source of contaminants

Thomas Maes (WGBEC): Litter – the plastic tide

Thomas Maes (CEFAS, UK) presented a comprehensive review of several aspects of the marine litter issue. The presentation was structured along three subtitles:

- Thrashing the waves
- Marine litter and the MFSD
- CEFAS and EU marine litter work

Thrashing the waves:

The term "Marine Litter" has been introduced to describe "any persistent, manufactured or processed solid material discarded, disposed of, or abandoned in the marine and coastal environment". It consists of articles that have been made or used by people and, subsequently, deliberately discarded or accidentally lost. They originate from ocean-based or land-based sources and can be found in marine environments around the globe. Most sources of marine pollution are land based. Marine litter, mainly plastic, poses a serious environmental threat to marine organisms, as well as a series of economic and social problems. The majority of marine debris is comprised of plastic materials (60-80% overall and 90% of floating debris).

All marine litter particles smaller than 5 mm are considered microparticles. Most microparticles consist of microplastics, although other types exist. The abundance and global distribution of microplastics in the oceans has steadily increased over the decades to around the year 2000 following the rising plastic consumption worldwide since the 1940s. However, there has been a decrease in the average size of plastic litter over this time.

- Primary microplastics are produced either for direct use, such as for defoliants, cosmetics, industrial abrasives or for indirect use as precursors (nurdles or virgin resin pellets) for the production of multiple plastic consumer products.
- Secondary: Microplastics formed in the environment as a consequence of the breakdown of larger plastic material, especially marine debris, into smaller and smaller fragments. The breakdown is caused by mechanical forces (e.g. waves) and/or photochemical processes triggered by sunlight (especially UV-B).
- Other types of microparticles:
    - Synthetic fibres shedding of textiles by domestic clothes washing
    - Rubber fragments from tires rubbing tarmac
    - Fly ash fine particles that rise with the flue gases after combustion
    - ...

The potential impacts of litter span both economic and ecological dimensions. The following section highlights the different aspects that are considered relevant.

- Economic
    - Losses to fishing and shipping industry
    - Clean up costs on beaches
    - Loss of tourist revenues
    - Aesthetic disturbance
- Ecological
    - Ingestion
    - Entanglement
    - Introduction of invasive species

- Bioavailability and transfer due to sorption/leaching
- Smothering
- Disturbance

Marine litter comes from a variety of land-based and sea-based sources and is essentially a consequence of poor waste management. However, the main sources can be grouped as follows:

- The main land-based sources of marine litter
  - Discharge of untreated municipal sewage, including storm water discharges and overflows
  - Tourism (recreational visitors to the coast; beach-goers)
  - Riverine transport of waste from landfills or other sources along rivers and other inland waterways and canals
  - Industrial facilities: Solid waste from landfills, and untreated waste water
  - Municipal landfills (waste dumps) located on the coast or inland
  - Direct littering
- The main sea/ocean-based sources of marine litter
  - Fishing vessels
  - Merchant shipping, ferries and cruise liners
  - Military fleets and research vessels
  - Pleasure craft
  - Offshore oil and gas platforms
  - Fish farming installations
  - ...

Marine litter and the MSFD:

The MSFD requires member states to manage their seas to achieve Good Environmental Status (GES) by 2020. MSFD Descriptor 10 requires litter to be at levels where the 'properties and quantities of marine litter do not cause harm to the coastal and marine environments'.

MSFD criteria and indicators require understanding and monitoring of:

- The characteristics of litter in the marine and coastal environment – including:
  - Trends in the amount of litter washed ashore and/or deposited on coastlines, including analysis of its composition, spatial distribution and, where possible, source (10.1.1);
  - Trends in the amount of litter in the water column (including floating at the surface) and deposited on the sea- floor, including analysis of its composition, spatial distribution and, where possible, source (10.1.2);
  - Trends in the amount, distribution and, where possible, composition of micro-particles (in particular micro- plastics).
- The impacts of litter on marine life – trends in the amount and composition of litter ingested by marine animals.

Reference

JRC (2013). Guidance on Monitoring of Marine Litter in European Seas. A guidance document within the Common Implementation Strategy for the Marine Strategy Framework Directive. MSFD Technical Subgroup on Marine Litter. JRC83985. ISBN 978-92-79-32709-4 (pdf).

CEFAS and EU marine litter work:

CEFAS is involved in several national and international marine litter projects. Thomas Maes (Cefas) focused on two EU projects MICRO and MARLISCO.

The EU Interreg 2 Seas MICRO

The Micro EU Interreg project is monitoring microplastics (MP) within the 2 Seas Region and will provide a risk assessment based on field observations, lab experiments and mathematical models. MICRO is a cross border cooperation to prevent environmental, technological and human risks attributed to MP. Furthermore the project will contribute to establish common strategies for environmental risk assessment by modelling the potential impacts on the environment, and by proposing follow-up tools and mitigation measures. The three main pillars of the project are:

- Scientific: a risk assessment of the current situation by combining distribution data, modelling and biological effect measurements with socio-economic endpoints.
- Educational/knowledge exchange: establishing good practices for adequate monitoring or impact determination across Europe.
- Public/scientific awareness: increase awareness of human behaviour in relation to waste production and management by creating co-responsibility among the different actors.

The EU FP7 MARLISCO project

MARLISCO activities take place in the **four European Regional Seas:** North-East Atlantic, Baltic, Mediterranean and Black Sea, by a consortium with members located in **15 coastal countries**. MARLISCO' s overarching goal is to **raise public awareness, facilitate dialogue** and **promote co-responsibility** among the different actors towards a **joint vision** for the **sustainable management of marine litter across all European seas**. It will do this by developing innovative mechanisms and tools. MARLISCO aims to effectively **engage**, **inform** and **empower society,** reaching the widest possible audience. Its activities include:

- A **scoping study** of the sources and trends regarding marine litter in each Regional Sea.
- A collection of **best practices** from all partner countries.
- A **survey** on the prevailing perceptions and attitudes of different stakeholders regarding marine litter.
- A European **video contest** for youngsters to collect their visions on the issue of marine litter and empower them as agents of change in society.
- **National debates** in 12 partner countries.

- Diversified, tailor-made **national activities** including exhibitions, workshops, festivals, clean ups, etc.

References

www.marlisco.eu
www.ilvo.vlaanderen.be/micro

Bavo de Witte (MCWG) and Lisa Devries (WGBEC): The role of microplastics and marine litter as a vector for chemical and microbial contamination

Bavo de Witte and Lisa Devries (both ILVO, Belgium) presented recent results of their research into the associations between litter and contaminants in terms of the following three presentations:

- Marine litter as a vector for contamination:

  A quantitative GC-MS screening was performed on marine litter, present within benthos beam trawl nets during fishing activities. No clear indication of chemical contamination was found on blue synthetic rope. None of the OSPAR -7 indicator PCBs were found at concentrations > 0.1 ng/g. The origin of determined PAHs, alkylated PAHs, alkanes, alkenes and alkylated aromatic compounds may be pyrogenic/petrogenic pollution as well as plastic production. Phenols and specific antioxidants and UV-absorbers can also be related to plastic production.

- Microplastics as a vector for PCBs:

  Few data are available on the role of microplastics as a vector for PCBs through the marine trophic levels and impact studies are required under controlled conditions. Benthic marine organisms such as the common shore crab and Norway lobster were exposed to PCB loaded microplastics under controlled laboratory conditions. In these experiments, 500-600 µm diameter polyethylene or polystyrene spheres were loaded with PCBs. The microspheres passed the digestive tract without accumulation in the organism and egestion of the spheres was observed within two days after uptake. Within this research, it was shown that PCBs could desorb from the microspheres during the short period in the digestive system, but only a very small uptake of PCBs was observed by Norway lobster. No additional effect caused by the microspheres could be observed.

- Plastic litter as a vector for bacteria:

  This work had been carried out by Lisa Devriese, Caroline de Tender and Sara Maes (all ILVO, Belgium). The possibility for microplastics and litter to act as a vector for bacteria and pathogens was suggested based on a bacterial screening on beach pellets, marine plastic litter and plastic beach litter. Diverse methods such as Next Generation Sequencing, TOPO TA cloning, PCR-DGGE were used to identify the bacterial communities of the different types of plastic.

Michiel Kotterman (MCWG): Microplastics as vectors of organic contaminants.

Michiel Kotterman (IMARES, The Netherlands) presented briefly the research on plastics at IMARES. Next to monitoring the presence of plastics in the environment (as monitored by trawling; bottom and egg surveys), in biota (fish, fulmars and seals) the main research topic is to determine the role of microplastics with regard to contaminants. Are they a vector of contaminants, enhancing the uptake of contaminants by biota, or are they a sink for some contaminants due to their high affinity for some contaminants, lowering the exposure?

This is being investigated with lugworms under environmentally relevant conditions, micro-PS in contaminated sediments (Besseling), and models for effects of plastic ingestions have been made (Koelmans). So far, plastics can be a vector as well as a sink, the effects under natural conditions are, from of risk assessment perspective, generally small. More data are required for proof and to improve the models. Therefore, research will be focussed on the net effects of plastic on the uptake of contaminants under natural conditions.

Within the EU project ECSAFESEAFOOD, IMARES is involved in feeding trials of fish. Salmon will be exposed to plastics and contaminants through their feed. In one treatment plastics will be equilibrated with the contaminants before feeding, while in another treatment clean plastics will be added to contaminated food while feeding. This may add to the understanding of processes (rates especially) during the digestion.

Reference

Koelmans, A.A.; Besseling, E.; Foekema, E.M. (2014). Leaching of plastic additives to marine organisms. Environ. Pollut. 187, 49-54.

Jakob Strand (WGBEC): Relationship between microplastic particles, sediment characters and contaminants in sediments from Danish waters

Jakob Strand (Aarhus University, Denmark) gave a presentation on the relationships between microplastic particles, sediment characteristics and contaminants in sediments from Danish waters based on a study on distribution of microplastic particles (38 μm – 5mm) in sediment in the Danish waters from the Baltic Sea towards the North Sea. The results indicate that normalisation of microplastic abundances to adequate sediment characters can reduce the variability caused by natural heterogeneity between samples and thereby increase the power of identifying more or less affected areas. Strong relationships between the content of microplastics in sediments and both %TOC and fine sediment fraction (< 63 μm) were found throughout the area supporting that microplastics will accumulate in sedimentary depositional areas – i.e. with parallels to organic pollutants sorbed to organic materials. Positive correlations were also established to contaminants, especially PAHs and to lesser extent to alkylphenols and phthalates in sediments. It could be due to co-variation with sources and TOC rather than due to chemical extraction of microplastic particles. However, at least antifouling agents like TBT in paint flakes from ship lanes and harbours can be one exception.

Bjørn Einar Grøsvik (WGBEC): Monitoring marine litter, a part of the joint Norwegian/Russian ecosystem survey in the Barents Sea

Bjørn Einar Grøsvik (IMR, Norway) presented a collaboration project with the Polar Research Institute of Marine Fisheries and Oceanography (PINRO) in Russia. Co-workers on this study were Elena Eriksen (IMR, Norway) and Tatiana Prokhorova and Pavel Krivosheya (both PINRO, Russia). Since 2004 these institutes have collaborated on ecosystem based surveys in the Barents Sea. From 2010 registration of marine litter has been a part of this collaboration.

Surface investigations and trawl catches have demonstrated highest occurrence of litter in the areas of intensive fishery and navigation. Plastic prevailed among observed litter. The main plastic concentration in the surveyed area was observed between 69° and 74°N and between 25° and 45°E, an area being under the influence of the Atlantic and coastal currents. Plastic might be brought further northwards and eastwards by the Novaya Zemlya and Kolguev-Pechora Currents. Floating timbers were observed in all investigated areas. Litter was observed in bottom trawls more frequently than in pelagic trawls. Other types of litter (metal, paper, rubber, textile, glass) were sporadically observed.

5.4.2 Review the literature with regard to the role of marine litter as a potential source of contaminants

Taking into account the presentations given during the marine litter session as well as the available literature, MCWG remarks that there is currently insufficient information to assume that the uptake of chemical contaminants by marine biota through digestion of microplastics is significant. In some cases, enhanced uptake of plastic additives can occur, if these are not yet in equilibrium with the surrounding environment. More plastic uptake might also occur at locations where marine litter accumulates by marine gyres. Major problems of marine plastic pollution seem to be related to obstruction by and/or uptake of large amounts of plastics.

WGBEC as well as MCWG stress their interest to work further in the field of marine litter as well as microplastics. MCWG would be particularly interested in further information on desorption studies in gastrointestinal tracts and work on uptake of chemical contaminants by organisms from marine litter.

With respect to the idea of starting a new ICES working group on marine litter and microplastics (see section 3.1.2), MCWG advises that MCWG should be involved where chemical contamination is concerned given MCWG's expertise in transport, distribution and uptake of chemical contaminants.

MCWG recommends to WGBEC to share new information with MCWG identifying plastics as a vector of enhanced contaminant transfer to biota (see Annex 4).

5.4.3 Combine information on plastics in sediment, on plastic/contaminant interactions ad on their effects in biota for a comprehensive problem description and assessment

The large amount of information provided through the presentations described in section 5.4.1 did not leave enough time to work on a comprehensive problem description. Activities in the field of marine litter have increased significantly, including a number of national and EU research projects as well as work in several fora towards marine litter monitoring in relation to MSFD. As described above a separate ICES working group dedicated to marine litter has been proposed by members of WGBEC.

MCWG suggests addressing marine litter in their draft ToRs for MCWG 2015, however, with a clear focus on contaminants associated with marine litter (see Annex 3).

5.5 ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested

In connection with agenda items 3.1.4 and 5.7.1, Hans Mose Jensen of the ICES Data Centre presented the changes that have been made to the ICES database to accommodate ocean acidification monitoring data. These changes were based on inputs of MCWG 2013 and SGOA 2012/2013. Hans Mose Jensen also presented general questions to MCWG regarding ocean acidification data as well as specific questions continuing the work on reporting requirements at MCWG 2013. These tasks were also described in a recommendation by SGOA 2013, see section 5.7.

5.5.1 Presentation of a draft format for litter reporting

The ICES Data Centre has set up new litter record to include litter information in Environmental Reporting Format 3.2. In the framework of the MSFD (descriptor 10) the task group marine litter at the ICES Data Centre defined different litter categories in 2013. It was, however, too complex, to include the variability of types and sizes within the existing framework, and it was decided to set up a separate litter record. This includes the following information: depths min/max, litter size, litter reference list, parameters/unit/value, litter source, litter use, number of entangled biota, state of litter, polymer type, attached organisms (non-microbial). ERF3.2.5 is available on the MCWG SharePoint and comments to the new record can be given to *marilynn.sorensen@ices.dk* by 1 April 2014.

It was suggested that one person of each group should give suggestions and that the database should be kept as lean as possible since this will lead to more people who will fill in the database.

5.6 Report on activities in other expert groups on the interface to MCWG (e.g. WGMS, WGBEC, WGEEL, SGONS)

Obvious links with **WGMS** and **WGBEC** had led to the suggestion by MCWG 2012 of a joint meeting with these two groups. WGMS and WGBEC met concurrently with MCWG 2014 and joint sessions had been arranged on passive sampling (see section 5.11) and marine litter (see section 5.4). WGMS and WGBEC also attended the plenary presentations arranged by MCWG (see section 4).

As further described in section 5.11, MCWG has approached passive sampling from a research as well as a monitoring point of view. The latter is based on the work of WKPSPD, which MCWG is interested in moving forward. The work on certain aspects of passive sampling and passive dosing, for example the development of environmental assessment criteria based on C_{free} and discussions of new developments within toxicity testing would benefit from joint efforts of all three groups, see also recommendations in Annex 4.

WGBEC chaired the session on marine litter and has established expertise in this field. MCWG is mainly interested in contaminant-related aspects of marine litter, e.g. the role of marine litter as a vector for contaminants. MCWG would appreciate more information by WGBEC on this topic as well as continuing collaborations (see recommendations in Annex 4). This will also apply to a potentially newly formed expert group on marine litter.

MCWG and WGMS collaborated on the revision of technical annexes of the JAMP Guidelines on contaminant monitoring (see section 5.13). Experts of WGBEC contributed to this work as well.

Two TIMES manuscripts on passive sampling are in preparation and will be drafted jointly by MCWG and WGMS members.

Katrin Vorkamp informed about contaminant-related work by **WGEEL**, based on the WGEEL 2013 report. WGEEL is a joint initiative by ICES and the European Inland Fisheries and Aquaculture Advisory Commission (EIFAAC) and held two meetings in 2013, each attended by approximately 30 participants. The WGEEL 2013 report includes a comprehensive literature review of contaminants in eel, covering nine papers published in 2013 on various contaminants and trace metals in eel and five papers on contaminant effects in eel. Further literature reviews include contaminants and genomics and the transfer of contaminants to fish offspring, however, the publications reviewed under this topic dealt with other fish species than eel. The report also includes information on monitoring programmes of contaminants in eel and information on the closure of eel fisheries due to elevated contaminant levels.

Interestingly, the WGEEL 2013 report announced a joint workshop with WGBEC on the subject "Are contaminants in eel contributing to their decline?" (WKBECEEL). The workshop will be chaired by Claude Belpaire and John Thain. The date remains to be settled, but 2015 has been suggested. Terms of Reference are given in the WGEEL 2013 report and include spatial and temporal trends of contaminants in eel. MCWG considered this workshop relevant for MCWG as well. Michiel Kotterman expressed his interest in participating in this workshop and reporting back to MCWG (see action list in Annex 6).

Michiel Kotterman also informed about an ICES/EIFAAC International Workshop on the subject "Development of standardized and harmonized protocols for the estimation of eel quality", which he would be interested in attending as well. MCWG would welcome further information on this workshop and its outcomes as well (see action list in Annex 6).

MCWG has close links to **SGOA**, as described in e.g. section 3.1.4.

According to information at previous MCWG meetings, the joint ICES/IOC Study Group on Nutrient Standards **(SGONS)** has been discontinued. The network still exists, but has no Terms of References. MCWG would be interested in any information on the topics previously addressed by SGONS.

The discussions at MCWG 2014 showed that it would be interesting to establish contacts to the following three ICES working groups because of potentially common interests:

- Working Group on Oceanic Hydrography (WGOH).
- Working Group on Phytoplankton and Microbial Ecology (WGPME).
- Working Group on Seabird Ecology (WGSE).

Contacts will be established according to the actions listed in Annex 6.

5.7 Ocean acidification

5.7.1 Report from the OSPAR/ICES Study Group on Ocean Acidification and provide comments and input as follows:
- Review and discuss developments of analytical methods
- Update QA/QC requirements
- Assist SGOA in elaborating reporting requirements

SGOA recommendation: Further review reporting requirements to ICES environmental database for OA data, specifically in relation to units and reference temperature for pH and other parameters as elaborated in Section 8 of the SGOA 2013 report.

Evin McGovern gave a presentation on the SGOA 2013 meeting to MCWG as described in section 3.1.4 and explained the recommendations to MCWG. Further background was provided by Hans Mose Jensen of the ICES Data Centre, as described in section 5.5.

The Chemical Oceanography Subgroup (COSG, see section 2) focussed on the questions of reporting requirements. COSG went through the DATSU excel form with Marilynn Sørensen to address the outstanding issues from SGOA and Marilynn Sørensen updated as per discussion. Marilynn Sørensen further explained the differences between warning, errors and critical errors noting that critical errors must be addressed for data to be accepted and that errors were more likely to be considered and addressed compared to warnings.

MCWG recommends the following:

- The unit of μmol kg^{-1} for TA and DIC is mandatory.
- The unit of μatm for pCO_2 is mandatory.
- The scale for pH must be specified (data refused entry if not).
- Method of analysis for pH is specified – there are 4 listed and a warning is issued if someone enters pH data which are not one of these 4.
- User will be warned if purpose of monitoring not set to O (Ocean Acidification monitoring) but they have entered 2 of the parameters from TA, DIC, pCO_2, pH.
- When pH and pCO_2 are reported, users must submit results at the measurement temperature together with that measurement temperature, which should be added as an additional parameter, and the in situ temperature must also be reported.
- Uncertainty of measurement is an important parameter. At present uncertainty will not be mandatory as there needs to be an agreed method of calculating uncertainty which has yet to be agreed. It should be an 'error' if uncertainty is not reported. There is a recommended method in the Dickson manual. OSPAR also have guidelines for calculating uncertainty for contaminant monitoring (OSPAR, 2011). This should be one of the subjects to be discussed at the QUASIMEME workshop (see section 5.1) and once agreed this should be implemented on the data filter. The method of calculating the uncertainty is also required.
- Only results for discrete samples will be reported to DOME, data from underway systems will not, but will continue to be reported to existing databases e.g. CDIAC.

With respect to alternative databases and the desire to facilitate OA-data exchange between data centres, such as CDIAC, MCWG also recommends:

- Cruise summary reports should be supplied with the data – it will be added to the DATSU and an error generated if it is not. The ICES Data Centre confirmed they could check if cruise reports have been submitted. This is not a critical error as not all data will pertain to samples collected on ship-based cruises.
- An additional text file with method details should be supplied which will give the additional detailed information required by CDIAC. This would trigger an error though not a critical error if not submitted.

MCWG defined the following action (see Annex 6): Further examine the CDIAC metadata requirements and consider whether these are directly appropriate for including in a form for the text file. Caroline Kivimae agreed to prepare this for the next SGOA and MCWG meeting.

Reference

OSPAR (2011). JAMP Guidelines estimation of a measure for uncertainty in OSPAR monitoring. Agreement 2011-3.

5.7.2 Present and discuss new chemical oceanographic data relating to ocean acidification

Caroline Kivimae presented an overview of the work which will happen in CANDYFLOSS which is work package 1 of the new NERC/Defra Shelf Sea Biogeochemistry programme in the UK (see section 5.3). As part of this work package, there will be one year of sampling (recently commenced) across the NW European Shelf for TA/DIC, inorganic and organic nutrients and pCO_2 to make an estimate of the air-sea CO_2 flux across the shelf.

CEFAS (UK) is purchasing a Seafet pH for initial installation in the underway system on RV Endeavour. Data will be compared with data from the existing Dartcom pCO_2 system and discrete TA/DIC results.

5.7.3 Report on QUASIMEME workshop on ocean acidification and discuss implications for ocean acidification monitoring

SGOA recommendation: Review progress on advancing ocean acidification QA/QC workshop

There was a discussion about the workshop when reviewing the 2013 action list (see section 2). Koen Parmentier informed that QUASIMEME would be happy to facilitate an OA workshop – this was reiterated by Steven Tito of the QUASIMEME Project Office (see section 5.1). If there are at least 25 participants then attendees' fees should be sufficient to cover speakers' travel and subsistence costs. NOC are still happy to host and Andrew Dickson would be happy to come over provided his costs are covered.

Pamela Walsham and Caroline Kivimae will progress organizing the workshop and will contact Andrew Dickson to find dates which he could make. COSG would prefer the workshop to be held in autumn 2014, before the next SGOA meeting. COSG recommends that participants are charged to cover the cost of organizing the workshop but would cover their own food and accommodation costs.

COSG further discussed the aims of the workshop discussed at SGOA and added discussion of uncertainty and data reporting. The updated aims are given below:

Proposed aims of the worksho:

1) Introduction to Quasimeme Quality assurance and Quality assessment.

2) Obtain a consistent approach to sampling, sample pre-treatment sample storage across the OSPAR contracting parties for all four carbonate parameters (TA/ DIC/ pCO2/ pH).

3) Discuss the key analytical techniques for all four carbonate chemistry parameter measurements; challenges, limitations and misconceptions affecting quality of results. The emphasis of the workshop will be on the parameters of TA/DIC since these are likely to progress to the OSPAR CEMP but considerations will also be given to pH and pCO2.

4) Obtain a consistent approach to the analysis of TA/DIC, and correct use of reference materials/standards across the OSPAR region.

5) Consider the limitations of reference materials across the OSPAR region i.e. salinity ranges, open oceans and coastal waters and needs for reference materials and proficiency testing to support monitoring. This could include reviewing the outcome of the intercalibration exercises performed by Scripps Institution of Oceanography.

6) Address issues with calculation of data using the various software packages.

7) Address data quality objectives needed for various assessment purposes, including method uncertainties. GOA-ON identified the need for two different levels of data quality to ensure the availability of data and permit assessment of short-term variability as well as longer term trends.

8) Highlight reporting requirements for both ICES and CDIAC.

Potential outcomes of the workshop:

- Workshop report and if deemed appropriate the preparation of a technical guide for carbonate chemistry sampling, sample pretreatment, sample storage, analysis, use of reference materials and calculation for use within OSPAR.
- Recommendations for future QA tools (ongoing proficiency testing and reference materials) that could support OSPAR and other monitoring of OA parameters.
- Potentially updates of the current OSPAR guidelines.

MCWG defined the following actions with regard to the workshop (see also Annex 6):

- Pamela Walsham will contact Andrew Dickson to arrange suitable date of the workshop.
- Caroline Kivimae will make arrangements at NOC at Southampton.
- Caroline Kivimae and Pamela Walsham will liaise with QUASIMEME to identify participants, develop a detailed programme and promote the workshop.

Regarding wider QA/QC, Caroline Kivimae reported that NOC participated in an interlaboratory exercise in autumn 2013 organized by Andrew Dickson to analyse two unknown samples.

5.7.4 Report from theme session on ocean acidification at the ICES Annual Science Conference 2013

See section 3.1.3.

5.7.5 Report on pH measurements in sediments, in a joint session with WGMS and WGBEC

Naomi Greenwood and David Pearce presented work on pH measurements carried out by colleagues at CEFAS (UK).

5.8 Chlorophyll and nutrients

5.8.1 Report from QUASIMEME workshop on chlorophyll and nutrient analysis

Steven Tito reported the outcomes of the recent chlorophyll and nutrients workshop to MCWG (see also section 5.1). QUASIMEME reported that unlike other PT determinands there had been no overall improvement in participant performance for chlorophyll. This had prompted an internal investigation, by QUASIMEME, into methods used by participants to report chlorophyll *a*. The approach and main results are further described in section 5.1.

There were no distinct differences in participant results using different extraction time or solvent volumes, however differences were observed in extraction and detection methods, for example, ethanol seemed to be a better solvent to extract chlorophyll *a*. In particular samples extracted by sonication alone resulted in underestimation of chlorophyll *a* concentrations. There was also a clear distinction between participants reporting chlorophyll *a* by either fluorometric/photometric or HPLC methods. The standard photometric and fluorometric methods for determining chlorophyll *a* do not separate the different chlorophyll pigments while this is possible by HPLC resulting in differences. Issues with poor performance when nannochloropsis was used as a material were shown not to be caused by the analytical technique (i.e. HPLC or fluorometry). However, QUASIMEME decided not to use nannochloropsis as a material in the future. QUASIMEME agreed to report results from participants undertaking HPLC analysis separately from those undertaking the fluorometric and photometric analysis.

The workshop also highlighted the need for harmonisation of methods used for the analysis of chlorophyll in marine waters. A sub-group of workshop participants have agreed to further investigate extraction and detection methods. MCWG agreed this would be useful and look forward to receiving a workshop report and update on progress with investigations.

Participants in the nutrient PT scheme are performing well with overall improvement in z-scores. QUASIMEME are considering whether the current proportional error is too high and should be lowered, this will be considered by the QUASIMEME Scientific Advisory Board (SAB) in autumn 2014. MCWG has representation on this board and can advise.

The workshop again highlighted the need for suitable reference materials when undertaking nutrient analysis. The concentration of reference materials currently available is often not applicable to North Atlantic or Baltic waters. QUASIMEME are in discussion with Kansco about the potential of producing a reference material suitable North Atlantic and Baltic waters. MCWG welcomed any improvement to methods.

As described in section 5.1, MCWG felt that the resulting information and recommendations of QUASIMEME's meta-analysis were very valuable. MCWG encouraged QUASIMEME to publish the data and recommendations issued at the workshop.

5.8.2 Review if OSPAR guidelines for chlorophyll determination are in line with outcomes of the QUASIMEME workshop on chlorophyll analysis and provide advice on most appropriate methodology

The COSG reviewed the JAMP Eutrophication monitoring guidelines for chlorophyll in water (OSPAR Agreement 2012-11). The guidelines state that "because the standard photometric and fluorometric methods used for determining chlorophyll *a* do not completely separate the different chlorophylls or distinguish between chlorophyll *a* and chlorophyllide *a* the term "total chlorophyll a" should therefore be used when reporting results from these methods. For chlorophyll data, analysed by HPLC, which considered the other chlorophyll derivatives as well the term "chlorophyll *a*" should be used".

The use of different analytical techniques in determining chlorophylls has implications for reporting data under WFD and MSFD. To meet statutory obligations contracting parties are increasingly relying on the use of remote sensing devices such as satellites for inclusion in data sets for their assessments. These devices are calibrated using discrete samples analysed by various techniques. It is important that a consistent analytical approach is taken to calibrate such devices to ensure comparability and correct assessment of GES.

MCWG further discussed the use of the different techniques in a plenary session. MCWG agreed a systematic difference in methods is obvious. It may be necessary to consider different methods for different end purposes, for example primary production studies may only require bulk information which fluorometric and photometric methods can provide while for regulatory purposes and calibrating sensors HPLC may be more applicable. MCWG decided that it should be recommended to OSPAR that OSPAR be aware of potential differences in results derived from fluorometric/photometric or HPLC methods, which may have implications for WFD monitoring (Annex 4). A more detailed description of the recommendations to OSPAR is given in Annex 9.

5.8.3 Discuss comparability of methods for chlorophyll analysis

MCWG had general discussions about the issues highlighted by QUASIMEMES. The group again highlighted the differences in concentrations observed when using different methodology, as described in points 5.8.1 and 5.8.2.

MCWG agreed that until the planned further work by QUASIMEME (see sections 5.1 and 5.8.1) had been undertaken this point could not be progressed. MCWG agreed that OSPAR needed to be made aware of the issue (see Annex 9). A TIMES paper publication will be considered next year (see section 5.12.4).

5.9 Report on new information on emerging contaminants in the marine environment

Philippe Bersuder: Alternative Brominated Flame Retardants (aBFRs) in UK harbour porpoise (Phocoena phocoena)

Philippe Bersuder reported on results of an investigation into the presence of alternative brominated flame retardants (aBFRs) in UK harbour porpoises. As controls have been put in place for some high volume brominated flame retardant (BFR) products such as some polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), manufacturers and users are moving to alternative chemicals as replacements. aBFRs are a heterogeneous group of compounds that include at least 75 different BFRs produced commercially, which for 2009, have been estimated to represent 100 000 to 180 000 tonnes per annum globally.

In order to ascertain the presence of these compounds in UK marine compartments, the blubber of 21 harbour porpoises (*Phocoena phocoena*) stranded or by-caught around the UK coast in 2008 were analysed for 28 aBFRs, PBDEs and the chlorinated dechlorane-plus isomers. A dedicated analytical method using gas chromatography with triple quadrupole mass spectrometry detection was developed and validated. Day to day Quality Control was achieved using a Laboratory Reference Material consisting of cod liver tissue spiked with aBFRs. Of the 28 aBFRs analysed, 19 were not present, and three compounds (tetrabromo-p-xylene (TBX), tetrabromo-o-chlorotoluene (TBCT) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE)) were detected in the blubber but below limits of quantitation. Of the remaining 6 brominated compounds (i.e. tribromotrichlorocyclohexane (TrBTrCcH), 2,3,4,5,6-pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), hexachlorocyclopentadienyldibromocyclooctane (DBHCTD), 2,2′,4,4′,5,5′-hexabromobiphenyl (BB153)), highest levels were detected for PBEB, but these were 3 orders of magnitude lower than the sum of PBDEs. The dechlorane-plus isomers were detected in all samples at part per trillion levels.

It was concluded that it was reassuring that the aBFRs studied here showed either low concentrations or were below limits of detection. However the compounds detected are not being used in large volumes in products placed on the UK market or in UK manufacture, or are being used reactively (and less likely to leach into the environment), and other alternative flame retardant products are likely to being used as replacements for the controlled PBDEs formulations.

Reference

Law, R.J., Losada, S., Barber, J.L., Bersuder, P., Deaville, R., Brownlow, A., Penrose, R., Jepson, P.D. (2013). Alternative flame retardants, dechlorane plus and BDEs in the blubber of harbour porpoises *(Phocoena phocoena)* stranded or bycaught in the UK during 2008. Environment International 60, 81-88.

5.10 Seabird eggs as a monitoring matrix for organic contaminants and trace elements

5.10.1 Review literature that has become available since MCWG 2013 on the monitoring of organic contaminants and trace elements in seabird eggs

Katrin Vorkamp and Michael Haarich presented a summary on new monitoring data published since MCWG 2013 on organic contaminants and metals in seabird eggs.

In the introduction it was reminded that these presentations will be completed by additional information and the discussion on seabird biology in order to get better view on the use of migratory species and historical processes that might influence contaminants uptake by these animals (see section 5.10.3). The main concern is if contaminant concentrations in the seabird eggs reflect local or more integrated pollution status over larger areas.

It was also reminded that seabird eggs had been included in the OSPAR JAMP guideline for monitoring of biota since 1998 and contaminants were monitored in seabird eggs in several monitoring programs (e.g. Trilateral Monitoring and Assessment Programme of the Wadden Sea (TMAP), Arctic Monitoring and Assessment Programme (AMAP), Swedish Environmental Monitoring Programme). More information on these monitoring activities had been summarized by MCWG 2013.

In their recent publication in *Science* Elliott & Elliott (2013) state that seabird monitoring studies may provide a global picture of an increasing range of marine pollutants and that it is a solid argument in favour of this approach. An uptake of contaminants by seabirds over larger geographical scales is considered an advantage of this matrix. The authors also discuss other advantages of seabird monitoring such as: lower variance in organochlorine concentrations (than in other biota species), smaller sample size required for comparable statistical power and reduced environmental impact and cost of sampling. Furthermore, such monitoring is conducted with non-lethal sampling of seabird feathers, blood or eggs and provides possibility of retrospective time trend studies on eggs archived in specimen banks. Finally the authors propose further progress of seabird studies, complemented by stable isotopes food web measurements and better determination of their migration routes with tracking devices development. They also draw attention to increasing threats related to the ingestion of litter plastics and related contaminants transfer to the seabirds.

Braune & Letcher (2013) communicated on a large suite of perfluorinated compounds determinations in the eggs of two species: Thick-billed murre *(Uria lomvia)* and northern fulmars *(Fulmarus glacialis)*. This study was conducted within the Canadian Arctic AMAP program and samples were collected between 1975–2011 at Prince Leopold Island. The perfluoroalkyl carboxylic acids (PFCAs) show significantly increasing temporal trends, whereas perfluoroalkane sulfonic acids (PFSAs) concentrations were more variable and did not show a particular trend. The analysis in additional eggs samples collected in 2008 of black-legged kittiwake *(Rissa tridactyla)*, black guillemot *(Cepphus grylle)* and glaucous gull *(Larus hyperboreus)* show high interspecies variation of PFCAs and perfluorooctane sulfonate (PFOS). PFCAs > PFOS was observed in glaucous gull and black-legged kittiwake, while the opposite trend was found in black guillemot and thick-billed murre. Similar concentrations of PFCAs and PFOS occurred in eggs of northern fulmar.

New data on PBDEs and HBCD concentrations in eggs of 7 seabird species from Iceland were reported by Jörundsdóttir *et al.* (2013). Geometric mean concentrations and ranges of PBDE congeners and HBCD were given for common eider *(Somateria mollissima)*, Arctic tern *(Sterna paradisaea)*, guillemot *(Uria aalge)*, northern fulmar *(Fulmarus glacialis)*, lesser black-backed gull *(Larus fuscus)*, great black-backed gull *(Larus marinus)*, great skua *(Stercorarius skua)*. In this publication, there is also an evidence of BDE 209 presence at detectable concentrations in seabird eggs, given thus some new insight about this compound's bio-accumulation potential.

Chen *et al.* (2012) reported on the Great Lakes monitoring programme of organic contaminants in herring gull eggs. They focused on potential new contaminants, i.e.

methoxylated polybrominated diphenoxybenzenes (MeO-PDBPBs - they might originate from the BFR tetradecabromodiphenoxybenzene -TDBDPB, major component of SAYTEX 120). Similar temporal trends (1982–2010) in Lake Huron were given for PBDEs and MeO-PDBPBs. Furthermore the concentrations in Lake Huron station were considerably higher than the concentration in other sampling station in Great Lakes probably due to some local inputs. The significantly diverse time trends at different monitoring stations of the Great Lakes were explained by possible changes in diet regimes of herring gull.

Hanley & Doucet (2012) have published original work on the influence of the level of contamination on the colouration of herring gull eggs. The question of this study was whether intensity of egg pigment expression such as biliverdin (blue-green colour) and porphyrin (brown colour) may be used as a bioindicator of contamination loads in the seabird eggs. The methodology was described in their paper, and the partial least square-linear discrimination analysis was used to discriminate the eggs in two clusters of low and high contamination loads. The results show negative association between blue-green chroma and contaminant load and correct classification of 84% of the eggs analysed for cross-validation.

More data were reported (Cipro *et al.*, 2013) on classic and new organohalogenated compounds in the eggs of a few seabird species from Antarctic: Skua *(Catharacta sp.)*, kelp gull *(Larus dominicanus)*, Antarctic tern *(Sterna vittata)*. The PCB concentration levels were apparently consistent with the birds' migration distance and opportunistic and scavenging feeding behavior. The highest concentrations were found in skua, lower in Antarctic tern and lowest in kelp gull.

Eens *et al.* (2013) presented results of organohalogenated contaminants monitoring on a worldwide scale in starling eggs. The egg samples from 15 countries (including New Zealand, USA, Canada and Europe) were analyzed for PCBs, DDTs, HCHs, HCB, chlordanes, and PBDEs. The results show that PCB levels were higher in urban than rural areas. The highest levels of DDT in New Zealand were likely related to its extensive use and late ban in 1989 while higher levels of chlordanes in the USA were probably related to the primary use of chlordanes in the USA. However, the question may be raised if samples were representative for a global comparison, as in several cases the contaminant content of the eggs seemed to be strongly affected by local factors .

The perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) were analyzed in 1980 and 2008 egg (and plasma) samples of great skua from Scotland (Leat *et al.*, 2013). The results of this study showed that levels had increased from 1980 to 2008 and this increase was more pronounced for PFCAs than for PFSAs. The authors discussed that PFAS levels were not particularly high, compared with other seabirds. It is also interesting to note that levels in male plasma samples were generally higher than concentrations in females.

Trefry *et al.* (2013) reported data on persistent organic contaminants and trace elements in egg samples of magnificent frigatebird from Barbuda (West Indies). The levels of contaminants from these samples were among the lowest ever reported for marine birds feeding at higher levels in food webs. According to the authors, these data suggest that the chemical contamination of marine food webs of breeding frigatebirds in the Caribbean is low and does not present major threats to the ecosystem. However the study was conducted on the relatively small sample size and only from a single colony.

Finally, mercury concentrations were studied in herring gull eggs over a 36-year period (1972–2008) from five sites in Atlantic Canada (Burgess *et al.*, 2013). The influence of dietary shifts on temporal trends was examined. The decreasing trends of Hg levels in two colonies (Manawagonish Island and Île du Corossol) were not significant anymore when adjusted for dietary shifts. The increasing trend of mercury is maintained when corrected for diet shift in herring gulls in Gull Island, Newfoundland.

References

Braune, B.M., Letcher, R.J. 2013. Perfluorinated sulfonate and carboxylate compounds in eggs of seabirds breeding in the Canadian Arctic: Temporal trends (1975-2011) and interspecies comparison. Environ. Sci. Techn. 47, 616-624.

Burgess, N.M., Bond, A.L., Hebert, C.H., Neugebauer, E., Champoux, L. 2013. Mercury trends in herring gull *(Larus argentatus)* eggs from Atlantic Canada, 1972-2008: Temporal change or dietary shift? Environmental Pollution 172, 216-222.

Chen, D., Letcher, R.J., Gauthier, L.T., Chu, S., McCrindle, R. 2012. Newly discovered methoxylated polybrominated diphenoxybenzenes have been contaminants in Great Lakes herring gull eggs for thirty years. Environ. Sci. Technol. 46, 9456-9463.

Cipro, C.V.Z., Colabuono, F.I., Taniguchi, S., Montone, R.C. 2013. Persistent organic pollutants in bird, fish and invertebrate samples from King George Island, Antarctica. Antarctic Sci. 25 (4), 545—552.

Eens, M., Jaspers, V.L.B., van den Steen, E., Bateson, M., Carere, C., Clergeau, P., Costantini, D., Dolenec, Z., Elliott, J.E., Flux, J., Gwinner, H., Halbrook, R.S., Heeb, P., Mazgajski, T.D., Moksnes, A., Polo, V., Soler, J.J., Sinclair, R., Veiga, J.P., Williams, T.D., Covaci, A., Pixten, R. 2013. Can starling eggs be useful as a biomonitoring tool to study organohalogenated contaminants on a worldwide scale? Environ. Int. 51, 141-149.

Elliott, J.E., Elliott, K.H. 2013. Tracking marine pollution. Science 340, 556-558.

Hanley, D., Doucet, S.M. 2012. Does environmental contamination influence egg coloration? A long-term study in herring gulls. J. App. Ecolog. 49, 1055-1063.

Jörundsdóttir, H., Löfstrand, K., Svavarsson, J., Bignert, A., Bergman, Å. 2013. Polybromianted diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD). Chemosphere 93, 1526-1532

Leat, E.H.K., Bourgeon, S., Eze, J.I., Muir, D.C.G., Williamson, M., Bustnes, J.O., Furness, R.W., Borgå, K. 2013. Perfluoroalkyl substances in eggs and plasma of an avian predator, great skua *(Stercorarius skua)* in the North Atlantic. Environ. Toxicol. Chem. 32 (3), 569-576.

Trefry, S.A., Diamond, A.W., Spencer, N.C., Mallory, M.L. 2013. Contaminants in magnificent frigatebirds from Barbuda, West Indies. Marine Pollution Bulletin 75, 317–321.

Discussion

In the discussion following this presentation it was again emphasized that some countries considered pollutant monitoring in seabird eggs in their descriptor 8 MSFD monitoring schemes (Ireland and Belgium, possibly Germany). The question if more Member States will use this approach is not yet clearly settled.

It was also remarked that a recommendation was sent to OSPAR from MCWG 2013 to note the information available from several monitoring programmes, besides the TMAP. MCWG feel that they need more information about why OSPAR is interested in seabird egg monitoring and in what aspects specifically. Bird eggs have been prov-

en to be a favourable matrix in various long-term monitoring programs in several countries (Sweden, Germany, Denmark/Greenland etc.).

5.10.2 Review if OSPAR guidelines on seabird eggs as a monitoring matrix present the current state of knowledge

Due to time constraints this topic was not discussed at MCWG 2014.

5.10.3 Collect biological information on seabird egg production to elucidate the transfer of contaminants from birds to eggs

Katrin Vorkamp had invited Anders Mosbech (Aarhus University) to present an overview on seabird biology, feeding habits, life cycles, geography distribution and migration behaviours.

Anders Mosbech explained the concept of income and capital breeder species. The feeding strategies vary considerably between species and geographical ranges extend from local feeders such as black cormorant and black guillemot (<20 km, <5 km ranges) to long range feeders such as puffin, common guillemot and kittiwake (10–200 km). The data on the worldwide seabird density show very high population density over northern and southern remote regions (from Karpouzi *et al.*, 2007). The presented examples of several studies covered:

- Little Auk tracking of foraging flights from breeding colony as well as tracking of their autumn migration to winter quarters;
- Thick-billed murre and Kittiwake studies provided also identification of their important foraging areas.

Reference

Karpouzi, V.S., Watson, R., Pauly, D. (2007). Modelling and mapping resource overlap between seabirds and fisheries on a global scale: a preliminary assessment. Mar. Ecol. Prog. Ser. 343, 87-99.

Discussion

MCWG welcomed this contribution and found the information on seabird biology highly interesting. MCWG felt that the biological complexity behind seabird egg monitoring should be considered to a larger extent when reviewing contaminant data derived from seabird eggs.

Various aspects were raised during the discussion. For example, whether the widespread use of gull eggs in monitoring programmes might lead to challenges in data interpretation because of the opportunistic and varying diet of the gulls? This was confirmed, however, their high trophic level usually means relatively high contaminant levels, which reduces other uncertainties. Another question was what parameters should be measured along with the contaminants. Anders Mosbech suggested that stable isotopes of nitrogen and carbon could give valuable ecological information. The age of the individual, an important parameter for other species, was probably of minor importance in the seabird egg monitoring.

Anders Mosbech informed MCWG about the Working Group on Seabird Ecology who might be interested in collaboration with MCWG on some of these questions. The differentiation between income and capital breeders was mainly based on nutrient data and MCWG wondered to what extent the contaminants follow the nutrients. This could be a relevant question to discuss in collaboration with the Working Group

on Seabird Ecology. Katrin Vorkamp will establish a contact to the Working Group (see Annex 6).

Kine Bæk informed that she was involved in a study in the Oslo Fjord, which also includes analyses of seabird eggs. She will be happy to report on this study at MCWG 2015 (see Annex 6).

5.10.4 Report and comment on OSPAR and HELCOM activities with regard to seabird eggs as a monitoring matrix

Evin McGovern informed about two documents describing OSPAR's current activities with regard to seabird eggs as a monitoring matrix. They show that the contaminant monitoring in seabird eggs is a high priority topic at OSPAR, however, no links exist currently to the MCWG activities in this field, despite a recommendation to OSPAR of MCWG 2013 to note the information that MCWG had collected.

The documents were not further discussed at MCWG 2014 and are only briefly described here.

The first document is the report of an Intersessional Correspondence Group (ICG) on bird eggs chaired by Harald Marencic of the Commen Wadden Sea Secretariat (OSPAR, 2013). The ICG had been established by HASEC, with the task to advise whether the monitoring of seabird eggs should be included in the pre-CEMP. The following points were addressed by ICG Bird Eggs:

- Submission of data to the ICES database
- EcoQO and Background Concentrations
- Replace or complement other monitoring
- Other contaminants
- Supporting parameters
- Birds species in the Convention area
- MSFD target and indicator

Based on their analysis of these items, the ICG Bird Eggs proposed, inter alia:

- Laboratories should not analyse the eggs of their region/country, but specialize in a certain parameter. The egg material should then be subsampled and all eggs should be analysed at the specialized laboratory.
- EcoQO/EACs should be developed for specific contaminants and bird species, taking into account food web accumulation processes.
- PFAS, PBDEs, HBCD, dioxin, furans and dioxin-like PCBs should be considered for inclusion in the monitoring programme.
- Eggshell thickness and breeding success should be monitored alongside the contaminants.
- Comparability studies with species occurring in the northern and southern part of the Convention area should be performed.
- Seabird eggs should be considered as a common indicator for D8 of the MSFD.

The second document is the MIME 2013 report as presented at HASEC 2014 (OSPAR, 2014). MIME considered that ICG Bird Eggs had completed their terms of references and would cease to exist. Following up on the presentation of the ICG Bird Eggs re-

port (see above) and discussions at MIME, MIME communicated the following points to HASEC, inter alia:

- The question of reporting seabird egg data to the ICES database requires more work, currently taken on by Sweden.
- MIME did not support the proposal of one laboratory analyzing all eggs (for a given parameter). MIME considered it pre-mature to involve QUASIMEME in the QA scheme because of a low number of laboratories.
- Development of EACs requires more work, but MIME considered it difficult to find resources.
- MIME supported combining the seabird egg monitoring with existing monitoring activities.
- Whether or not additional contaminants should be included should be decided at the national level.
- MIME agreed that eggshell thickness was an important parameter to include, while monitoring of breeding success should be a national decision.
- Questions about the bird species remained unanswered for the time being.
- The OSPAR common indicators "metals in biota", "PCBs in biota" and "PBDEs in biota" could also integrate contaminants in seabird eggs.

References:

OSPAR (2013). Report of the ICG Bird Eggs. Meeting of the Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME), Copenhagen, Denmark, 25 – 29 November 2013. MIME 13/3/3-E.

OSPAR (2014). Report on the outcome of MIME 2013. Meeting of the Hazardous Substances and Eutrophication Committee (HASEC), Bonn, Germany, 17 – 21 March 2014. HASEC 14/6/1-E.

5.10.5 Discuss potential of concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace elements

MCWG discussed that the data collected at MCWG 2012, MCWG 2013 and MCWG 2014 might form the basis of a publication, for example a review article on the use of seabird eggs as a monitoring matrix. It was generally agreed that it was not optimal that a large amount of information was spread over three MCWG reports. Furthermore, several MCWG members were in favour of publications in the peer-review literature which would reach a broader audience. However, time constraints might limit what can be achieved.

Katrin Vorkamp and Michael Haarich are going to consider options of publishing the information compiled on seabird eggs at the last three MCWG meetings (see Annex 6). This will most likely also involve other experts.

5.11 Passive sampling (joint session with WGBEC and WGMS)

The session was opened with a plenary presentation by Prof. Philipp Mayer (Technical University of Denmark), see section 4.2.

In the remainder of the session, three further presentations were given by members of MCWG and WGMS.

Foppe Smedes (WGMS/MCWG): A comparison of lipid based concentrations of PCBs and PAHs obtained through passive sampling with lipid normalized concentrations in biota

Foppe Smedes (DELTARES, The Netherlands) illustrated the use of passive samplers for deriving equivalent lipid-based concentrations (C_{lipid}), which are easier to interpret for risk assessments than C_{free}, and allow for direct comparison with lipid-based concentrations in biota. He showed that different types of passive samplers yielded the same values of C_{lipid}, indicating the robustness of this method. The work had been conducted in collaboration with Tatsiana P. Rusina and Philipp Mayer.

Foppe Smedes (WGMS/MCWG): Passive sampling in sediments in and around the North Sea – ICES ICON project.

Within the ICES ICON project silicone rubber passive samplers were exposed to 13 sediment samples taken from the Mediterranean to Iceland, including estuarine as well as open sea sediment. PAHs, PCBs, musk compounds, organo-phosphates, several organochlorine pesticides (including chlordanes), PBDEs and dioxins could be detected in samplers from virtually all locations. Higher concentrations were observed in estuaries for compounds that enter the marine environment through that route. Compounds that primarily enter the marine environment from diffuse sources, e.g. atmospheric deposition, showed concentrations much more equal for estuaries and open sea. For example chlordane, a pesticide not used in Europe, was present in open sea samples at the same levels as in estuaries. The results indicate that passive sampling allows very sensitive analyses of the contaminant levels in sediments. Furthermore, the same time and spatial comparison is possible as in conventional sampling, without the need for normalisation of the data for sediment characteristics. Foppe Smedes acknowledged contributions of Henry Beeltje (TNO-Utrecht, NL), Petr Kukucka (RECETOX, Brno, CZ) and Dick Vethaak (Deltares, Delft, NL).

Maria J. Belzunce (WGMS): Utilising DGT–labile metal measurements to explain differences in bioaccumulation occurring in identical sediment deployed in field and laboratory

Maria J. Belzunce (AZTI-Tecnalia, Spain) presented results from a study in Australia, with collaboration partners at the Centre for Environmental Contaminants Research (CSIRO, Sydney) and the School of Chemistry, University of Wollongong, NSW, Australia. Collaboration partners were M.J. Belzunce-Segarra, S. Simpson, E. Amato, D. Spadaro, I. Hamilton, C. Jarolimek, D. Jolley. The aims of the study were: (a) to investigate the metal bioavailability-organism response relationship utilising DGT techniques in sediments and metal accumulation in benthic bivalves (b) to evaluate in which extent metal bioavailability and bioaccumulation measured in situ conditions are comparable with data obtained under laboratory conditions.

A field and laboratory based experiments were conducted simultaneously over 31 days. *In situ* deployment system was prepared with two stainless steel cages containing a range of metal contaminated marine sediments. The cages were submerged (0.5 m depth from the water surface) in Woronora estuary (Sydney, Australia). A total of 8 metal contaminated sediments (plus replicates) were prepared and placed into plastic beakers inside the cages. Seven individuals of the bivalve *Tellina deltoidales* of similar size (0.5–1.0 cm length) were added to each beaker. Under laboratory conditions clean and filtered sea water was used; the overlaying water was changed 2 times a week and the bivalves were fed 2 times a week. DGT-probes were deployed in each sediment twice during the test period, and overlying waters were also sampled throughout the laboratory test. At the end of the experiment the cages were retrieved from the field site and transported to the laboratory. For all treatments, sub-samples

from three sediment depths were analysed for metals, organic carbon and AVS-SEM. The surviving bivalves were isolated, counted, and then allowed to depurate in clean seawater for 24 h, before being analysed for metal content.

Results show differences in metal concentration in sediments after 31 days deployment in field with respect sediments exposed in laboratory conditions that influence metal bioavailability. The DGT-metal flux measurements show differences in metal content in pore waters and in the overlaying water in the two scenarios (laboratory and field deployments) that explain the higher metal bioaccumulation obtained in the laboratory tested bivalves. DGT probes are useful tools that allow describing the relationships between the metal bioaccumulation by the bivalves and metal in the sediments and the various factors influencing metal bioavailability.

Lutz Ahrens (MCWG): Calibration and Field Evaluation of Passive Samplers for Monitoring Pesticides in Water

Lutz Ahrens (SLU, Sweden) presented preliminary results on calibration and field evaluation of passive samplers for monitoring pesticides in water. The objectives of this study were i) to characterize six passive sampler types in a laboratory uptake study, ii) to apply three passive sampler types in two Swedish river systems, and iii) to compare passive sampling and active sampling. In this study, the passive samplers were characterized for about 150 individual pesticides including 20 priority substances of the EU Water Framework Directive (WFD). The passive sampler adsorbents included i) POCIS A: Pharmaceutical-POCIS, polar organic chemical integrative sampler (Oasis hydrophilic–lipophilic balance (HLB) sorbent), ii) POCIS B: Pesticide-POCIS, triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500) enclosed in a polyethersulphone membrane, iii) Chemcatcher® SDB-RPS: Styrene divinyl benzene EmporeTM disk, iv) Chemcatcher® C18: EmporeTM disk, v) silicone rubber (SR), and vi) low-density polyethylene (LDPE). Overall, passive sampling is a promising tool for monitoring of pesticides in water with minimal infrastructure and low contaminant concentrations. However, more research is needed to improve our understanding of the concept, challenges, and application of passive sampling for future monitoring strategies.

5.11.1 Report on QUASIMEME exercise on passive sampling

A development exercise is planned to start in September 2014 by QUASIMEME, with support of WGMS (Foppe Smedes) and MCWG (Kees Booij) – see also section 5.1. The required minimum of ten participants has not yet been reached, and Foppe Smedes and Kees Booij will try to further raise the present number of participants via e-mail to the networks of MCWG, WGMS, NORMAN, IPSW, after consultation of QUASIMEME. Koen Parmentier and Peter Lepom will forward this e-mail to selected members of their networks. MCWG noted that this exercise may also be relevant for people working on freshwater environments. Inclusion of the analysis of mussels deployed at the same site as the passive samplers was deemed too complicated and costly.

5.11.2 Review and discuss information on effects of freely dissolved concentrations, with a view of developing environmental assessment criteria, in a joint session with WGMS and WGBEC

It was noted that the discussion on the relevance of passive sampling methods for environmental risk assessment of contaminants was presently limited to non-polar contaminants.

WGMS recognised the relevance of these methods for the risk assessments of contaminated sediments. Some members felt, however, that sediment characteristics might also be important in this respect, therefore discussion within WGMS is ongoing.

WGBEC expressed interest to further look into the use of passive sampler based C_{free} as a proxy for toxicity for benthic and pelagic organisms. MCWG expressed interest to continue discussing the above issues with WGMS and WGBEC. MCWG would welcome the interaction with WGBEC and WGMS in relation to its discussions of C_{free} and sediment properties in relation to toxicity.

It was highlighted in the discussion that some of this work was initiated by WKPSPD. As the workshop was a one-off event, the only possibilities of following up on e.g. the knowledge gaps described by WKPSPD was in MCWG, WGMS and WGBEC. In order to keep the momentum from the workshop, MCWG would be interested in further collaboration with WGMS and WGBEC on specific aspects of passive sampling, amongst these the long-term goal of developing environmental assessment criteria. See also recommendations in Annex 4.

5.11.3 Review and discuss information on mixture toxicity derived from passive dosing, in a joint session with WGMS and WGBEC

As described in section 5.11.2, MCWG would welcome interactions with WGMS and WGBEC on specific aspects of passive sampling/passive dosing. MCWG felt that WGBEC could contribute significantly to the work on passive dosing techniques for toxicity testing of contaminant mixtures. WGBEC agreed that they would be interested in this topic.

It was agreed between MCWG and WGBEC (and WGMS) that a recommendation (see Annex 4) would be given that describes MCWG's interest in contributions from WGBEC. MCWG recommended using the information provided by Prof. Philipp Mayer (see section 4) including the references in Annex 7 as a starting point.

5.11.4 Report and comment on OSPAR and HELCOM activities with regard to passive sampling

Due to time constraints this was not further discussed. For a general discussion of MCWG's interest in OSPAR and HELCOM activities, see section 6.

5.12 Publications

5.12.1 Present final draft manuscript on atmosphere-water exchange of PFAS in the marine environment

Lutz Ahrens presented a draft manuscript on "Atmospheric-Water Exchange of Poly- and Perfluoroalkyl Substances (PFASs) in the Marine Environment – a Review" by the authors Lutz Ahrens, Katrin Vorkamp, Zhiyong Xie, Norbert Theobald, Ralf Ebinghaus.

The background of this publication is as follows: In 2010, OSPAR had raised the question whether atmospheric monitoring of PFOS and/or other PFASs would be useful for assessments of their input into the oceans. This question led to a literature review on non-polymeric PFASs in the abiotic marine environment, as presented to MCWG at the annual meetings in 2011–2013. At MCWG 2013, it was decided that the main authors of the annual literature reviews would compile and update this information, for publication in a peer-reviewed journal.

The draft manuscript covers the following topics: i) Analytical challenges for the analysis of PFASs in the atmosphere and water, ii) overview on PFAS concentrations in marine atmosphere and seawater, iii) pathways and distribution of PFASs in the marine environment, iv) investigation of atmospheric-water exchange including the role of wet and dry deposition and volatilization and sea spray, v) implications for monitoring, and vi) conclusions and future perspectives.

Jacek Tronczynski, Kine Bæk and Philippe Bersuder agreed to provide comments on the draft presented at MCWG 2014. The authors plan to submit the manuscript in 2014.

5.12.2 Review final draft TIMES manuscript on passive sampling in sediments

The manuscript on passive sampling in sediments was not addressed due to time constraints.

5.12.3 Review draft TIMES manuscript on determination of sampler–water partitioning coefficients

A subgroup of members of WGMS and MCWG (see section 2) outlined this draft during the meeting and agreed on the details of the methods that will be recommended. It is expected that a final draft can be produced intersessionally. MCWG hopes to invite a number of laboratories to test the recommended methods before finalising the manuscript, but recognises that there may be time and budget constraints for the invited laboratories, since external funding may not be available.

Shortly after the MCWG 2014 meeting, the MCWG chair was contacted by SCICOM with regard to the draft resolutions originally submitted by WKPSPD for TIMES papers (see section 3.1.2). It was advised that these draft resolutions should be resubmitted via active working groups. After consultation with the lead author of the TIMES manuscript on determination of sampler-water partitioning coefficients, the draft resolution was revised as follows:

Draft resolution

The following manuscript is proposed for publication in ICES Techniques in Marine Environmental Sciences:

Publication title	MCWG Lead	Estimated page numbers
Determination of sampler-water partition coefficients and sampler-sampler partition coefficients	Kees Booij	20

Supporting Information

Priority	WKPSPD recommended the use of passive sampling for the monitoring of hydrophobic contaminants in the marine environment (e.g. for WFD, MSFD and OSPAR) and a TIMES document on the use of one type of passive sampler was recently published (no. 52). However, the passive sampling technique is reliant upon having accurately determined partition-coefficients for each compound of interest. Hence, the technique will only be accepted for monitoring purposes when these can be produced using a standardised approach that is compliant with EU Directives.
Scientific justification	Passive sampler-water (Ksw) partition coefficients are required in order to determine aqueous concentrations of hydrophobic analytes using passive sampling. Ksw values are required for every analyte of interest, and differ depending upon which passive sampler material is used. It is important that a standardised methodology is available for determining Ksw values, to encourage more laboratories to produce them and thus reduce uncertainty in their values. Determination of Ksw requires determining the concentration of hydrophobic contaminants i

	both the sampler material and in water, which is difficult. However, determination of partition coefficients between different sampler materials allows calculation of Ksw for one material, if the Ksw for the other is already known. For the propagation of analytical error calculations, it is important that the uncertainties on Ksw values are also calculated in a consistent manner.
Resource requirements	Cost of production and publication.
Participants	MCWG and WGMS members, potentially additional experts, external reviewers.
Secretariat facilities	Help with document preparation/publication. Final editing.
Financial	Publication costs.
Linkages to advisory committees	-
Linkages to other committees or groups	Experts from WGMS will contribute to the manuscript.
Linkages to other organizations	This documentation is relevant to OSPAR, and in relation to monitoring for the EU WFD and MSFD.

5.12.4 Discuss potential of a TIMES publication on chlorophyll measurements

As described in section 5.1 and section 5.8, there are a number of methodological issues in relation to chlorophyll measurements. These might include questions about solvent use, extraction techniques and instrumental analyses, in particular HPLC vs. photometric determination. MCWG discussed that a method paper might be useful taking into account the latest findings with regard to method biases, including the meta-analysis performed by QUASIMEME (see section 5.1). It was agreed that the method paper should also await results of the data analyses still ongoing at QUASIMEME and MUMM (see sections 5.1 and 5.8).

Pamela Walsham agreed to collect relevant information on this topic, for follow up at MCWG 2015 (see Annex 6). She also agreed to take the lead on a potential method paper, with further contributors to be defined at MCWG 2015.

5.13 Review and update, as necessary, the following existing technical annexes to JAMP Guidelines (OSPAR request)

The full text of the OSPAR requests to MCWG is given in Annex 5. The technical annexes for metal determination in biota and sediment and organotin determination in sediment were reviewed and revised with focus on new technical developments since the present versions. The sediment-related technical annexes were reviewed and revised jointly with WGMS.

5.13.1 Contaminants in biota: Technical Annex 2 (Determination of metals)

The subgroups working on the revision of the technical annexes on metal determination in biota and sediment, respectively, paid particular attention to new key references to be included and found it important to provide a list of commercially available certified reference materials, to support guidance on quality assurance/quality control.

The technical annex on metal determination in biota was reviewed and revised by an MCWG subgroup (Victoria Besada, Gert Asmund, Jens Søndergaard, Michael Haarich, see section 2) with assistance from Martin M. Larsen of WGMS. The draft revised technical annex is given in Annex 10 of this report.

5.13.2 Contaminants in sediments: Technical Annex 4 (Determination of mono-, di- and tributyltin in sediments: analytical methods)

The technical annex for the determination of organotin compounds in sediments was reviewed and revised in a joint MCWG/WGMS subgroup consisting of Els Monteyne, Thi Bolam (both WGMS), Norbert Theobald and Koen Parmentier (both MCWG). Because of his expertise in this field, Jakob Strand (WGBEC) contributed to this work as well.

The subgroup provided a significant amount of new information on laboratory procedures in particular, including extraction, digestion, derivatisation and purification methods. The draft revised technical annex is given in Annex 11 of this report.

5.13.3 Contaminants in sediments: Technical Annex 6 (determination of metals in sediments – analytical methods)

The overall approach was the same as for the technical annex on determination of sediments in biota (section 5.13.1). As this OSPAR request had also been given to WGMS, a joint MCWG/WGMS subgroup worked on this technical annex. The subgroup consisted of Victoria Besada, Gert Asmund, Jens Søndergaard, Michael Haarich (MCWG) and Martin M. Larsen and Carla Palma (WGMS), see also section 2. The draft revised technical annex is given in Annex 12 of this report.

6 Plenary discussion of draft report

During the meeting, specific sections of the report were discussed, in order to agree on the content as well as the precise wording. The rest of the report was discussed by correspondence.

It was mentioned in the discussion that MCWG would welcome more interactions with OSPAR and HELCOM, for example in terms of a brief status on the documents and recommendations provided for OSPAR. It would also be interesting for MCWG to be informed about topics within marine chemistry discussed at OSPAR working group and committee meetings (e.g. ocean acidification, passive sampling, seabird eggs). As some MCWG members attend the OSPAR meetings, this information could probably be provided relatively easily. To ensure progress on this, an internal recommendation has been given to MCWG (Annex 4).

7 Any other business

Katrin Vorkamp will reach the end of her term as chair of MCWG in 2015. She therefore suggested appointing a co-chair for MCWG 2015 who could gradually take over the work of the chair and continue as chair after MCWG 2015. MCWG voted for a new chair and Koen Parmentier accepted the function as incoming chair of MCWG.

8 Recommendations and action list

Recommendations and actions were discussed in plenary and are summarized in Annex 4 (recommendations) and Annex 6 (action list).

9 Date and venue of the next meeting

MCWG received an invitation by Carlos Borges for the MCWG 2015 meeting to be held at the Instituto Hidrográfico at Lisbon, Portugal, 2–6 March 2015. MCWG gladly accepted this invitation.

10 Closure of the meeting

The meeting was closed at 1 p.m. on 7 March 2014.

Annex 1: List of participants

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Annex 2: Agenda

ICES MARINE CHEMISTRY WORKING GROUP
36TH MEETING

ICES, COPENHAGEN, DENMARK

3TH – 7TH MARCH 2014

1 OPENING OF THE MEETING

The meeting will begin at 10.00 am on the first day, and 09.00 am thereafter.

2 ADOPTION OF THE AGENDA

Updates of MCWG action list, discussion of timetable, formation of subgroups.

3 REPORT OF ICES ACTIVITIES

i) MCWG 2013 recapitulation
ii) Intersessional activities
iii) 2013 Annual Science Conference
(see also 5.7)
iv) OSPAR/ICES Study Group on Ocean Acidification (SGOA)
(see also 5.7)

4 PLENARY PRESENTATIONS

4.1 Hans Sanderson (Aarhus University): Sea dumped chemical munition in the Baltic Sea – a review with regards to fish community risk.

4.2 Philipp Mayer (Technical University of Denmark): Passive sampling

5 MAIN AGENDA

General

5.1 ToR a: Quality assurance of marine chemistry.

i) Report and discuss new developments in QUASIMEME.
Presentation by Steven Tito (QUASIMEME)
(see also 5.7, 5.8 and 5.11)
ii) Provide information on other proficiency testing schemes with relevance to MCWG.

iii) Demonstrate new software developed by the Finnish Environmental Institute for estimations of measurement uncertainty.

5.2 ToR b: Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD):

i) Review and discuss developments of WFD, in particular regarding new priority (hazardous) substances and associated EQS values.
ii) Review and discuss developments in MSFD, in particular regarding the monitoring of descriptors 5, 7, 8 and 9.

5.3 ToR c: Present projects of relevance to MCWG activities.

Bavo de Witte: Presentation of the 4DEMON project

Lutz Ahrens: New information on perfluoroalkyl substances in the marine environment
Jacek Tronczynski: Transfer and bioaccumulation of contaminants at first trophic levels in short pelagic food webs
Jacek Tronczynski: Historical records of Hg, Pb and PAH in a dated sediment core from the Eastern Mediterranean
Michael Haarich: Contaminants in fish – Monitoring in the North Sea and the Baltic Sea
Caroline Kivimae: Presentation of the Shelf Sea Biogeochemistry project

5.4 ToR d: Marine litter and its role as a potential source of contaminants
(joint session with WGBEC and WGMS)

i) Report on new information on marine litter and its role as a potential source of contaminants.
ii) Review the literature with regard to the role of marine litter as a potential source of contaminants.
iii) Combine information on plastics in sediment, on plastic/contaminant interactions and on their effects in biota for a comprehensive problem description and assessment.

5.5 ToR e: ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested
i) Presentation of a draft format for litter reporting.

5.6 ToR f: Report on activities in other expert groups on the interface to MCWG
(e.g. WGMS, WGBEC, WGEEL, SGONS).

Chemical Oceanography

5.7 ToR g: Ocean acidification:

i) Report from the OSPAR/ICES Study Group on Ocean Acidification and provide comments and input as follows:
– Review and discuss developments of analytical methods
– Update QA/QC requirements
- Assist SGOA in elaborating reporting requirements;
i) SGOA recommendation: Further review reporting requirements to ICES environmental database for OA data, specifically in relation to units and reference temperature for pH and other parameters as elaborated in Section 8 of the SGOA 2013 report.

ii) Present and discuss new chemical oceanographic data relating to ocean acidification.

iii) Report on QUASIMEME workshop on ocean acidification and discuss implications for ocean acidification monitoring.
SGOA recommendation: Review progress on advancing ocean acidification QA/QC workshop.

iv) Report from theme session on ocean acidification at the ICES Annual Science Conference 2013.

v) Report on pH measurements in sediments, in a joint session with WGMS and WGBEC.

5.8 ToR h: Chlorophyll and nutrients

i) Report from QUASIMEME workshop on chlorophyll and nutrient analysis.

ii) Review if OSPAR guidelines for chlorophyll determination are in line with outcomes of the QUASIMEME workshop on chlorophyll analysis and provide advice on most appropriate methodology.

iii) Discuss comparability of methods for chlorophyll analysis

Contaminants

5.9 ToR i: Report on new information on emerging contaminants in the marine environment.

ii) Philippe Bersuder: Alternative flame retardants in marine mammals

5.10 ToR j: Seabird eggs as a monitoring matrix for organic contaminants and trace elements

i) Review literature that has become available since MCWG 2013 on the monitoring of organic contaminants and trace elements in seabird eggs.

ii) Review if OSPAR guidelines on seabird eggs as a monitoring matrix present the current state of knowledge.

iii) Collect biological information on seabird egg production to elucidate the transfer of contaminants from birds to eggs.
iv) Report and comment on OSPAR and HELCOM activities with regard to seabird eggs as a monitoring matrix.
v) Discuss potential of concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace elements.

5.11 ToR k: Passive sampling
(joint session with WGBEC and WGMS)

i) Report on QUASIMEME exercise on passive sampling.
ii) Review and discuss information on effects of freely dissolved concentrations, with a view of developing environmental assessment criteria, in a joint session with WGMS and WGBEC.
iii) Review and discuss information on mixture toxicity derived from passive dosing, in a joint session with WGMS and WGBEC.
iv) Report and comment on OSPAR and HELCOM activities with regard to passive sampling

iii)

iv) Publications

v)

5.12 ToR l: Publications

i) Present final draft manuscript on atmosphere-water exchange of PFAS in the marine environment.
ii) Review final draft TIMES manuscript on passive sampling in sediments.
iii) Review draft TIMES manuscript on determinations of sampler-water partitioning coefficients.
iv) Discuss potential of a TIMES publication on chlorophyll measurements.

vi)

vii) OSPAR requests

5.13 Review and update, as necessary, the following existing technical annexes to JAMP Guidelines:

i) Contaminants in biota: Technical Annex 2 (Determination of metals)
ii) Contaminants in sediments: Technical Annex 4 (Determination of mono-, di- and tributyltin in sediments: analytical methods)
iii) Contaminants in sediments: Technical Annex 6 (determination of metals in sediments – analytical methods)

6 PLENARY DISCUSSION OF DRAFT REPORT

7 ANY OTHER BUSINESS

8 RECOMMENDATIONS AND ACTION LIST

9 DATE AND VENUE OF THE NEXT MEETING

10 CLOSURE OF THE MEETING

Annex 3: MCWG draft resolution for the next meeting

The **Marine Chemistry Working Group** (MCWG), chaired by Katrin Vorkamp, Denmark and Koen Parmentier, Belgium, will meet in Lisbon, Portugal, 2 - 6 March 2015 to:

1) Quality assurance of marine chemistry

i) Report and discuss new developments in QUASIMEME.

ii) Provide information on other proficiency testing schemes with relevance to MCWG.

2) Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)

i) Review and discuss developments of WFD, in particular regarding new priority (hazardous) substances and associated EQS values.

ii) Calculate and discuss conversions of EQS_{biota} values from fish to mussels.

iii) Review and discuss developments in MSFD, in particular regarding the monitoring of descriptors 5, 7, 8 and 9.

3) Developments at OSPAR and HELCOM

i) Discuss activities at OSPAR and HELCOM with direct relevance to MCWG and consider input from MCWG.

4) Present projects of relevance to MCWG activities, including information on emerging contaminants.

5) Marine litter and its role as a potential source of contaminants.

i) Report on new information on marine litter and its role as a potential source of contaminants, with particular focus on field studies demonstrating elevated contaminant levels associated with plastics.

ii) Present information on contaminant desorption from plastic in the digestive system after plastic uptake by biota, if available.

6) ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested.

7) Report on activities in other expert groups on the interface to MCWG

i) WGMS

ii) WGBEC

iii) WGEEL

iv) Working Group on Oceanic Hydrography (WGOH)

v) Working Group on Phytoplankton and Microbial Ecology (WGPME)

8) Ocean acidification

i) Report from the OSPAR/ICES Study Group on Ocean Acidification and address potential recommendations from this group to MCWG.
ii) Report from OA workshop and discuss implications of workshop results for OA monitoring.
iii) Present and discuss new chemical oceanographic data relating to ocean acidification.

9) Chlorophyll

i) Report on QUASIMEME initiative of assessment of chlorophyll data in the QUASIMEME database, in particular regarding data comparability, and discuss potential implications for existing measurement guidance.
ii) Collect information in preparation of TIMES manuscript or similar publication on chlorophyll determination methods.

10) Seabird eggs as a monitoring matrix for organic contaminants and trace metals

i) Review and discuss potential contributions from the Working Group on Seabird Ecology.

11) Passive sampling

i) Report on QUASIMEME exercise on passive sampling and review data with a view to adjustment of background assessment concentrations.
ii) Obtain information from WGBEC and WGMS regarding the use of C_{free} as a proxy of the effects of non-polar compounds, with a view to determining environmental assessment criteria.
iii) Review and discuss information on mixture toxicity derived from passive sampling, supported by WGBEC.

12) Publications

i) Review and comment on TIMES draft manuscript on passive sampling in sediments, produced by WGMS.
ii) Review and complete TIMES draft manuscript on the determination of sampler/water and sampler/sampler partition coefficients.
iii) Discuss initial work on concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace metals.

MCWG will report by 15 April 2015 to the attention of the SCICOM and ACOM.

Supporting Information

Priority	This group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. MCWG provides input across the field of marine chemistry, which underpins the advice given by ICES, and also supports the work of national and international collaborative monitoring programmes, e.g. within OSPAR
Scientific	1. MCWG has a particular interest in quality assurance and maintains strong links with QUASIMEME with a view to supporting quality

justification	assurance activities in this field. MCWG has initiated several new activitites in QUASIMEME. 2. This work was inititated by MCWG and will be of interest to EU/OSPAR/HELCOM. 3. MCWG feels that OSPAR and HELCOM work with several topics within marine chemistry which MCWG could provide input to. 4. MCWG members are interested in receiving reports on relevant projects and activitites from other members. 5. This is a new focus area within marine chemistry (MSFD descriptor 10) and an area of common interest for MCWG, WGMS and WGBEC. MCWG focusses on contaminant-related issues of marine litter. 6. This is in direct respons to possible requests by the ICES Data Centre. 7. Collaboration between expert groups, with new additions which may be relevant for information exchange within chemical oceanography. 8. These items will support the OSPAR/ICES study group on Ocean Acidification. 9. This item was identified by MCWG 2012 as a relevant area for more in-depth discussions, and will be of interest to OSPAR. 10. This was initiated by MCWG 2011 as an item of general interest to the group and will probably be of interest to OSPAR. 11. This continues work by WKPSPD and MCWG 2013 and will be of interest to OSPAR. 12. Specific parts of MCWG's work might be of interest to a larger scientific community, i.e. relevant for publication beyond the annual report
Resource requirements	The research programmes which provide the main input to this group are already underway, and resources are already committed..
Participants	The Group is normally attended by some 20–25 members and guests.
Secretariat facilities	None.
Financial	No financial implications.
Linkages to advisory committees	ACOM
Linkages to other committees or groups	SCICOM WGMS, WGBEC OSPAR/ICES study group on Ocean Acidification (SGOA) ICES Data Centre
Linkages to other organizations	The work of this group is closely aligned with EU working groups under the Water Framework Directive (e.g. Working Group on Chemicals) and EU expert networks with regard to contaminants under the MSFD. Specific agenda points will be directly relevant for QUASIMEME. The group provides the basis for some advice to OSPAR.

Annex 4: Recommendations

Recommendation	Adressed to
1. For QUASIMEME to obtain data on relevant indicator compounds of the compound group to be analysed in the contaminant exercises, to ensure appropriate concentrations for the exercise. The concentration range provided in the protocol should agree with the actual concentrations.	QUASIMEME (quasimeme@wur.nl)
2. For QUASIMEME to note that while freshwater species are acceptable, the focus should be on marine species.	QUASIMEME (quasimeme@wur.nl)
3. For OSPAR to note that different methods of chlorophyll a determination might lead to significantly different results, as outlined in Annex 9 of the MCWG 2014 report.	OSPAR
4. For WGBEC and WGMS to coordinate with MCWG in order that a database of publications concerning toxicity of contaminants based on freely dissolved concentrations is developed in order to enable this data to be made available for the further development of environmental assessment criteria.	WGBEC and WGMS
5. For WGBEC to review information on mixture toxicity derived from passive dosing, for example starting from the references given in the MCWG 2014 report (section 4 and Annex 7).	WGBEC
6. For WGBEC to share new information with MCWG identifying plastics as a vector of enhanced contaminant transfer to biota.	WGBEC
7. For MCWG members also attending OSPAR and HELCOM working group and committee meetings to provide relevant information to MCWG regarding i) status on documents/topics to which MCWG previously provided input and ii) new topics of interest to OSPAR in the field of marine chemistry.	MCWG/OSPAR

Annex 5: OSPAR requests to MCWG 2014

Review and update of the Technical Annexes to JAMP Guidelines for Monitoring of Contaminants in Biota and in Sediments:

> To review and update, as necessary, the following existing technical annexes to JAMP Guidelines:

a) contaminants in biota: Technical Annex 2 (Determination of metals)

b) contaminants in sediments: Technical Annexes 4 (Determination of mono-, di- and tributyltin in sediments: analytical methods) and 6 (determination of metals in sediments – analytical methods)

Examination of the current versions downloaded from the OSPAR website (section 'agreements') indicates that these are in need of review and update primarily in terms of updated literature and analytical detection limits (where given). The information is still relevant and there is nothing in there which prevents their being useful guidance.

In the light of the fact that TBT concentrations in the marine environment as shown around UK and the North Sea are now declining rapidly following completion of the implementation of the worldwide IMO ban on the use of TBT in antifouling paints on large vessels (Verhaegen *et al.*, 2012; Law *et al.*, 2012), when reviewed, consideration should also be given to refocusing the butyltins method on dibutyltin as the primary determinand rather than tributyltin, as this compound is still widely used in e.g. plastics and clothing.

The direct measurement of metals in environmental matrices such as biota and sediments is a recent development (cf. e.g. Maggi *et al.*, 2009). This technique should be included in the technical guidelines.

The updates should build on the latest developments as available to the relevant ICES working groups.

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Verhaegen, Y.; Monteyne, E.; Neudecker, T.; Tulp, I.; Smagghe, G.; Cooreman, K.; Roose, P.; Parmentier, K. 2012. Organotins in North Sea brown shrimp *(Crangon crangon)* after implementation of the TBT ban. Chemosphere 86, 979-984.

Annex 6: Action list of MCWG 2014

The actions below are given in alphabetical order based on first names.

Bavo de Witte:

- Present new information on the Micro project.

Caroline Kivimae:

- Make arrangements at NOC for hosting QUASIMEME workshop on ocean acidification.
- Liaise with QUASIMEME to identify participants, develop a detailed programme and promote the workshop.
- Inform MCWG about activities of relevance to MCWG in Working Group on Oceanic Hydrography (WGOH).
- Further examine the CDIAC metadata requirements and consider whether these are directly appropriate for including in a form for the text file.
- Report on progress of Sea Shelf Biogeochemistry project to MCWG 2014.

Evin McGovern:

- Provide relevant background material for MCWG's work on conversion of EQS_{biota} from fish to mussels.

Jacek Tronczynski:

- Provide comments to authors of the PFAS draft manuscript (first author: Lutz Ahrens).
- Present new information on contaminants at lower trophic levels of a Mediterranean foodweb.

Katrin Vorkamp:

- Provide MCWG's comments on monitoring under descriptor 8 and 9 of the MSFD (Annex 8) to Georg Hanke
- Provide MCWG 2014 draft and final report to QUASIMEME.
- Provide MCWG 2014 draft and final report to the chairs of WGMS and WGBEC.
- Contact Working Group on Seabird Ecology with regard to biological information of relevance for contaminant monitoring (WGSE).
- Contact chairs of WGMS and WGBEC prior to MCWG 2015 for coordination and information exchange, in particular regarding passive sampling and marine litter.
- Follow up on considerations of publishing a concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace metals.
- Enquire at ICES about the Workshop on linking contaminant issues with integrated ecosystem assessment (WKLINCON) planned for 2014.

Kees Booij:

- Coordinate finalization of guideline for partition coefficents.

Kine Bæk:

- Provide comments to authors of the PFAS draft manuscript (first author: Lutz Ahrens).
- Report on study in Oslo Fjord including seabird eggs.

Koen Parmentier:

- Prepare draft proposals for 3 year ToRs including relation to Science Plan and potential outputs.
- Present outcome of the intercalibration exercise organized by CEN /TC 230 on the analysis of PBDEs, PAHs, chlorinated pesticides and organotins in water.

Michiel Kotterman:

- Plan participation in joint WGEEL/WGBEC workshop on effects of contaminants in eel.
- Plan participation in ICES/EIFAAC International Workshop of a Planning Group on the Monitoring of Eel Quality under the subject "Development of standardized and harmonized protocols for the estimation of eel quality." (WKPGMEQ), held in Brussels, 20 – 22 January 2015.
- Present new information of the ECsafeseafood project.
- Update MCWG on current eel studies at IMARES.

Pamela Walsham:

- Contact Andrew Dickson with regard to availability for OA workshop and settle date together with QUASIMEME.
- Liaise with QUASIMEME to identify participants, develop a detailed programme and promote the workshop.
- Collect information on different chlorophyll a results from different determination methods, with a view to write TIMES manuscript.

Peter Lepom:

- Provide information on other proficiency testing schemes with relevance to MCWG.

Philippe Bersuder:

- Provide comments to authors of the PFAS draft manuscript (first author: Lutz Ahrens).

Solveig Olafsdottir:

- Inform MCWG about activities of relevance to MCWG in Working Group on Phytoplankton and Microbial Ecology (WGPME).

Annex 7: References to the plenary presentation by Prof. Philipp Mayer (Section 4.2)

Equilibrium sampling

Cui, X., Mayer, P., Gan, J. (2012). Methods to assess bioavailability of hydrophobic organic contaminants: Principles, operations and limitations. Environmental Pollution 172, 223-234.

Hunter, W., Yang, Y., Reichenberg, F., Mayer, P., Gan, J. (2008). Measuring pyrethroids in sediment pore water using matrix-solid phase microextraction. Environmental Toxicology and Chemistry 28(1), 36-43.

Jahnke, A., Mayer, P., McLachlan, M.S. (2012). Sensitive Equilibrium Sampling to Study Polychlorinated Biphenyl Disposition in Baltic Sea Sediment. Environmental Science and Technology 46, 10114−10122.

Jahnke, A., Mayer, P., McLachlan, M.S., Wickström, H., Gilbert, D., MacLeod, M. (2014). Silicone passive equilibrium samplers as 'chemometers' in eels and sediments of a Swedish lake. Environmental Science: Processes & Impacts 16, 464-472.

Mayer, P. (2013). Equilibrium sampling of hydrophobic organic contaminants in sediments. Kolloquium Bioakkumulaiton in aquatischen Systemen: Methoden, Monitoring, Bewertung, Koblenz, Germany, March 2013.

Mayer, P., Parkerton, T.F., Adams, R.G., Cargill, J.G., Gan, J., Gouin, T., Gschwend, P.M., Hawthorne, S.B., Helm, P., Witt, G., You, J. (2014). Passive sampling methods for contaminated sediments: scientific rationale supporting use of freely dissolved concentrations. Integrated Environmental Assessment and Management 10 (2), 197-209.

Witt, G., Liehr, G.A., Borck, D., Mayer, P. (2009). Using solid phase microextraction to measure freely dissolved concentrations and chemical activities of PAHs in sediment cores of the western Baltic Sea. Chemosphere 74: 522-529.

Witt, G., Lang, S.C., Ullmann, D., Schaffrath, G., Schmidt, K., Schulz-Bull, D., Mayer, P. (2013). A passive sampler for in situ measurements of freely dissolved concentrations of hydrophobic organic chemicals in sediments. Environmental Science & Technology 47, 7830−7839.

Linking polymer based concentrations to lipid based concentrations

Jahnke, A., McLachlan, M.S., Mayer, P. (2008). Equilibrium sampling: partitioning of organochlorine compounds from lipids into polydimethylsiloxane. Chemosphere 73 (10), 1575-1581.

Jahnke, A., Mayer, P., Adolfsson-Erici, M., McLachlan, M.S. (2011). Equilibrium sampling of environmental pollutants in fish: comparison with lipid-normalized concentrations and homogenization effects on chemical activity. Environmental Toxicology and Chemistry 30 (7), 1515-1521.

Mäenpää, K., Leppänen, M.T., Reichenberg, F., Figueiredo, K., Mayer, P. (2011). Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment: comparison of two approaches to determine equilibrium partitioning concentrations in lipids. Environmental Science & Technology 45, 1041-1047.

Passive dosing of hydrophobic organic chemicals and their mixtures (toxicity studies)

Engraff, M., Solere, C., Smith, K.E.C., Mayer, P., Dahllöf, I. (2011). Aquatic toxicity of PAHs and PAH mixtures at saturation to benthic amphipods: lining toxic effects to chemical activity. Aquatic Toxicology 102 (3-4), 142-149.

Rojo-Nieto, E., Smith, K.E.C., Perales-Vargas-Machuca, J.A., Mayer, P. (2012). Recreating the seawater mixture composition of HOCs in toxicity tests with Artemia franciscana by passive dosing. Aquatic Toxicology 120-121, 27-34.

Smith, K.E.C., Dom, N., Blust, R., Mayer, P. (2010). Controlling and maintaining exposure of hydrophobic organic compounds in aquatic toxicity tests by passive dosing. Aquatic Toxicology 98 (1), 15-24.

Smith, K.E.C., Schmidt, S.N., Dom, N., Blust, R., Holmstrup, M., Mayer, P. (2013). Baseline toxic mixtures of non-toxic chemicals: "solubility addition" increases exposure for solid hydrophobic chemicals. Environmental Science & Technology 47: 2026-2033.

Analytical passive dosing (determining free fractions)

Birch, H., Mayer, P., Lützhøft, H.-C.H., Mikkelsen, P.S. (2012). Partitioning of fluoranthene between free and bound forms in stormwater runoff and other urban discharges using passive dosing. Water Research 46 (18), 6002-6012.

Birch, H., Gouljarmou, V., Lützhøft, H.-C.H., Mikkelsen, P.S., Mayer, P. (2010). Passive dosing to determine the speciation of hydrophobic organic chemicals in aqueous samples. Analytical Chemistry 82 (3), 1142-1146.

Gouljarmou, V., Smith, K.E.C., de Jonge, L.W., Mayer, P. (2011). Measuring binding and speciation of hydrophobic organic chemicals at controlled freely dissolved concentrations and without phase separation. Analytical Chemistry 84 (3), 1601-1608.

Annex 8: MCWG's comments to MSFD expert network on contaminants

Descriptor 8

OSPAR published an MSFD Advice document in 2012 on *Good Environmental Status - Descriptor 8: Contaminants - Approaches to determining good environmental status, setting of environmental targets and selecting indicators for Marine Strategy*, which has been submitted to the European Commission for discussion at the MSFD workshop on Eutrophication and Contaminants held at JRC Ispra on 23/24 October 2012. MCWG supports the approaches described in this document but would like to make some additional suggestions in view of the provisions made in Directive 2013/39/EU of the parliament and of the council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

Seven out of eleven EQS_{biota} laid down in Directive 2013/39/EU have been set to protect humans from adverse health effects via consumption of fishery products and therefore, they are not relevant for contaminant monitoring under descriptor 8.

However, some of these substances for which $EQS_{biota\ hh}$ have been set are indicators in OSPAR and HELCOM, such as PBDEs and PFOS, and are monitored within the CEMP and COMBINE monitoring programmes. Therefore, they should be considered in marine monitoring under D8 as well. So far, neither background assessment concentrations (BACs) nor environmental assessment concentrations (EACs) are available, which would allow the assessment of the measured concentrations of PFOS and PBDE in fish. Hence, MCWG suggests applying $EQS_{biota\ sec\ pois}$ derived under the WFD for compliance checking. These EQSs have not been set out in Directives 2008/105/EC and 2013/39/EU, but are available from EQS dossiers published in 2011.

Member States may apply an EQS for an alternative taxon or matrix once the same level of protection is offered. Monitoring of bivalve molluscs is widespread and offers some advantages as a monitoring matrix. MCWG is willing to provide advice on conversions of EQS_{biota} set for fish to mussels, noting the different trophic levels. This would aid member states in using mussels in their WFD/MFSD monitoring and would avoid member states taking independent approaches to this.

Descriptor 9

Substances for which maximum levels are established for products destined for human consumption should be monitored under descriptor 9. According to COMMISSION REGULATION (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs and subsequent amendments of this regulation, the minimum set of compounds in edible portions of unprocessed fisheries products comprises:

- Sum of dioxins (WHO-PCDD/F-TEQ)
- Sum of dioxins and dioxin-like PCBS (WHO-PCDD/F-PCB-TEQ)
- Sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180 (ICES – 6)
- Lead
- Cadmium
- Mercury
- Benzo(a)pyrene and sum of benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, chrysene (4 indicator PAHs) (in bivalve molluscs only)

MCWG would like to stress that different approaches are required for environmental monitoring (D8) and food safety control (D9). The latter is typically carried out as part of food safety control programs under the auspices of consumer protection/health authorities. Samples for this purpose are typically collected from a variety of points along the processing chain: collection at sea, at fishery landing points or at retail level. Often, the further away the sampling occurs from the initial point of capture of the fish, the lower the degree of certainty is as to the geographical origin of the sample. Hence, an important issue is to ensure and where necessary to improve traceability of geographical origin of the fish used in D9 monitoring.

Annex 9: MCWG's recommendation to OSPAR regarding the determination of chlorophyll

Requirement for harmonisation of analytical techniques used for estimating chlorophyll concentrations in marine waters

Chlorophyll measurements are made to estimate the phytoplankton biomass in the marine environment and are probably the most frequently measured biochemical parameter in oceanography. Chlorophyll *a* is the primary pigment of interest in monitoring programmes, but several pigments and degradation products may be found at any one time in a given sample. Due to spectral overlap between chlorophylls, carotenoids and degradation products, under- or overestimation of chlorophyll *a* can occur.

It is widely reported that the equations used for calculating chlorophyll *a* and phaeophytin *a* from fluorometric measurements are accurate when these are the only two components present in the sample, which is not the case in algae samples collected from the marine environment (Gibbs, 1997; Trees *et al.*, 1985; Arar and Collins, 1997; Smith *et al.*, 2007). It is evident that complex mixtures of pigments, such as those found in the marine environment cannot be assayed accurately using simple photometric or fluorometric methods for chlorophyll *a*. Separation techniques have been developed to allow for a more accurate assessment of chlorophyll compounds, with HPLC methods of increasing complexity being used (Jeffrey *et al.*, 1997).

The current JAMP Eutrophication monitoring guidelines for chlorophyll in water also highlight this issue, stating that "because the standard photometric and fluorometric methods used for determining chlorophyll *a* do not completely separate the different chlorophylls or distinguish between chlorophyll *a* and chlorophyllide *a* the term "total chlorophyll *a*" should therefore be used when reporting results from these methods. For chlorophyll data, analysed by HPLC, which considered the other chlorophyll derivates as well the term "chlorophyll *a*" should be used"(OSPAR, 2012).

QUASIMEME reported to MCWG 2014 that unlike other PT determinands there has been no overall improvement in participant performance for chlorophyll (Figure 1). This has prompted an internal investigation, by QUASIMEME, into methods used by participants to report chlorophyll *a*. There was a clear distinction between participants reporting chlorophyll *a* by either fluorometric or photometric methods with those using HPLC. QUASIMEME now operates with two different assigned values based on photometric and HPLC methods.

The use of different analytical techniques in determining chlorophylls has implications for reporting data under WFD and MSFD. To meet statutory obligations contracting parties are increasingly relying on the use of remote sensing devices such as satellites for inclusion in data sets for their assessments. These devices are calibrated using discrete samples analysed by various techniques. It is important that a consistent analytical approach is taken to calibrate such devices to ensure comparability and correct assessment of GES which does not distinguish between "chlorophyll *a*" and "total chlorophyll *a*".

MCWG recommends that OSPAR is aware of potential differences in results derived from fluorometric/photometric or HPLC methods, which may have implications for WFD monitoring.

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Gibbs, C. F. (1979). Chlorophyll *b* interference in the fluorometric determination of chlorophyll *a* and phaeopigments. *Australian Journal of Marine and Freshwater Research*, **30**, 597 - 606.

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Trees, C. C., Kennicut, M. C. and Brooks, J. M. (1985). Errors associated with the standard fluorometric determination of chlorophylls and phaeopigments. *Marine Chemistry*, **17**, 1 - 12.

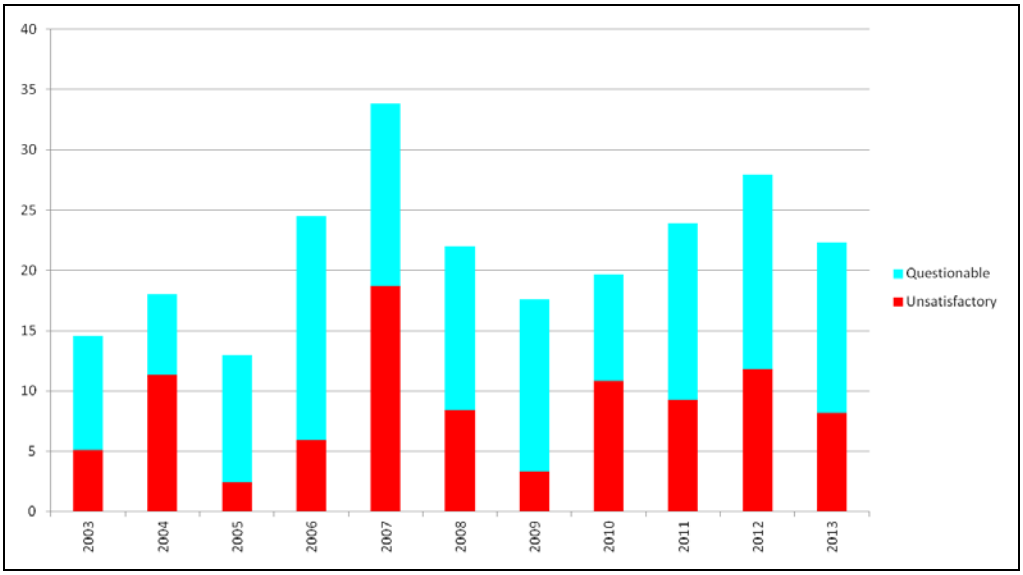

Figure 1: QUASIMEME chlorophyll proficiency test performance

Annex 10: Draft revised technical annex 2 to OSPAR JAMP Guidelines for monitoring contaminants in biota – metals

This annex is intended as a supplement to the general guidelines. It is not a complete description or a substitute for detailed analytical instructions.

1. Species

1.1 Fish and shellfish

1.1.1 Criteria for the selection of species for temporal trend monitoring

Species for temporal trend monitoring can only be selected in the light of information on fish stock composition and history. It is essential that long time series with one species are obtained. Care should be taken that the sample is representative of the population and can be repeated annually. Fish and shellfish species currently used for trend monitoring are listed in Tables 1 and 2 of the main guidelines.

1.1.2 Criteria for the selection of species for spatial distribution monitoring

To standardise results the first choice species *Limanda limanda, Gadus morhua* and *Mytilus edulis* or *Mytilus galloprovincialis* should be used if possible. The second choice species *Merlangius merlangus, Merluccius merluccius, Platichthys flesus* and *Crassostrea gigas* should be used when none of the first choice species are available.

First choice species

Limanda limanda (dab)

Dab is a ground dwelling species confined to the shelf seas. It has replaced the previously recommended plaice and flounder for the following reasons:

a. its migration is less pronounced, thus it is more likely to represent the area in which it is caught;

b. it has been used successfully in disease studies, thus complementary information from such studies would be available (in fish disease studies a length range for individual fish of 20-25 cm is used).

The southern distribution limit of dab is the north coast of Spain.

Gadus morhua (cod)

Cod normally live near the seabed but may also be pelagic. Cod occur in coastal areas and to 600 m depth. Cod may also be found in the open ocean and so may also be used for monitoring oceanic regions. The southern distribution limit of cod is at 45°N. A sampling size range of 30-45 cm is specified because cod of that size and age tend to feed on a fairly uniform diet.

Mytilus sp. (mussel)

Mytilus edulis occurs in shallow waters along almost all coasts of the Contracting Parties. It is therefore suitable for monitoring in nearshore waters (Bellas *et al.*, 2014; Green *et al.*, 2012; IFREMER, 2006). No distinction is made between *M. edulis* and *M. galloprovincialis* because the latter, which may occur along Spanish and Portuguese

coasts, cannot easily be discerned from *M. edulis*. A sampling size range of 3-6 cm is specified to ensure availability throughout the whole maritime area .For monitoring in polluted areas, mussels may be transplanted from an unpolluted area and then left in the polluted area (Benedicto *et al.*, 2011; Søndergaard *et al.*, 2011) for e.g. one year before sampling and analyses. The results will reflect the last years contamination in contrast to resident mussels that will reflect several years of contamination.

Second choice species

Platichthys flesus (flounder)

The distribution of flounder extends further south than that of dab and might therefore represent the flatfish of choice for certain Portuguese coastal areas and Spain's northwestern coastal areas. Flounder is not suitable for monitoring in open sea areas due to its migration pattern. A sampling size range of 15-35 cm ensures individuals of the 2-year age class.

Merlangius merlangus (whiting)

Whiting can be caught in coastal waters and to 200 m depth. Its distribution is from Portugal to Iceland and Norway, thus covering all the maritime area subject to monitoring by Contracting Parties. It is a suitable substitute for cod. The sampling size range, 20-35 cm, may need adjustment in the light of future experience.

Merluccius merluccius (hake)

Hake live at 100-300 m along the shelf margins. The sampling size range is 20-35 cm. The sampling size interval suggested is arbitrary and may need adjustment in the light of future experience.

Crassostrea gigas (Pacific oyster)

The Pacific oyster should be sampled in areas where *Mytilus sp.* is not available. The sampling size should be within the length range 9-14 cm to ensure individuals of the 2 year age class.

1.2 Seabirds

Relevant references concerning the use of seabirds in contaminant monitoring programmes include Gilbertson (1987), Becker (1989; 1991); Becker *et al.* (1991; 1992), Walker (1992), Herzke *et al.* (2009), Miljeteig *et al.* (2009) and Dittmann *et al.* (2012).

Sterna hirundo (common tern)

The common tern is widely distributed over the European and North American Atlantic coasts as well as the Baltic Sea, but does not occur in Iceland. It feeds in marine, brackish, and fresh waters.

Haematopus ostralegus (oystercatcher)

The oystercatcher is widely distributed along the coasts of the North-West Atlantic, including Iceland, and also occurs in the Baltic Sea. The species is not strictly marine as it also feeds inland. It feeds on benthos. In contrast to other seabirds, nest sites are accessible and the eggs within reach.

Uria aalge (guillemot)

The guillemot feeds in the open sea and nests on the coasts of northern Europe, in the Baltic Sea and on the North American coast.

2. Sampling

Two alternative sampling strategies are described: sampling to minimise natural variability and length-stratified sampling.

2.1 Sampling to minimise natural variability

Gain in precision of the contaminant data can be obtained by minimising variance from the biological covariables (Viñas *et al*., 2012). For fish, this can be achieved by sampling and analysing individually at least 12 young fish of the same sex, e.g. 2-3 year old female fish. To assist the selection of the relevant length range in order to find individuals of the recommended age, it is advised to produce specific species and region related correlation graphs by use of existing data from the respective monitoring data base. An example is given in Appendix 1.

For shellfish, a sample should be collected with the number of individuals large enough to be divided into at least 3 equal pools with each pool consisting of at least 20 animals and enough soft tissue for all analyses. The length of the individuals collected should be constant from year to year at each station, or should at least fall within a very narrow range, e.g. within 5 mm. To reflect recent levels of contamination, young individuals should be chosen. In selecting the sample, care should be taken to ensure that it is representative of the population and that it can be obtained annually.

2.2 Length-stratified sampling

Where successfully ongoing, length-stratified time series should be continued.

2.2.1 Fish

Gain in precision of the contaminant data can also be obtained from stratification using biological variables. Although several biological parameters are appropriate length appears to be the parameter which can most easily be applied onshore and at sea and which has also been shown to be significant in many analyses. Much discussion has been devoted as to whether simple linear or log-linear (multiplicative) models give the better fit. General experience with other fish and other types of data indicate a preference for the log-normal model at least for the present.

As the length dependence of the contaminant concentration is not well understood, sampling should keep the length/contaminant relationship under constant surveillance, i.e. the entire length range should be covered evenly. Care should be taken that the samples are not unduly clustered within a particular length-interval. More length intervals could be used and the test of the hypothesised contaminant/length relationship becomes stronger if the lengths are evenly distributed. It is essential to keep the length stratification identical from one year to the next. The length range should be defined on the basis of practical considerations. For fish, the upper limit should be chosen in such a way that at least 5 fish in the largest length interval can easily be found. The length stratification should be determined in such a way that it can be maintained over many years. The length interval should be at least 2 cm in size. The length range should be split into 5 length intervals, which are of equal size after log

transformation. For example, if the length range is 18-36 cm, then the interval boundaries could be (rounded to 0.1 cm) as follows:

18-20.7 20.8-23.8 23.9-27.3 27.4-31.3 31.4-36 cm.

2.2.2 Shellfish

For shellfish, the upper limit should be chosen in such a way that at least 20 mussels in the largest length interval can easily be found. The length stratification should be determined in such a way that it can be maintained over many years. The length interval should be at least 5 mm in size. The length range should be split into at least 3 length intervals (small, medium and large) which are of equal size after log transformation. For example, if the length range is 40-70 mm, then the interval boundaries could be (rounded to 1 mm) as follows:

a. 5 intervals: 40-45 46-50 51-56 57-63 64-70

b. 3 intervals: 40-48 49-58 59-70

2.3 Seabird eggs

2.3.1 Permission

Permission to collect the eggs must be received from the appropriate national authorities.

2.3.2 Sampling period and frequency

Eggs should be sampled annually at each site in May or June. Only clutches from the first laying cycle within a single year should be selected.

2.3.3 Number of eggs and sampling procedure

Eggs should only be taken from full clutches (i.e. common tern 3 eggs, oystercatcher 3-4 eggs). Eggs should not be taken from abandoned clutches. Only one egg should be taken from each clutch. Ten eggs should be selected in total (i.e. one egg from 10 separate clutches) and it is important to choose the egg from each clutch randomly. As the eggs must be fresh (i.e. between 1-5 days incubation) information about the incubation stage of each egg is required. Two methods are recommended for determining incubation stage:

a. locate 12-15 clutches containing one egg only and mark these by placing a peg about 1 m from the nest. Check the clutches every other day until they are complete. Take one egg randomly from the completed clutch;

b. fill a 1 litre plastic beaker with water and place the egg in the water:

   i. fresh eggs (*i.e.* of 1-2 days incubation) will lie on the bottom with the long axis parallel to the bottom;

   ii. eggs of 3-6 days incubation will rest with the small end on the bottom of the beaker and the long axis forming an angle of 30-45°;

   iii. eggs which float or stand vertically with the small end on the bottom are of more than 7 days incubation and should not be selected.

Each nest from which an egg has been taken should be marked, using a peg or some other type of marker, to ensure that a second egg is not taken. While still in the field the egg selected should be put into a numbered plastic egg box. The number of the box should be written on the shell of the egg in soft pencil. The clutch size from which the egg was taken, the nest number and the sampling date should be recorded.

2.3.4 Materials

For each species, area and year the following are required:

- nest pegs;
- a non-toxic, waterproof marker;
- a 1 litre plastic beaker;
- numbered egg boxes (e.g. for oystercatcher: 100 ml, polypropylene polyethylene, ø 55*73 mm, and for common tern: 50 ml, polystyrol/polyethylene, ø 41*49 mm).

3. Transportation

3.1 Fish and shellfish

Samples should be kept cool and frozen at below -20°C as soon as possible after collection. Length and weight should be determined before freezing. Live mussels should be transported in closed containers at temperatures between 5-15°C, preferably <10°C. Frozen samples should be transported in closed containers at temperatures below -20°C. More rigorous conditions will be necessary for samples for biological effects monitoring, e.g. storage in liquid nitrogen.

3.2 Seabird eggs

Eggs should be kept cool and frozen at -18°C as soon as possible after collection.

4. Pre-treatment and storage

4.1 Contamination

Sample contamination may occur during sampling, sample handling, pre-treatment and analysis (Oehlenschläger, 1994a), from the environment, the containers or packing material used, the instruments used during sample preparation or from the chemical reagents used during the analytical procedures. Controlled conditions are therefore required for all procedures, including the dissection of fish organs on board ship Relevant references concerning clean laboratories include Moody (1982), Mitchell (1982a), Boutron (1990) and Schmidt and Gerwinski (1994).

4.2 Fish

4.2.1 Dissection, storage and drying

Ungutted fish should be wrapped separately in suitable material (e.g. polyethylene or polytetrafluorethylene) and frozen. The frozen samples should be stored in suitable containers to avoid damage. Sub-samples (e.g. of liver) should be stored in a suitable acid-cleaned container and frozen or freeze-dried immediately. During freeze-drying, sample temperature should be maintained below 0°C to avoid the loss of volatile compounds. The individual samples should be clearly labelled and stored together in a suitable container. The frozen samples should be maintained at below -20°C until

analysis. Freeze-dried samples should be stored in a dessicator. Sub-samples for enzyme tests should be stored in vials suitable for storage in liquid nitrogen, labelled clearly and stored in liquid nitrogen until analysis.

The dissection must always be done by trained personnel on a clean bench, wearing clean gloves and using clean stainless steel knives which may be equipped with blades made of ceramics or titanium to reduce the risk of Cr and Ni contamination. Colourless polyethylene tweezers are recommended for holding tissues during dissection. After each sample has been prepared, the tools should be cleaned regularly. The following procedure is recommended:

- wash in acetone or alcohol and high purity water;
- wash in HNO_3 p.a./high purity water diluted 1+1 (for tweezers diluted 1+6);
- rinse with high purity water.

4.2.2 Sub-sampling

To sample fish muscle, care should be taken to avoid including any epidermis or subcutaneous fatty tissue in the sample. Samples should be taken underneath the red muscle layer. In order to ensure uniformity the right side dorso-lateral muscle should be sampled. If possible, the entire right dorsal filet should be homogenised or freeze-dried and sub-samples taken for replicate dry weight and contaminant determinations. If however the amount of material to be homogenised would be too large, a specific portion of the dorsal musculature should be chosen. It is recommended that the portion of the muscle lying directly under the first dorsal fin be used in this case. As both fat and water content vary significantly in the muscle tissue from the anterior to the caudal muscle of the fish, in order to ensure comparability it is important to obtain the same portion of the muscle tissue for each sample (see Oehlenschläger, 1994b).

When dissecting the liver, care should be taken to avoid contamination from other organs (Viñas *et al.*, 2012). The whole liver should be homogenised or freeze-dried. If however the amount of material homogenised would be too large, a specific portion of the liver should be chosen. In order to ensure comparability, this should always be the same part of the liver, preferably the middle part. Liver samples can be freeze-dried. However, for very fatty samples, freeze-drying can be difficult. In this case, the lipids can be extracted prior to freeze-drying. It has to be ensured that no metals are extracted together with the lipids.

Where pooling of tissues is necessary, an equivalent quantity of tissue must be taken from each fish, e.g. a whole fillet from every fish. If the total quantity of tissue so yielded would be too large to be handled conveniently, the tissue may be sub-sampled, but a fixed proportion of each tissue must then be taken, e.g. 10% of each whole fillet or 10% of each whole liver or for muscle tissue 10% of the fish.

Personnel must be capable of identifying and removing the desired organs according to the requirements of the investigations.

4.3 Shellfish

4.3.1 Depuration

Mussels should be placed on a polyethylene tray elevated above the bottom of a glass aquarium. The aquarium should be filled with sub-surface sea water collected from

the same site as the samples and which has not been subject to contamination from point sources. The aquarium should be aerated and the mussels left for 20-24 hours at water temperatures and salinity close to those from which the samples were removed.

4.3.2 Opening of the shells

Mussels should be shucked live and opened with minimum tissue damage by detaching the adductor muscles from the interior of one valve. The mussels should be inverted and allowed to drain on a clean towel or funnel for at least 5 minutes in order to minimise influence on dry weight determinations.

4.3.3 Dissection and storage

The soft tissues should be removed and deep frozen (-20°C) as soon as possible in containers appropriate to the intended analysis. The dissection must always be done by trained personnel on a clean bench wearing clean gloves and using clean stainless steel knives which may be equipped with blades made of ceramics or titanium to reduce the risk of Cr and Ni contamination. Colourless polyethylene tweezers are recommended for holding tissues during dissection. After each sample has been prepared, the tools should be cleaned regularly. The following procedure is recommended:

- wash in acetone or alcohol and high purity water;
- wash in HNO_3 p.a./high purity water 1+1 (for tweezers 1+6). This does not apply to parts of metal e.g. stainless steel knives.
- rinse with high purity water.

4.4 Seabird eggs

Before thawing, each egg should be placed in a previously weighed goblet. The weight of the egg (to the nearest 0.1 g including the shell), the length of the egg between poles and the breadth of the egg at the equator (to the nearest 0.1 mm using callipers) should be recorded. The egg should then be opened (if this has not already happened during thawing) and the content carefully separated from the shell. If the egg contains an embryo, the eye diameter or the "crown-tail" length of the embryo should be measured (to the nearest 0.1 mm using callipers). The content of the egg (*i.e.* the albumen and yolk) should be weighed (to the nearest 0.1 g) and homogenised in the same goblet for each egg (e.g. by an Ultra Turrax). The samples can then be analysed or deep frozen for later analysis. The shell (including the shell-skin) should be washed with water and dried in laboratory air for at least a week before weighing (to the nearest 0.01 g). The shell thickness should be measured at three points along the egg equator.

5. Analysis

5.1 Preparation of equipment and reagents

Glassware and Teflon equipment should be washed extensively with diluted nitric acid, distilled water and acidified metal-free deionised water, and should be rinsed immediately before use with the acids or solvents used according to the following procedure. The blank from all plastic and glassware after the purification procedure should be controlled. Acids, solvents, chemicals and adsorption materials should be free of trace metals or organometallic compounds. If not they should be purified by

appropriate methods. Acids should be checked by measuring blanks using the analytical procedure applied to the samples. If necessary, the acids should be purified by distillation, preferably under sub-boiling point conditions in a quartz distillation apparatus. If appropriate, chemicals and adsorption materials should be purified by exhaustive extraction with the solvents used for extraction of the metal compounds. Care should be taken to avoid contamination from laboratory air dust particles. Relevant references concerning reagents and materials include Moody *et al.* (1982; 1989); Tschöpel *et al.* (1980), Kosta (1982), Mitchell (1982b), Paulsen *et al.* (1989) and Luque de Castro and Luque García (2002).

5.2 Dry weight determination

Dry weight determinations should be carried out by air-drying homogenised subsamples of the material to be analysed to constant weight at 105°C. Freeze-drying could also be used for the dry weight determination.

5.3 Determination of metals

5.3.1 Homogenisation and drying

When the analysis is undertaken, all fluids that may initially separate on thawing should be included with the materials homogenised. Wet or freeze-dried tissues should be homogenised. Homogenisation of wet tissues should be performed immediately prior to any subdividing of the sample. Fresh tissue should be thoroughly homogenised to include any moisture and lipids that may have separated from the solid parts of the sample. Aliquots should be taken as soon as possible, either for direct analysis or for drying. When grinding samples after drying, classical techniques using a ball mill made of different materials should be used. References concerning sample pre-treatment include Klussmann *et al.* (1985), Luque de Castro and Luque García (2002) and Larsen *et al.* (2011).

5.3.2 Digestion

The minimum requirements for the digestion procedure are the following:

- complete destruction of all organic material and mineralisation of the sample;
- avoidance of loss of the elements to be determined;
- avoidance of contamination;
- a sampling size of minimum 200 mg dry material

The following aspects should be considered as well:

- Digestion methods will be favoured with use only small amounts of ultra pure reagents and chemicals;
- The method should be safe to handle (e.g. avoiding hydroperchloric acid);
- Some methods analyse directly and dissolution is not necessary e.g. AMA-254 for mercury analyses.
- A microwave digestion closed system is preferred for biota samples.
- The use of automated procedures is preferred.

Trace element analysis in biological tissues normally involves digestion of the sample with acids. Very pure acids are essential to ensure acceptable blanks. If "matrix-effects" prevail after sample digestion, three strategies may be followed:

- standard addition for calibration;
- chemical separation procedures;
- matrix modifiers.

5.3.3 Instrumental determination

The appropriate instrumental equipment has to be chosen with regard to (i) the elements to be analysed (ii) the concentration levels to be detected (iii) the matrix and the sampling processing prior to the measurement (e.g. digestion, pre-cleaning), but for economic reasons also taken into account (iv) the typical throughput number of samples and (v) investigation and operational costs.

For marine biota samples, all relevant monitoring programmes include mercury, cadmium and lead as mandatory parameters. For analyzing Cd and Pb from open sea samples, e.g. flatfish liver of dab and plaice, Graphite Furnace Atomic Absorption Spectometry (GFAAS) and ICP-MS are appropriate. For higher concentrated metals such as Cu and Zn, Flame-AAS, ICP-AES or ICP-OES (weak for Pb) and Total Refection X-Ray Spectrometry (TXRF, weak for Cd) may also be used, but are not suitable to cover all obligating measurements in the required concentration range at very low concentrations without additional preconcentrating procedures.

For mercury cold vapour AAS-systems are commonly used, as stand-alone device or addition to AAS-systems. In recent years, direct measuring systems for analysing mercury from liquid and solid samples without any preceeding digestion have become available (e.g. AMA, PE SMS 100 and MLS DMA-80), which have been proven to produce accurate and reliable results. Also a GFAAS-system equipped with a solid sample (autosampler) device for direct measuring and a high-resolution continuum source has become available, which reduces the pretreatment of the samples and has only one source for all elements. Direct methods for analysing mercury using pyrolysis combined with a gold trap and fluorescence or atomic absorption detection are sensitive enough to measure biota sample directly (Carbonell *et al.*, 2009; Maggi *et al.*, 2009; Torres *et al.*, 2012). For the detection of hydride forming elements, such as arsenic, selenium or antimony, nearly all manufactorers of AAS offer additional hydride add-on devices.

6. Analytical quality assurance

The programme planners must decide on the accuracy, precision, repeatability, limit of detection and limit of determination required for each specific programme. Achievable limits of determination are as follows:

Cd	5 µg/kg wet weight
Hg	5 µg/kg wet weight
Pb	20 µg/kg wet weight
Cu	200 µg/kg wet weight

Relevant references concerning QA include HELCOM (1988), QUASIMEME (1992), Harms (1994) and ICES (1995).

6.1 Calibration and preparation of calibrands

For calibration purposes, single element standard stock solutions at a concentration of 1000 mg/l are commercially available or can be prepared from the highest quality

elements available (generally 99,999% purity) dissolved in high purity acid (usually 1 molar nitric acid). Single or mixed working element standard solutions for calibration purposes are prepared by taking aliquots of the standard stock solutions which are diluted using diluted acid as required. Both standard stock and working solutions are stored in polyethylene, borosilicate or silica volumetric flasks. Borosilicate flasks must not be cleaned with alkaline solutions or heated above 70°C.

Working standard solutions at concentrations less than 100 µg/l should be prepared immediately before use, which is particularly important for mercury. The actual concentration of the element should be stated on the label together with the date of the preparation of all standard solutions. The calibration procedure must meet some basic criteria or assumptions in order to give a best estimate of the true (but unknown) element content of the sample analysed. These are as follows:

- the masses or concentrations of standards for the establishment of the calibration function must be prepared without bias;
- the chemical and physical properties of the calibration standards must closely resemble those of the sample under investigation;
- sample and calibration standard should be subject to the same operational steps of the analytical procedure;
- signals of repeatedly analysed calibration standards must be randomly distributed on either side of the calibration line.

Application of chemical separation procedures: Although relatively simple standards with a minimum of matrix matching are required, separation procedures that consist of several stages are prone to systematic errors due to both uncontrollable contamination and analyte losses, respectively.

6.2 Blanks

A procedural blank should be measured for each sample series and should be prepared simultaneously using the same chemicals and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will lead to errors in quantification. Detailed information how to reduce and control contamination is given by ICES (1995).

6.3 Accuracy and precision

A Laboratory Reference Material (LRM), preferably a Certified Reference Material (CRM), should be included in the analyses, at least one LRM/CRM sample for each series of identically prepared samples.

The LRM must be homogeneous, well characterised for the determinands in question and stability tests must have shown that it produces consistent results over time. The LRM should be of the same type of matrix (e.g. liver, muscle tissue, fat or lean fish) as the samples, and the determinand concentrations should occur in a comparable range to those of the samples. If the range of determinand concentrations in the sample is large (> factor of 5) at least two LRMs should be included in each batch of analyses to cover the lower and upper concentrations. It is good practice to run duplicate analyses of a LRM to check within-batch analytical variability. The use of a freeze-dried LRM is a practicable alternative to a homogenised and frozen LRM. However, the efficiency of the preceding steps such as homogenisation and drying cannot be checked. A quality control chart should be recorded for each metal. When introducing a new LRM or when it is suspected from the control chart, that there is a system-

atic error possibly due to an alteration of the LRM, another LRM (preferably a CRM) with a matrix as close as possible to the material analysed, should be used to check the reference material. Table 1 contains information on CRMs commercially available for use in marine monitoring.

Table 1. Certified Reference Materials for metals in marine organisms.

Code	Organization	Matrix
ERM-CE278k	IRMM[1]	Mussel tissue
ERM-BB422	IRMM	Fish muscle
BCR-463	IRMM	Tuna fish
DOLT-4	NRC[2]	Dogfish liver
DORM-4	NRC	Fish
LUTS-1	NRC	Non defatted lobster hepatopancreas
TORT-3	NRC	Lobster hepatopancreas
SRM 2976	NIST[3]	Mussel tissue
SRM 1946	NIST	Lake fish tissue

[1]**IRMM: Institute for Reference Materials and Measurements (Europe)**

[2]**NRC: National Research Council (Canada)**

[3]**NIST: The National Institute of Standards and Technology (USA)**

Additionally a duplicate of at least one sample should be run with every batch of samples. Each laboratory should participate in interlaboratory comparison studies and proficiency testing schemes on a regular basis, preferably at an international level.

6.4 Data collection and transfer

Data collection, handling and transfer must take place using quality controlled procedures.

7. Data recording and reporting parameters

Data reporting should be in accordance with the requirements of the respective monitoring programmes and with the latest ICES reporting formats. Results should be reported according to the precision required for the programme. In practice, the number of significant figures is defined by the performance of the procedure.

The following parameters should be recorded although they may serve different purposes, e.g. internal sampling protocols, and QA or requirements of the data base of the assessing body:

7.1 Sampling and biological parameters

Fish

- location of catch (name, latitude, longitude);
- date of collection and time (start and end time of trawling operations, GMT);
- mean trawling depth;
- type of gear;
- irregularities and unusual conditions;
- name and institution of sampling personnel;
- for each individual:
  - the species, its length, total weight, sex, age, reproductive status (GSI);
  - sample type (e.g. muscle, liver);
  - total tissue weight of the dissected organ;
- the number of individuals and data specified for pooled samples.

Shellfish

- location of sampling site (name, latitude and longitude);
- date and time of sampling (GMT);
- sampling depth with respect to low tide (for sub-tidal sites only);
- irregularities and unusual conditions;
- name and institution of sampling personnel;
- number of pooled samples;
- number of individuals in pool;
- mean, minimum and maximum length and standard deviation;
- mean dry shell weight;
- mean soft tissue weight (wet weight);
- condition index.

Seabird eggs

- location of sampling site (name, latitude, longitude);
- species;
- estimated number of pairs of the species breeding in the sampling area;
- date of collection;
- estimated or known laying date;
- size of clutch from which the egg was taken;
- number of eggs in the sample from the site;
- irregularities and unusual conditions;
- name and institution of sampling personnel;
- for each egg:
  - weight (to the nearest 0.1 g);
  - length and breadth (between poles and the equator to the nearest 0.1 mm);
  - content weight exclusive of shell (to the nearest 0.1 g);
  - shell thickness (to the nearest 5 μm) taking the mean of triplicate measurements with a micrometer;
  - shell weight (to the nearest 0.01 g);
  - embryo length (to the nearest 0.1 mm) or eye diameter of the embryo (to the nearest 0.1 mm).

7.2 Analytical and quality assurance parameters

- LRM and CRM results for the metals listed in section 7.3 reported.;
- mean soft tissue dry weight and method of determining water content if this differs from air drying to constant weight at 105°C;
- descriptions of the digestion and instrumental determination methods used;
- the determination limit for each element. The limits should not exceed the values in section 6;
- measurement uncertainty
- the relevant QA information according to the requirements specified in the programme;
- the mean tissue lipid weight and method of extraction could also provide valuable information.

7.3 Parameters

- Elements of interest for monitoring programmes for which these guidelines apply:
  1) cadmium (total);
  2) mercury (total);
  3) lead (total);
  4) zinc;
  5) -copper.

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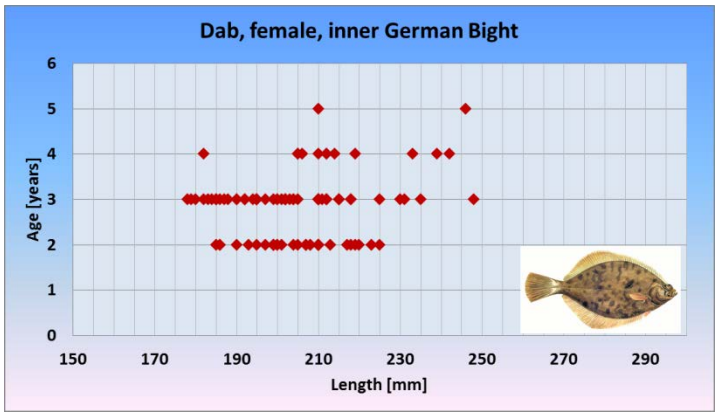
Appendix

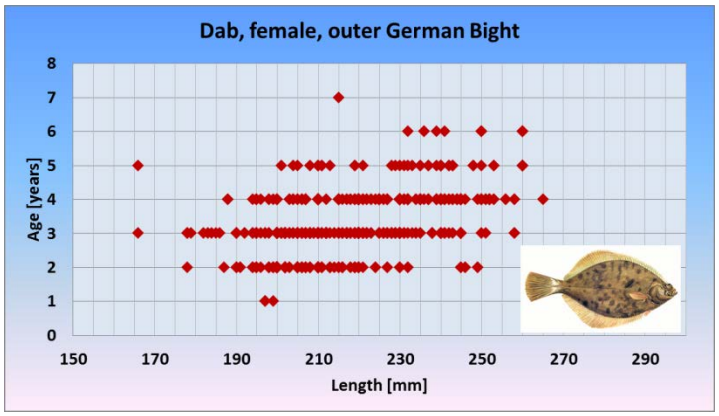
Examples of length-age relations of fish for different species and regions.

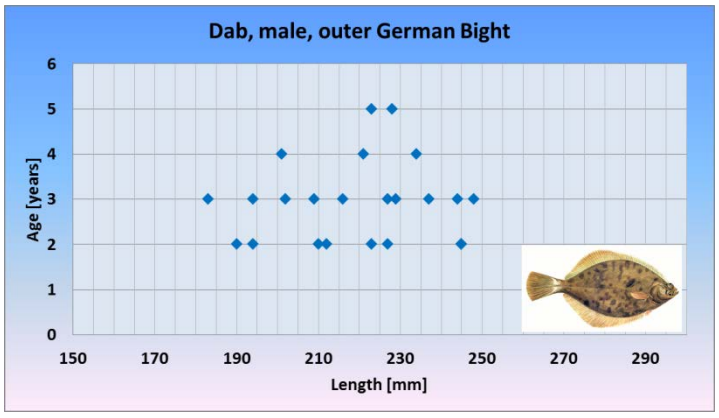
These relationships can be used to select individuals of the recommended age by using the length measurement when sampling onboard ship.

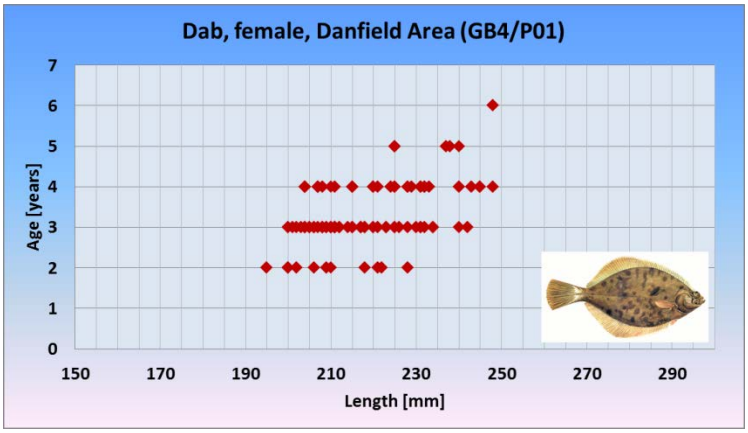
The laboratories of the contracting parties performing metal analysis in biota should use their databases to produce comparable information for their specific species and regions.

Dab, Southern North Sea

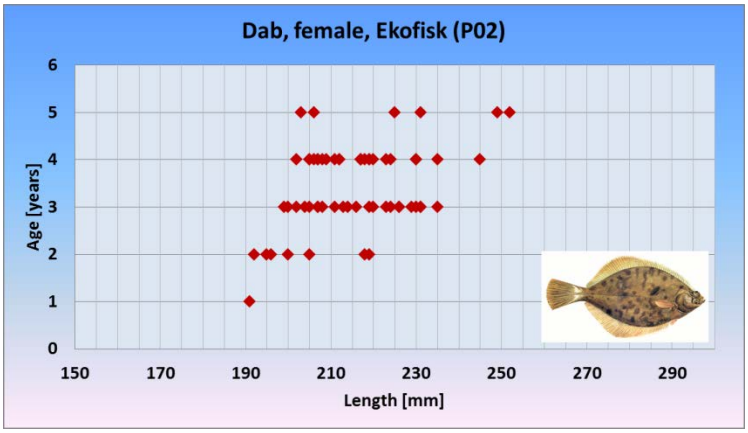




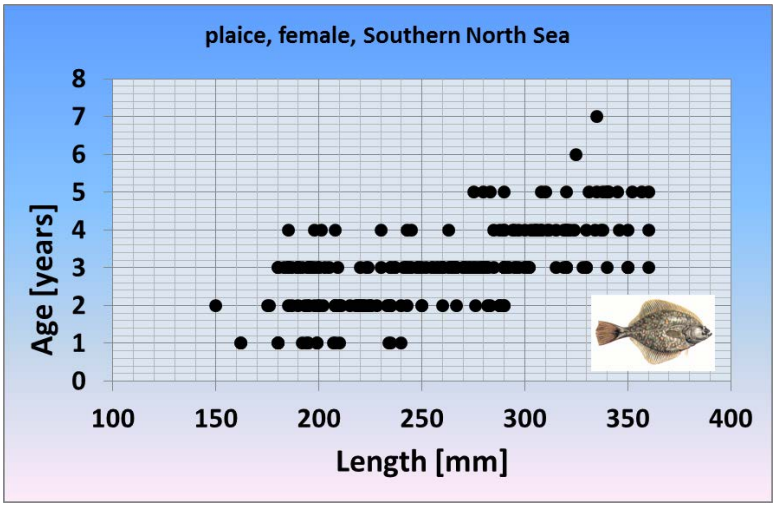


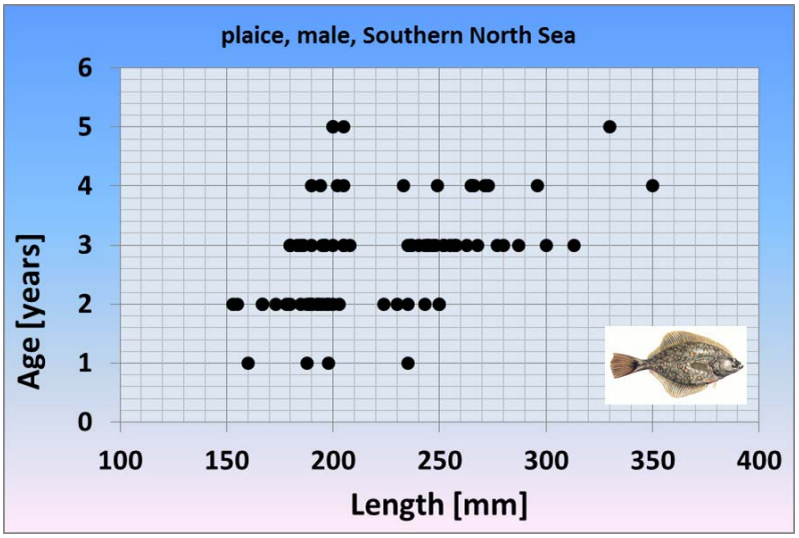


Dab, Central North Sea



Plaice, Southern North Sea, outer German Bight




plaice, male, Southern North Sea
Age [years]
0
1
2
3
4
5
6
100
150
200
250
300
350
400
Length [mm]

Annex 11: Draft revised technical annex 4 to OSPAR JAMP Guidelines for monitoring contaminants in sediments – organotins

This annex is intended as a supplement to the general guidelines. It is not a complete description or a substitute for detailed analytical instructions. The annex provides guidelines for the measurement of organtins in marine sediment in monitoring programmes. Organotins can origin from several sources. In addition to the previous use of antifouling agents on ship hulls, organotins can also be emitted to the environment from their use as fungicides or stabiliserrs for plastic materials (Fent, 2006; Fent and Muller, 1991; Hoch, 2001).

Target compounds include tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) and also triphenyltin (TPhT), diphenyltin (DPhT), and monophenyltin (MPhT). The method can be optimized to analyse other target organotins such as octyltins.

In order to assess the analytical results of organotin compounds in sediments, covariables must be measured as potential normalisers (e.g. grain-size distribution, organic carbon content, carbonate content). For samples 'diluted' with sand, the sample intake size can be increased. For very sandy samples, isolation of the fine fraction by sieving might be required.

1. Sampling and storage

Storage of samples is preferably done in glass, but containers of other materials such as polycarbonate or aluminium are also suitable. Nevertheless, possible adsorption of and contamination by organotin compounds need to be checked. Since photochemical degradation during storage has been reported for the aqueous phase (Quevauviller and Donard, 1991), the samples should be protected from light. Samples should be frozen after collection. For longer-term storage, the samples should be placed in a freezer (below –20°C) with or without freeze-drying. Under these conditions, samples can be stored for over a year (Gomez-Ariza *et al.*, 1994).

2. Transportation

Samples should be kept cool and ideally frozen below -20°C as soon as possible after collection. Sediment should be transported in closed containers at temperatures between 5-15°C, preferably <10°C. Frozen samples should be transported in closed containers at temperatures below -20°C.

3. Blanks and contamination

The complete analytical procedure should be checked for blank values, i.e. all solvents, chemicals, and adsorptive materials should be checked for potential sources of contamination or interference. If a contamination has been localised, measures must be taken to avoid it (e.g., cleaning, different suppliers etc.).

Although butyltin compounds are not likely to occur in the laboratory environment or in solvents or most chemicals, commercial derivatisation reagents sometimes contain significant concentrations of various (butyl)tin species. This can be solved by purchasing from other suppliers or by preparing the reagent in the laboratory.

Glassware should be treated thoroughly with concentrated HCl or HNO_3 and rinsed with deionised water and acetone prior to use. Alternatively, the glassware can be

heated in an oven at 450°C or above after going through the standard glassware cleaning procedure.

4. Pre-treatment

Before taking a subsample for analysis, samples should be sufficiently homogenised. Especially samples from harbours can contain paint particulate matter irregularly distributed in the sample, thereby affecting the representativeness of the subsample. This can only be avoided when intensive mixing techniques (e.g. ballmill) are applied. Homogeneity can be checked by analysing several subsamples (e.g. five). Sediment samples from the marine environment are more homogeneous than those from harbour areas, as contamination in marine sediments usually derives from the water phase as mediated by tidal water movements. Less polluted samples are often more homogeneous than highly polluted samples. Because the size of the sample intake for analysis is inversely related to the pollution level, the intake will be small when the risk for heterogeneity is high. For this reason, multiple analyses might be appropriate for the higher concentration levels. The sample intake is usually around 1–5 g (dry weight), but some methods do not allow the use of more than 1 g (see also section 5.5).

Most extraction methods can deal with wet as well as dry samples. Analysis of wet samples saves laborious drying procedures, but dry samples are more easily homogenised and stored. In general, organotins can be analysed from the same sample collected to monitor other substances such as polychlorinated biphenyls (PCBs). Since mono-, di-, and tributyltin are ionic compounds and strongly sorbed to the sediment, it is unlikely that losses through evaporation during air-drying or freeze-drying will occur. Air-drying has been reported possible up to 50°C, but because other related compounds (i.e. phenyltins) decompose, freeze-drying is preferred (Gomez-Ariza *et al.*, 1994). Whichever drying procedure is used, the suitability with regard to cross-contamination and losses should always be tested (Quevauviller and Donard, 1991). If sieving is required, avoid contact with plastics. The use of stainless steel equipment is strongly recommended.

5. Analysis

5.1 Preparation of materials

Solvents, chemicals and adsorption materials must be free of organotin compounds or other interfering compounds (see also section 3). If they are not they should be purified using appropriate methods or replaced with clean materials. Solvents should be checked by concentrating the volume normally used in the procedure to 10% of the final volume and then analysing for the presence of organotin compounds and other interfering compounds by gas chromatography (GC). If necessary, the solvents can be purified by redistillation. Chemicals and adsorption materials should be purified by extraction and/or heating. Glass fibre materials (e.g. thimbles for Soxhlet extraction) should be pre-extracted. Alternatively, full glass thimbles with a G1 glass filter at the bottom can be used. Generally, paper filters should be avoided in filtration and substituted for by appropriate glass filters. As all super cleaned materials are prone to contamination (e.g. by the adsorption of organotin compounds and other compounds from laboratory air), materials ready for use should not be stored for long periods. All containers, glassware etc. which come into contact with the sample must be made of appropriate material and must have been thoroughly pre-cleaned.

5.2 Dry weight determination

Dry weight determinations should be carried out by air-drying homogenised sub-samples of the material to be analysed to constant weight at 105°C.

5.3. Calibration and preparation of calibrant solutions

5.3.1 Calibration

Multilevel calibration with at least five calibration points is preferred to adequately define the calibration curve. Standard preparation can be done in two ways depending on the methods of extraction/derivatisation used:

i) by using alkyltins salts then proceed to the derivatisation step as for samples (for hydridisation or ethylation followed by purge-and-trap analysis, there is no other appropriate way than using alkyltin salts);

ii) by using commercially readily available derivatised standards.

Standard solutions can be prepared in (m)ethanol or another solvent depending on the instrumental method used. Addition of an internal standard to all standard and samples solutions is recommended, e.g. tripropyltin chloride TPrTCl or ^{13}C labelled or deuterated TBT if using GC analysis with mass selective detection. When using tripropyltin chloride, which is an underivatised standard, the recovery efficiency of the whole procedure can be determined.

A new calibration solution should always be cross-checked to the old standard solution.

Calibrant solutions should be stored in a refrigerator in gas tight containers to avoid evaporation of solvent during storage. It is important to determine the expiry date of standard dilutions in order to avoid a concentration shift due to deterioration of analytes or evaporation of solvents.

5.3.3 Isotope Dilution–Mass Spectrometry

Isotope Dilution-Mass Spectrometry technique (IDMS), can be used as an alternative quantification method (Monperrus *et al.*, 2003; Centineo *et al.*, 2004).

5.4 Extraction

Organotin compounds are strongly bound to particulate matter. The binding forces to the sediment have a dualistic character. Whereas tributyltin is mainly bound by hydrophobic forces, mineral binding dominates for monobutyltin because of its high electrical charge (e.g. the binding characteristic of trace metals). To achieve complete extraction, the butyltin compounds have to be released from the sediment, i.e. the binding must be diminished and the solubility in the extraction solvent must be maximised.

Different approaches can be applied to extract organotins from sediments:

- Acidic digestion followed by *in situ* derivatisation with simultaneous extraction to an organic phase.
- Leaching under acidic conditions with simultaneous extraction of the compounds to an organic phase, as applied with different acids, solvents and complexing agents.

To maintain a logical order, '*in situ* derivatisation' will be discussed as a derivatisation technique (see below) and not as an extraction technique. Furthermore, the use of recovery internal standards (RIS) to check the procedural steps is discussed separately below.

5.4.1 Acidic digestion followed by *in situ* derivatisation

Digestion techniques by adding hydrochloric acid or acetic acid can be used to extract organotins, while stirring or shaking the sample. Another possibility is the use of ultrasonic treatment.

5.4.2 Leaching and subsequent extraction to an organic phase

When extracting organotin compounds with an organic phase immiscible with water (e.g. DCM, diethylether, hydrocarbons etc.), much higher acid concentrations (6 M HCl) can be applied without obstructing the derivatisation. High acid concentrations will leach most of the monobutyltin from the sediment, but the high electrical charge of the monobutyltin^{3+} ion will not allow complete extraction to an organic phase. Under these strongly acidic conditions, the addition of complexing agents, e.g. tropolone (2-hydroxy-2,4,6-cycloheptatrienone) or diethyldithiocarbamate (Zhang *et al.*, 1991; Quevauviller, 1996) is not expected to have much effect. Just like the sediment, the agent will be protonated and consequently lose (much of) its complexation ability. When applied, the effectiveness of complexing agents should be critically evaluated. Furthermore, large amounts of agents in the extract may affect the chromatography.

Quantitative extraction of all butyltin compounds to pentane is possible only under strongly acidic conditions when HBr (6 M) is used (Gomez-Ariza *et al.*, 1995). The presence of bromide ions is essential to promote the extraction to the organic phase (pentane) through the formation of neutral ion-pairs. For tributyltin, it was shown that the distribution coefficient between octanol and water increased from 10^2 to 10^6 after the addition of 1 M bromide (Weidenhaupt, 1995).

Gomez-Ariza *et al.* (1995) used a 'sediment:6 M HBr: pentane' ratio of 1:5:10 (g/v/v) for extraction. The leaching time was set to one hour, followed by an extraction of one hour. For completeness a second extraction with pentane is recommended. The pentane extract obtained can safely be concentrated, as the ionic butyltin compounds will not evaporate easily. This low risk for evaporation also allows transfer to other solvents if required for derivatisation or analysis. The residue can be subjected to chromatographic methods such as high performance liquid chromatography (HPLC) that directly analyses the butyltin compounds in their ionic form. For GC methods, the butyltin compounds are derivatised to their hydride or tetra-alkyl form.

5.5 Derivatisation

Derivatisation can either be performed after extraction or simultaneously with extraction.

Sodium Tetraethylborate ($NaBEt_4$): Derivatisation with this reagent has been developed to minimise the analysis time. The $NaBEt_4$ procedure allows a simultaneous extraction-derivatisation in a buffered medium (optimum pH 4-5). $NaBEt_4$ derivatisation produces more thermally stable derivatives. However, $NaBEt_4$ is extremely air sensitive, since it is considered as pyrophoric, care must be taken to keep its chemical integrity. Although solutions in water have been shown to be stable for about 1 month at 4°C, it is recommended to prepare them freshly for use.

Solutions of the reagent in an organic solvent (e.g.tetrahydrofuran, methanol or ethanol) seem to be more stable (Smedes *et al.*, 2000). After the addition of sodium tetraethylborate (e.g. 1 to 4 ml of 2 to 5 % solution in water or organic solvents), the mixture is shaken vigorously (Wilken *et al.*, 1994).

Although ethylation in the aqueous phase is very fast, the derivatisation is limited by the desorption kinetics. Multiple additions have been applied, but a continuous addition of the reagent using a peristaltic pump supported by effective mixing conditions is more appropriate. In this way, the reagent is always present and every butyltin molecule desorbed from the sediment is immediately derivatised and extracted, which also makes the desorption process continuous. However, this very intensive derivatisation may lead to the formation of boroxin, a six-angle ringed ethylborane. This compound is very reactive to the (bonded) phases used in gas chromatographic columns, affecting the column efficiency and mass spectrometric (MS) response. The boroxin is not removed by the normal phase column clean-up procedure usually applied, but can be degraded by the addition of an alkaline aqueous solution with a pH above 12. Ethylated organotin compounds will not be affected.

Since organic matter also reacts with the sodium tetraethylborate, the amount of sample that can be used is limited. As a rule of thumb, the sample intake should represent about 20–50 mg organic carbon which is, in practice, 1 g fine material (dry weight).

If simultaneous extraction and *in situ* derivatisation is used, 5 to 10 ml of organic solvent (hexane or pentane) has to be added before derivatisation. The extraction of the derivative itself is quantitative but to isolate the whole organic phase, a second extraction is necessary. Usually centrifugation is required to separate the phases.

Grignard reagent, sodium diethyldithiocarbamate (NaDDTC) and sodium borohydrate ($NaBH_4$) are alternative derivatisation agents which can be used on organic phase extracts from sediment leachates. These reagents are not widely used anymore. Methods are described in Waldock *et al.* (1989) and Morabito *et al.* (2000).

5.6 Clean-up

Whether a clean-up step must be applied depends on the sample type, separation (GC or LC), and detection method used. Furthermore, the nature of the extract determines whether a clean-up step is possible. In the literature, no clean-up procedures are reported for aqueous/methanol leachates. Clean-up is not necessary when the butyltin compounds are determined by purge and trap analysis, which acts as a superb clean-up. However, extraction methods using an organic solvent will co-extract many kinds of other compounds from the sample, such as sulphur and sulphur-containing compounds, oil, and many other natural and anthropogenic compounds.

In addition to co-extracted substances, the extract will contain by-products of the derivatisation. Using sodium tetraethylborate for derivatisation, compounds such as boroxin, diethylsulphide, and diethyltrisulphide can be formed in rather large quantities (section 5.5). If the basic wash has not yet been conducted, it should be added here as a clean-up step. The ethylsulphides usually do not disturb the instrumental analysis. Also, co-extracted substances usually do not visually disturb the chromatogram because most detection methods are very selective. Nevertheless, a large amount of matrix in the sample can affect the chromatography when the loading capacity of the column is exceeded, and can influence the detector response (e.g. MS). A decrease in the amount of matrix is always favourable for instrumental analysis and therefore a clean-up is recommended.

Generally, a simple SiO_2, Al_2O_3 or Florisil column clean-up is sufficient for sample clean-up. Alkylated tin compounds are as non-polar as PCBs and elute rapidly with hexane. Nevertheless, highly activated materials are not recommended, as the organotin compounds may degrade during elution. Using 2 g of SiO_2 deactivated with 1–5% water or Al_2O_3 with 5–10 % water in a glass column, organotin compounds usually elute in 5–10 ml hexane or pentane. Elution patterns should always be checked for each batch of column material.

5.7 Pre-concentration

Evaporation of solvents using a rotary evaporator should be performed under controlled temperature and pressure conditions, and the sample volume should be kept above 2 ml. Evaporation to total dryness should be avoided. To reduce the sample volume even more, e.g. to a final volume of 100 µl, solvents like pentane or hexane can be removed by concentration with a gentle stream of nitrogen. Only nitrogen of a controlled high quality should be used. Iso-octane is recommended as a keeper for the final solution to be injected into the GC.

5.8 Instrumental determination

Most of the analytical techniques developed for the speciation of organotin compounds are based on GC. GC remains the preferred separation technique owing to its high resolution and the availability of sensitive detectors such as (pulsed) flame photometry ((P)FPD), mass spectrometry (MS) or inductively coupled plasma- mass spectrometry (ICP-MS).

High performance liquid chromatography is an alternative approach. It mainly uses fluorescence, ultraviolet, and more recently inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and mass spectrometry detectors such as atmospheric pressure chemical ionisation mass spectrometry (APCI-MS-MS) and electrospray ionisation mass spectrometry (ESI-MS).

ICP-MS and (P)FPD detectors, equipped with a 610 nm band-pass filter selective for tin compounds have been applied widely because of their inherent selectivity and sensitivity. (P)FPD has been shown to have greater selectivity and lower detection limits (by a factor of 25 to 50 times) for organotin compounds than those obtained with conventional FPD (Bravo *et al.*, 2004).

5.8.1 Gas chromatography

Possible injection modes are splitless, large volume and on-column injection. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. If splitless or large volume injection is used, the liner should be of sufficient capacity to contain the injected solvent volume after evaporation. Helium must be used for GC-MS, GC-FPD and GC-ICP-MS. The preferred column length is 25–30 m, with an internal diameter of 0.15 mm to 0.3 mm. Film thicknesses of 0.3 µm to 1 µm are generally used. The most commonly used stationary phase for organotin analysis is 5% phenyl methyl siloxane. Mass spectrometric analyses are usually conducted in electron-impact mode at 70eV.

5.8.2 High Performance Liquid Chromatography

All stainless steel parts of the HPLC system that come into contact with the sample should be replaced by polyether ketone (PEEK) components. Reverse phase columns (e.g. octadecylsilane C18) are commonly used (Wahlen and Catterick, 2003) and the mobile phase can consist, for example, of a mixture of acetonitrile, water and acetic acid with 0.05% triethylamine, pH 3.1–3.4 (65:25:10, variable depending on columns used).

6. Quality assurance

References of relevance to QA procedures include HELCOM (1988), HELCOM COMBINE manual, QUASIMEME (1992), Oehlenschläger (1994), ICES (1996) and Morabito *et al.* (1999).

6.1 System performance

The performance of the instrumentation should be monitored by regularly checking the resolution of two closely eluting organotin compounds. A decrease in resolution points to deteriorating instrumental conditions. A dirty MS-source can be recognised by the presence of an elevated background signal together with a reduced signal-to-noise ratio. Chromatograms should be inspected visually by a trained operator.

6.2 Recovery

The recovery should be checked and reported. It does not guarantee that extraction is complete for the more aged compounds already present in the sample, but nevertheless complete recovery is a minimum requirement for the assumption that extraction is complete. One method is to add an internal (recovery) standard to each sample immediately before extraction (e.g. tripropyltin) and a second (quantification) standard immediately prior to injection (e.g. tetrapropyltin).

Correction for recovery is advised against as it is most likely not representative of the actual recovery of aged compounds and is only a measure of how well the procedure has been performed. However, when it is local practice to correct for recoveries, three recovery standards (a mono-, di-, and trialkyltin) are required because of the different properties of the three butyltin compounds. The uncorrected values should be reported in brackets to show the elevation due to the recovery correction. Results of analyses that show recoveries lower than 50% should be rejected or the samples should be re-analysed.

When using Isotope Dilution-Mass Spectrometry technique, the loss of target analytes is compensated. However, the recovery should still be calculated and should be between 50% and 150%.

6.3 Blanks

A procedural blank should be measured for each sample series and should be prepared simultaneously using the same chemicals and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will lead to errors in quantification. Even if an internal standard has been added to the blank at the beginning of the procedure, a quantification of peaks in the blank and subtraction from the values obtained for the determinands must not be performed, as the added internal standard cannot be absorbed by a matrix.

6.4 Accuracy and precision

A Laboratory Reference Material (LRM) or Certified Reference Material (CRM) should be included, at least one sample for each series of identically prepared samples. The LRM/CRM must be homogeneous, well characterised for the determinands in question and stability tests must have shown that it produces consistent results over time. The LRM/CRM should be preferably of the same type of matrix as the samples, and the determinand concentrations should occur in a comparable range to those of the samples. If the range of determinand concentrations in the samples is large (> factor of 5) two reference materials should be included in each batch of analyses to cover the lower and upper concentrations.

The data produced for the LRM/CRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM/CRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision, but a certified reference material (such as CRM 646 or PACS-2) of a similar matrix should be analysed periodically in order to check the method bias, ideally twice a year as a minimum. Additionally a duplicate of at least one sample should be run with every batch of samples. Each laboratory should participate in interlaboratory comparison studies and proficiency testing schemes on a regular basis, preferably at an international level.

6.5 Data collection and transfer

Data collection, handling and transfer must take place using quality controlled procedures.

7. Data recording and reporting parameters

The calculation of results and the reporting of data can represent major sources of error, as has been shown in intercomparison studies for organotin coumpounds. Control procedures should be established in order to ensure that data are correct and to avoid transcription errors. Data stored in databases should be checked and validated, and checks are also necessary when data are transferred between databases.

Data reporting should be in accordance with the requirements of the monitoring programme and with the latest ICES reporting formats. Results should be reported according to the precision required for the programme. In practice, the number of significant figures is defined by the performance of the procedure.

7.1 Analytical and quality assurance parameters

- LRM and CRM results for a set of organotin compounds, reported on a dry weight basis;
- descriptions of the extraction, cleaning and instrumental determination methods;
- the detection limit for each organotin compound. Specific performance criteria, including detection limits and precision, are usually set by the programme. A typical detection limit for single contaminants is 1 μg/kg as Sn on a dry weight, although this might be difficult to achieve for phenyltins compounds.
- QA information according to the requirements specified in the programme.

7.2 Parameters

- Organic contaminants of interest to monitoring programmes for which these guidelines apply: butyltin compounds: tributyltin (TBT) and dibutyltin (DBT).
- This technical annex also provides guidance on the determination of monobutyltin (MBT), phenyltin and octyltin compounds.

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Annex 12: Draft revised technical annex 6 to OSPAR JAMP Guidelines for monitoring contaminants in sediments – metals

1. Introduction

This technical annex provides advice on the determination of metals (including metalloids and some non-metals like Se) in whole sediment and in sieved fractions. Determinations of trace metals can be achieved by acid digestion of the sediment followed by analysis of the digest solution by spectroscopic or spectrometric methods, or non-destructive techniques such as X-ray fluorescence analysis (XRF), instrumental neutron activation analysis (INAA) etc. The guidelines are intended to assist analytical chemists both in starting up metal analyses in sediments, and to those already performing such analyses. They do not provide full details on specific laboratory procedures. Further guidance may be sought from specialised laboratories and publications (e.g. Loring and Rantala., 1991; Popek, 2003) or general guidance for selection of analytical methods (e.g. Larsen *et al.*, 2011). Analyses should be carried out by experienced staff and the procedure should be validated.

Trace metals may occur in both fine and sand fractions of sediments. However, most natural and anthropogenic substances (metals and organic contaminants) show a much higher affinity to fine particulate matter than the coarse fraction. Iron and manganese oxy-hydroxide coatings, and constituents such as organic matter and clay minerals, contribute to the affinity for contaminants for this fine material.

Total methods, such as procedures involving total dissolution of sediment samples with hydrofluoric acid (HF) prior to analysis, or non-destructive methods without digestion such as neutron activation analysis (INAA) and X-ray fluorescence analysis, determine total trace metal contents in the whole sediment sample. In contrast, methods using a partial digestion with only strong acids, e.g. nitric acid or aqua regia, mainly measure trace metals in the fine fraction, and only extract small amounts of trace metals from the coarse fraction. For fine material, similar results have been obtained using both total and strong partial methods (Smedes *et al.*, 2000; QUASH/QUASIMEME intercalibrations).

2. Sampling, pre-treatment and storage

Sampling sediments for metals analysis should preferably be done using cleaned plastic equipment, but this may not always be possible (e.g. at sea). Where metal sampling gear such as grabs must be used, care must be taken to avoid contamination of the sample, for instance by sub-sampling only sediment that has had no contact with the walls of the sampling device (maintain at least 1 cm distance from sides). Sample thickness should be chosen according to the monitoring proposes.

For ordinary surveys, the upper 2 cm of the sediment are sampled, but for other purposes like retrospective surveys, core samples can be taken. If knowledge exists about about the sedimentation rate, the sampling strategy can be based on this (e.g. Wadden Sea sampling of the upper 1 mm).

Sediments can be stored in closed plastic or glass containers. Samples must be sieved to 2 mm after sampling to remove large debris as well as large detritus and benthic organisms. Otherwise during further sample handling like storage, freezing or ultrasonic treatment, biotic material will deteriorate and become part of the sediment sample. Samples may then be further wet sieved to a smaller size fraction. Further

details on sieving procedures are available in the Technical Annex 5: Normalisation of Contaminant Concentrations in Sediments.

For total analysis, metals are usually not very sensitive with regard to storage conditions, so other measured parameters may determine how to store the samples. For total analysis of metals the sample can be stored at 4°C for a few weeks and for extended periods when frozen at –20°C, although direct wet sieving is preferred. For prolonged storage freeze-drying of samples can be considered. In this case contamination and losses of contaminants during freeze-drying have to be checked, in particular for volatile parameters (e.g. volatile organics) to be analysed in the same samples. Air-drying is not appropriate due to high contamination risks. Besides, samples may be difficult to disaggregate and mineral structures may be affected.

Once sieved and dried, samples should be homogenised and ground to a fine powder in a non-contaminating mill (e.g. made of agate or silicon nitride), and stored in plastic or glass containers until analysis.

3. Blanks and contamination

Any contact between the samples and metals should be avoided. If metallic implements are required during sampling (e.g. grab jaws), they should be of stainless steel and contact between the sub-sample and metal should be minimised.

Plastic and glassware should be cleaned using a laboratory washing machine incorporating an acid wash, or by an equivalent cleaning procedure. Some plastic ware may not need to be cleaned before first use for metals work, but this feature must be thoroughly examined (e.g. using acid leaching tests) before proceeding with any real samples.

Blanks should be taken through the whole procedure. In practice, this will generally represent the time from acid addition to a sample container through to the final measurement. There should be at least one analytical blank in a batch of 10–20 samples, representing 5–10% of the sample number.

For core-samples, care should be taken not to contaminate lower samples with upper samples in the process of cutting up the sediment core.

4. Digestion

4.1 Hydrofluoric acid digestion

HF digestions should be performed in polytetrafluorethylene (PTFE or PFA) vessels or equal quality, since the vessel must be metal-free and resist attack by the acid itself. Dried samples (normally 0.2–1g) should be accurately weighed into the vessel. Under fume extraction, the acid(s) are added. Some workers add HF first and leave the mixture to stand overnight, others add HF, nitric acid or *aqua regia* (see below); others use a perchloric acid mixture etc. In general, the mixtures are left to stand for a certain period of time (1 hour – overnight) to avoid problems with violent reactions, which may be prompted by the presence of organic matter in the sediment. Note that perchloric acid and organic matter can promote an explosive reaction, so this acid must be handled with great caution if applied to sediments. Specially designed fume hoods should be used for HF and perchloric acid treatments.

HF is corrosive and toxic. It is therefore necessary to either remove the acid or render it less harmful to the measurement instruments. The acid may either be boiled off,

which requires specialised facilities to extract the toxic fumes, or neutralised with boric acid (H_3BO_3), which is toxic itself.

Samples may be digested in a programmable heating block, with HF removal by evaporation. Alternatively, microwave digestions provide a rapid way to digest sediments. Some systems may allow the evaporation of HF, but in general microwaves use closed systems which allow pressure and temperature effects to rapidly dissolve the sediment. The most common methods use polytetrafluorethylene (PTFE or PFA) lined and sealed digestion vessels (Nakashima *et al.* 1988; Loring and Rantala, 1990). Since these closed systems retain the HF, boric acid is added after the HF digestion to complex remaining HF and make the resulting solution less hazardous, as well as preventing aluminium fluoride precipitation. The solution should be made up to volume with ultra-pure water and left to stand for at least 24 hours prior to analysis to precipitate excess boric acid. Others use adjusted amounts of boric acid and heat the digest to accelerate the process (Maham *et al.* 1987). Typical methods are described, for example, in Cook *et al.* (1997), Jones and Laslett (1994), Wu *et al.* (1996), Quelle *et al.* (2011).

If HF is to be removed by evaporation, care should be taken to ensure that mercury is not lost from sample solutions (Delft and Vos, 1988). It can be difficult to avoid mercury contamination with total digestion, but usually mercury is not bound strongly, so mercury can alternatively be analysed using strong acid digestion or by direct analysis (Taylor *et al.*, 2012).

4.2 Strong acid digestion

Partial digestions follow broadly similar procedures to HF digestions, as described above, for example using HNO_3 or *aqua regia* and deionised water to ca. 0.5 g sample. Microwave digestion is the preferred technique, but alternative methods applying high pressure and temperature can be used. The method used needs to be checked. Adequate performance is achieved when the digestion dissolves all the Al and Li from the clay fraction. It can easily be tested whether a method meets this requirement through parallel analyses of very fine grained samples by the partial method in use and a total method e.g. HF. If results for Al and Li do not differ significantly, the partial method used is sufficiently strong. To optimise the tests and to further normalize results, sieving to 20 or 63 μm grain size can be used, also reducing problems with detection limits in sandy sediments. A more general discussion on normalization can be found in the Technical Annex 5: Normalisation of Contaminant Concentrations in Sediments.

If the partial method results in lower contents than the total method, the conditions for the partial digestion such as time, temperature, acid concentration etc. need to be adjusted. Usually boiling with *aqua regia* is insufficient for a complete dissolution of Al. Historically, *aqua regia* has been used for strong acid digestions, but hydrochloric acid produces interferences for multi-element analysis by ICP and Cd in graphite furnace, so concentrated nitric acid alone may be used as a substitute (Christensen *et al.*, 1982; Krumgalz and Fainshtein, 1989; Koopmann and Prange, 1991). However, collision or reaction cell technology in ICP-MS can be used to reduce the interfering effect of chloride and other multi-element interferences, down to levels of <1% mass overlap for double charged or multi-element species, thus minimising correction formulas for standard mass-corrections.

5. Analysis and detection

Analysis of metals in solution resulting from digestion may be performed by a variety of means, but usually involves spectrometric or spectroscopic detection. Flame or graphite furnace atomic absorption spectroscopy used to be the primary method for analysis of metals (Welz, 1985). Alternatively, non-destructive methods, i.e. XRF (e.g. Jenkins, 1999; Potts, 1992; Williams, 1987; Bertin, 1984; Parsons *et al.*, 2013) and INAA (Alfassi, 1998), which do not require a preceding digestion step, can be used. Multi-element techniques like inductively coupled plasma attached to either an emission spectrometer (ICP-AES) or mass spectrometer (ICP-MS) allow much more rapid analysis of a wide range of metals (Kimbrough and Lauenstein, 2006; Duzgoren-Aydin *et al.*, 2011; Castillo *et al.*, 2012).

Interferences in the analysis may arise through the presence of other components in the sample. Use of at least 3-point standard additions may highlight where these occur and can be used to correct for suppression or enhancement effects. Interferences occurring with multi-element analytical techniques can be complex and require skilled personnel to identify and minimise such effects (Cook *et al.*, 1997).

Mercury can be detected by fluorescence spectrometry or cold vapour atomic absorption spectrometry. Direct methods for analysing mercury use pyrolysis combined with a gold trap and fluorescence or atomic absorption detection are sensitive enough to measure sediments directly (Maggi *et al.*, 2009; Kelly *et al.*, 2012). ICP-MS is also sufficiently sensitive to measure Hg, but care should be taken about controlling carry over memory effects.

It should be ensured that the limits of detection of the analytical technique selected meets the requirements of the respective monitoring programme. Typical detection limits using different methods are given in Table 1.

Table 1. Typical limits of detection for the determination of trace metals with different techniques (in mg/kg d.w.) based on typical sample intakes (0.5–1 g)

	Al	Li	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
AAS / flame	5	0.2		0.5	5	2		5	5	10
AAS / graphite furnace, hydride technique, cold vapour	<1	<1	0.2	0.02	<1	<1	0.05	<1	<1	-
ICP – AES with hydride generation	10	10	10 1	0.5	1	1	-	2	5	1
ICP – MS	40	0.1	1	0.01	0.2	0.1	0.05	0.2	0.2	2
X-ray fluorescence analysis (XRF)	1000	-	-	-	10	10	-	10	10	20
Neutron activation analysis (INAA)	-	-	0.3	1	0.8	-	0.1	-	-	2
Fluorescence, AAS spectrometry (direct or cold vapour/hydride generation)	-	-	0.2	-	-	-	0.005	-	-	-
Direct Mercury Analyzer (AA)							0.005			

6. Metal speciation

Several methods are in use to examine metal speciation in sediments, mainly by use of sequential extraction (e.g. Gleyzes *et al.*, 2002; Scouller *et al.*, 2006; Sutherland, 2010; Duzgoren-Aydin *et al.*, 2011), but currently also by passive samplers (for metals primarily DGTs) in porewater (Peijnenburg *et al.*, 2014).

7. Limits of detection

The limit of detection for each metal is normally determined by analysing a blank solution (containing acid to the dilution it is present in the sample) at least ten times. The limit of detection is calculated from 3 times the standard deviation of the blank taken through the whole procedure. For typical limits of detection, see Table 1.

8. Calibration and standards

Calibrations are usually performed using multi-element stock solutions and at least a 4-point calibration covering the range of concentrations expected in the samples. Multi-element solutions are commercially available, and may be used provided that they are of a similar matrix to the analyte. A crosscheck solution from a separate batch, or from a different supplier or an internal reference standard, should be used to check the calibration. Differences should not exceed 10%.

For non-destructive methods, appropriate certified reference sediments are required for calibration purposes.

9. Quality assurance

Every determinand should have its own Quality Control and Quality Assessment (QC – QA) scheme that includes regular blanks and calibration checks, the use of internal reference materials and certified reference materials and quality control charts. A system suitability check should be included in each batch to confirm that the measuring instrument is operating correctly. In each batch of samples at least one standard addition (from the start of the digestion) should be included to demonstrate that matrix effects do not occur, and also a duplicate sample.

At least one laboratory reference material should be included in each batch of samples in order to check the long-term performance. A quality control chart should be constructed for selected trace metals. If the warning limits are exceeded, the method should be checked for possible errors. When alarm limits are exceeded, the results should not be reported.

Certified reference materials (CRMs) for sediments are commercially available for both total methods and partial digestion methods. The data provided by such materials allow an independent check of the analytical performance. Table 2 contains information on certified reference materials available for use in marine monitoring.

Table 2: Certified Reference Materials for metals in marine sediments.

Code	Organization	Matrix
BCR 277R	IRMM[1]	Estuarine sediment
BCR 320R	IRMM	Channel sediment
BCR CC580	IRMM	Estuarine sediment (only Hg and CH_3Hg)
BCR 667	IRMM	Estuarine sediment
HISS-1	NRC[2]	Marine sediment
MESS-3	NRC	Marine sediment
PACS-2	NRC	Marine sediment (Harbour)
SRM 1646a	NIST[3]	Estuarine sediment
SRM 1944	NIST	Marine sediment
SRM 2702	NIST	Marine sediment

[1]**IRMM: Institute for Reference Materials and Measurements (Europe)**

[2]**NRC: National Research Council (Canada)**

[3]**NIST: The National Institute of Standards and Technology (USA)**

Participation in an international proficiency-testing scheme e.g. QUASIMEME is highly recommended to improve comparability between laboratories. Relevant quality assurance data should be reported e.g. to ICES, together with concentration data.

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Annex 13: Technical minutes by RGMON

Technical peer review of material from ICES Expert Groups for OSPAR request concerning:

A. 'Recommended method to determine the geographic representativeness of existing sediment monitoring stations' and
B. 'Review and update of the Technical Annexes to JAMP Guidelines for Monitoring of Contaminants in Biota and in Sediments'.

Reviewers: Jos Brils (The Netherlands, chair), Paul Keizer (Canada), Carlos Vale (Portugal) and Jarle Klungsøyr (Norway).

Chair WGMS: Craig Robinson and Lucia Vinas

Chair MCWG: Katrin Vorkamp

Secretariat RG: Claus Hagebro

Review process

The Review Group (RG) conducted its work by correspondence, from 7 to 23 April 2014. The RG members reviewed the Expert Group (EG) material mentioned above independently, and then exchanged their summaries that were compiled by the RG chair to form the RG technical report, agreed by all. The RG report will be annexed to the EG material and considered by the ICES Advice Drafting Group ADGMON, meeting 28-30 April 2014.

The RG focused in its review on:

- The completeness of the EG material (and not on style or general editing);
- Whether the EG missed important points relevant to the request;
- Agreement or disagreement to any conclusions made.

Where the RG found that an aspect of the issue was overlooked entirely, the RG drafted text to address the point in question, including references.

General comments

The RG acknowledges the EG effort executing the tasks related to the above OSPAR requests.

However, it appeared to the RG that one part of the material that we reviewed, seems in significantly 'higher state of maturity' (i.e. the technical annexes 6 and 7 to JAMP guidelines for monitoring contaminants in sediments) than the second part of the material (i.e. the technical annex 2 to JAMP Guidelines for monitoring contaminants in biota as well as the recommended method to determine the geographic representativeness of existing sediment monitoring stations).

Hence, especially that second part of the material could benefit from further elaboration.

A. Method on geographic representativeness of existing sediment monitoring stations

The material provided by the EG starts by stating "*although several members of WGMS were present at MIME, they could not recall discussion of this subject and were unable to assist in interpreting the meaning of the question. As a result, WGMS 2014 had several different interpretations of the question that it decided to attempt to answer*." Maybe a silly question, but why not have gone back to OSPAR for obtaining more clarity on the request – i.e. better framed the question(s) – before having started and executed the work?

Might this thus also be the reason why there is unfortunately very little advice for this request provided in the material?

The EG tackled several aspects of the request but along with other ICES EGs they are still uncertain as to how to deal with the issue of scale for the indicators of GES. The usefulness of statistical approaches, such as kriging, has been thoroughly explored and they provide some useful information. However one area that appears not to have been addressed is the potential usefulness of physical oceanographic circulation models that include simulations of the movement of the benthic boundary layer.

The only available information used by the EG to try to answer the questions raised by OSPAR was from southern North Sea. This is a highly dynamic area with shallow water depths (<50 m). It is well known from literature that strong and variable hydrographical conditions in this area lead to re-suspension and big sediment movements especially during stormy weather conditions. Both for spatial studies and for time trend studies it is generally recommended to sample sediments in areas where you have stable depositional conditions. You do not easily find these conditions in the southern North Sea. The RG feels that the EG should have commented on this in their report, and maybe also recommended to use data from other areas of the North Sea (e.g. the Norwegian Trench) when trying to answer the questions raised by OSPAR.

The specific request was "*Except for some work on sediment (Warren 1994, 1995), little is known of what geographical area each station represents. Given the current state of ocean models combined with measured changes at each station, OSPAR is requesting ICES (WGMS) whether a method can be recommended to determine the geographic representativeness of existing sediment monitoring stations*." The RG would take this to mean how much confidence do we have in contaminant distribution maps for sediments; i.e. what is the likelihood of missing a hot-spot or falsely identifying a hot spot, type 1 and type 2 errors? The RG notes in particular the phrase "(g)iven the current state of ocean models" which indicates to the RG that OSPAR is interested in knowing if and how these models might compliment the statistical approaches (e.g. kriging) to estimating concentrations between sampling locations. The RG would therefore support Q1 "*Suitability of sediment transport models to inform on the required spatial distribution of monitoring stations?*" as being the question of primary interest to OSPAR. Maybe it would be useful to recommend the application of normalisation to Al, Li or fine fraction, when extrapolation of metal concentrations between sampling locations are needed. That approach is valid to areas with a weak diagenetic signal in the surface sediments.

The sections on the "bubble plots" and concentration variability related to the size of a geographic area / strata are of limited usefulness. Both approaches are qualitative at best. The rationale for exploring concentration variability as a function of study area size is not apparent.

B. Technical Annexes for Monitoring of Contaminants in Biota and in Sediments

It would be useful for requests like this to update an existing document to either provide the original document or indicate the parts of the document that have been revised. There are several references to recent publications in both documents indicating that parts of the documents have been updated.

Consideration should be given to also revising or creating the relevant TIMES documents to keep these documents current with the OSPAR guidelines.

Please note that this is a comment rather than a criticism of the text. In the introduction of each of the annexes it is noted that these annexes do not contain all of the detailed information needed to conduct specific analyses and directs the reader to more some detailed documents. It would be useful if there was some organization of the potential sources for detailed information on specific analytes or techniques, e.g. a table. Also in keeping with the suggestion that these updates be captured in the TIMES series, there are references to other technical annexes in this annex that for "non-OSPAR" laboratories can be difficult to access. The TIMES series is readily accessible on-line without charge or restriction and provides an editorial service to the authors to ensure the quality of the final document.

B1 - Annex 2: Metals in biota

Sections 1.1 – 2.2.2 seem to be in a significant less (too low?) state of maturity compared to the rest of the sections and could benefit from further elaboration.

Most critical issue is the (presumed?) relation between length and age. E.g. studying the appendix provided, it seems very difficult – not to say impossible – to ensure that a certain length matches to a certain age. Maybe there are better relations to be found in literature, but there are no references provided to such evidence in the provided material. Hence, statements like "*A sampling size range of xx – xx cm ensures individuals of the x-year age class*" (in **section 1.1.2** for flounder, hake and Pacific oyster) and "*selection of relevant length range in order to find individuals of the recommended age*" (**section 2.1**) seem to lack scientific underpinning.

B2 - Annex 6: Metals in sediments – analytical methods

The provided material appears to be complete and well laid out.

B3 - Annex 7: Organotin compounds in sediments

The provided material appears to be complete and well laid out.

The nature of the specific request from OSPAR should be included in the introduction, i.e. "*consideration should also be given to refocusing the butyltins method on dibutyltin as the primary determinant rather than tributyltin, as this compound is still widely used in* e.g. *plastics and clothing*. "

In annex 6 it often mentions that trained/skilled personnel are needed to perform the analysis. It seems that this is even more a prerequisite for performing the analysis as described in annex 7. But it seems to be less pronounced in annex 7.

Technical comments

A. Method on geographic representativeness of existing sediment monitoring stations

Q1

- It would be useful to have a physical oceanography group comment on this discussion. Considerable work has been done on the movement of particulate material in the water column and in the benthic boundary layer in relation to contaminant discharges from marine gas and oil exploration and production platforms. This type of approach would seem to be relevant here.

- The provided material states "*Existing understanding (of) hydrodynamic models can predict the dispersion of suspended particles from riverine input* (e.g. *Ferrer et al., 2009), but require input on the contaminant concentrations of these before they can be used to model the input of contaminants to a given sampling area*." There is no further discussion or advice offered. Is it not possible that these models could be used to predict the distribution in the coastal zone of contaminants from riverine sources?

- "*… to trace the source of contaminated sediments …*" or is it/should it no be "*to trace the source of the contaminations in the sediment*"?

- *"… but require input on the contaminant concentrations of these …" Of these*: Of what? Anyhow a strange formulation '*require input of the contaminant concentrations*" Please be more precise.

Q2

- This does not appear to be new advice but rather a reiteration of the advice provided in 2013

- Please each occasion you provide acronyms please also give full terms, so please do this for GES, ERL, EAC, MSFD

- *"… to obtain sufficient statistical power to assess concentrations against the assessment criteria …*" You mean: " *… to obtain sufficient statistical power to determine whether there is a significant exceeding of the assessment criteria …*"?

- *"… time trend monitoring …"* Is this the 'official' JAMP jargon? If not, please for consistency use that jargon

Q3

- It is not apparent why there should be a relationship between the size of sampling area and the variability in the concentration. This would seem to be of little use to OSPAR

- Question not formulated precisely:
  1. be more specific on "… *concentration variability* …": i.e. variability of the concentrations of contaminants in sediment?
  2."… *relate to the size of a geographic area / strata* …": i.e. relate to the size and/or biophysical features of the sampling area and the number of sampled spots in that area?

- **Table 4.1**: Figure X should be Figure 4.1

- Page 3: " … *Knowledge on the variability of concentration data for many more boxes* …" Please be more precise on "*variability of concentration data*"

- **Figure 4.2**: "*Effect of spatial area* …" should it not be "E*ffect of the size of the sample area* …"?

Q4

- While this discussion is somewhat useful the RG feels that it suffers greatly from the omission of any discussion of the oceanographic processes dominant in the chosen areas and the potential sources of elevated contaminants in these areas. If elevated levels are observed then knowledge of the source of those elevated levels will contribute to the understanding of how the levels will vary in that area.

- Especially here the RG misses text that catches in a few words the key conclusions from the presented figures addressing Q4

- The text on the "bubble plots" is too qualitative to have any application to the request. The discussion on statistical estimation draws largely on the earlier work of Warren. There appears to be some benefit to certain types of statistical estimation but it should be done in the context of the knowledge that we have about the source of the contaminants and the physical and biological processes that influence their distribution. From a practical perspective an important question for the sampling design becomes how can I reduce the likelihood of a type 1 or type 2 error?

- Page 3: "… *sediment contaminant and co-factor concentration data* …" Please mention (as example) some of these co-factors.

- Page 3: "*… this may be due to a scaling effect.*" Please add 'to' and explain why it is due to that effect

- Page 3: "*It is apparent that, as expected* …" Please explain why this was expected

- **Figures 4.4 – 4.6**: In header of these figures it indicates CORG, but below the figures it mentions total organic carbon. Is CORG same as TOC? If yes, for consistency please use (preferred) TOC

- Why Pb contamination seems more evenly distributed over the North Sea than all other parameters, that show a tendency towards higher concentrations in Scheldt estuary and along the Dutch – Denmark coastline? Any explanation? Atmospheric deposition of Pb?

The summary (page 9)

- The answers to the questions could use some further elaboration, especially the answer to Q2 and Q4

B. Technical Annexes for Monitoring of Contaminants in Biota and in Sediments

B1 - Annex 2: Metals in biota

- **Section 1.1.1**: "*… can only be selected in the light of information on fish stock composition and history …*": How about shellfish?

- **Section 1.1.1**: " *… Care should be taken that the sample is representative of the population …*": Any suggestions on how to do that in practice?

- **Section 1.1.2**: "*… To standardise results …*": What does that mean? Please be more precise

- **Section 1.1.2**: "*a. its migration is less pronounced, thus it is more likely to represent the area in which it is caught …*": Please be more precise/explain this better

- **Section 1.1.2**: "*Mytilus edulis occurs in shallow waters along almost all coasts of the Contracting Parties. It is therefore suitable for monitoring in nearshore waters*": Are all nearshore waters shallow?

- **Section 1.1.2**: "*… M. galloprovincialis because the latter, which may occur along Spanish and Portuguese coasts, cannot easily be discerned from M. edulis*": what is/could be the implication of the fact that they cannot easily be discerned? In other words: do both species behave in same way if it concerns the uptake and accumulation of contaminants?

- **Section 1.1.2**: "*For monitoring in polluted areas, mussels may be transplanted …*": To make this more specific, insert 'caged' before mussels. Thus it relates **to**

section 4.3.1 of the generic part of the JAMP guidelines, where 'caged mussels' are mentioned.

- It would anyhow be good to make more references to the generic part of the JAMP guidelines

- **Section 1.1.2**: "*Flounder is not suitable for monitoring in open sea areas due to its migration pattern. …*": Please add a few words/explain that pattern.

- **Section 1.1.2**: "*Whiting …... It is a suitable substitute for cod.*": Why is that the case?

- **Section 1.1.2**: "*Hake ….. The sampling size interval suggested is arbitrary and may need adjustment in the light of future experience.*" Please elaborate, better explain why this is the case.

- **Section 2.1 as well as 2.2.1**: "*Gain in precision of the contaminant data …*" Please elaborate, be clearer in what you mean here.

- **Section 2.1**: "*In selecting the sample, care should be taken to ensure that it is representative of the population and that it can be obtained annually*" Any suggestions on how to do that in practice?

  Section 2.2.1: "*… using biological variables. Although several biological parameters are appropriate …*" Please either use variables or parameters.

- **Section 2.3.3**: "*…it is important to choose the egg from each clutch randomly.*" Can you provide some guidance on how to do that?

- **Section 4.3.1**: "*….. sub-surface sea water.*" Please be more precise: how deep is that?

  Section 4.3.1: "*…..has not been subject to contamination from point sources.*" How to ensure that?

- **Section 4.4**: "*The egg should then be opened ….*" Should that not be preceded by thawing? Thus sentence could then be "*After thawing the egg should be opened …*"

- **Section 5.1:** Statements such as "*Glassware and Teflon equipment should be washed extensively with diluted nitric acid, distilled water and acidified metal-free deionised water*" need to be identified during the editing process. "*Diluted nitric acid*" and "*acidified metal-free deionized water*" need to be technically specified, e.g. 1N HNO3.

- In general, the provided material requires extensive editing, e.g. "*calibrands*" is not a word.

- **Section 5.3.2 and 5.3.3**: especially here (more) references to more detailed analytical methods would be welcomed

- **Section 5.3.3**: full terms for GFAAS and TXRF are provided, please do same for all other acronyms in this section

- **Section 6**.1: "*the masses or concentrations of standards for the establishment of the calibration function must be prepared without bias*." What does that mean: without bias? Please be more explicit

- **Section 7**: "*… the latest ICES reporting formats*." Please provide the reference.

- **Appendix**: please add 1, so "Appendix 1".

B2 - Annex 6: Metals in sediments – analytical methods

- **Section 1**: metals (first sentence) versus trace metals (rest of the annex 6): maybe give definition of trace metals and only/consistently use trace metals?

- **Section 1**: first sentence mentions 'advice'. Maybe only use the word guidelines or guidance for consistency?

- **Section 1**: "*Analysis should be carried out by experienced staff*" Is it possible to be more explicit on what that means? What kind of level/training is required?

- **Section 1**: "*… procedure should be validated*." What does 'validated' mean? Is it possible to be more explicit? E.g. , is it recommended to use an ISO (or comparable) standard operation procedure?

- **Section 2**: "*For ordinary surveys …*" What does this mean in terms of the generic part of the JAMP guidelines, i.e. to which types of monitoring of section 2 of those guidelines does it relate?

- **Section 2**: "*… for other purposes like retrospective surveys, …*". Is a survey not always retrospective?: sediment that you sample now, has been deposited in the past, i.e. before it is sampled ...

- **Section 2**: "*Samples must be sieved to 2 mm after sampling …*". Is total concentration to be expressed on fraction < 2 mm, or on weight of total original sample before sieving?

- **Section 2**: " *… other measured parameters may determine how to store the samples*." Please provide a few examples of the "*other measured parameters*".

- **Section 2**: is it possible to be more explicit (references to literature) on storage time of samples under specific conditions?

- **Section 2**: "*Air-drying is not appropriate due to ….*". This is a deviation from the generic part of the guidelines where it mentions "*Alternatively, the sediments may be dried at any temperature below 105^{0}C.*" Please make reference to that, i.e. that – if applicable – the generic guidelines are no longer appropriate regarding this aspect.

- **Section 5**: "*… skilled personnel …*" Is it possible to be more explicit on what that means? What kind of level/training is required?

- **Section 9:** "*… demonstrate that matrix effects do not occur …*". Can you be more explicit in what "*matrix effects*" means in this context?

- **Section 9:** "*When alarm limits are exceeded …*". Can you be more explicit on "*alarm limits*"?

- **Section 9**: "*… such materials allow an independent check …*" Can you be more explicit in what "*independent*" means in this context?

B3 - Annex 7: Organotin compounds in sediments

- **Section 1**: "*… possible adsorption of and contamination by organotin compounds need to be checked …*" Can you give an indication/reference to a method on how to do so?

- **Section 2**: First sentence mentions "*Samples*". Then second sentence continues with "*Sediment*". Samples and sediment mean the same thing in this context? If yes, try to be more consistent in word use.

- **Section 5.8**: Please use complete terms for each abbreviation when mentioned first time: e.g. gas chromatography (GC). PFPD seems to be abbreviation of 'pulsed flame photometry'. But where does the "D" then stand for?

- **Section 5.8.1**: "*… The preferred column length is 25–30 m …*". This should be '*mm*' we suppose?

- **Section 5.8.2**: "*… mixture of acetonitrile, water and acetic acid with 0.05% triethylamine, pH 3.1–3.4 (65:25:10, variable depending on columns used) …*" For readability please change to "*… mixture of acetonitrile, water and acetic acid (65%:25%:10%, variable depending on columns used) with 0.05% triethylamine, pH 3.1–3.4 …*" And please note that we suggested to add '%'.

- **Section 6.1**: "*A dirty MS-source …*" What is that?

- **Section 6.1**: "*Chromatograms should be inspected visually by a trained operator*". Is it possible to be more explicit on what that means? What kind of level/training is required? And please also see the general comments related to this aspect.

- **Section 6.3**: "*… interfering compounds …*" Can you please give a few examples of such compounds?

- **Section 1**: "*Even if an internal standard has been added to the blank at the beginning of the procedure, a quantification of peaks in the blank and subtraction from the values obtained for the determinands must not be performed, as the added internal standard cannot be absorbed by a matrix*." This sentence needs more explanation.