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20–24 February 2012

Southampton, United Kingdom



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Executive summary

The Marine Chemistry Working Group (MCWG), chaired by Katrin Vorkamp, Denmark, met at the National Oceanography Centre (NOC) in Southampton, UK, 20–24 February 2012. The meeting was attended by 20 participants representing nine different countries. MCWG worked in a combination of plenary work, subgroups and specific task groups. The chemical oceanography subgroup (COSG) established at MCWG 2010 continued at this meeting and consisted of nine MCWG members.

MCWG 2011 addressed the following four **OSPAR requests**:

- i) Develop a **guideline on monitoring of contaminants in seawater**: This work had been started at MCWG 2011 and continued intersessionally, including comments by the 2011 Review Group and the 2011 Advice Drafting Group. The draft guideline was completed at MCWG 2012.
- ii) Revise the **JAMP guideline on monitoring of nutrients**. The approach was discussed and decided upon at MCWG 2011. The guideline was revised accordingly at MCWG 2012 including comments provided by OSPAR Contracting Parties.
- iii) Revise the **JAMP guideline on monitoring of dissolved oxygen**. This guideline was revised at MCWG 2012, including comments provided by OSPAR Contracting Parties.
- iv) Review **Environmental Assessment Criteria (EACs)** developed by an OSPAR working group. The development deviated from the approach originally chosen by the OSPAR working group, mainly due to lack of suitable data. Some of the resulting EAC values appeared questionable, i.e. much higher or lower than anticipated from observations in the environment. MCWG also expressed concern about calculations with a high degree of uncertainty. In conclusion, MCWG discouraged the calculations of EAC on a very uncertain data and calculation basis and recommended further efforts to retrieve suitable data and information.

In response to Terms of References given to MCWG by the ICES **Marine Strategy Framework Directive** Strategic Group (MSFD SG) MCWG described its area of expertise in relation to MSFD descriptors, essentially covering Descriptors 5 (“Eutrophication”), 8 (“Contamination”) and 9 (“Human consumption”). Challenges in determining good environmental status were seen in the lack of toxicological thresholds (see EAC review) and the scale issue, i.e. lack of data from the open sea. MCWG members reported on the developments under the MSFD in their respective country. Details of the proposed amendments of **Water Framework Directive** priority substances were presented to MCWG. MCWG provided comments and expressed an interest in more scientific dialogue with the relevant EC working groups on these issues.

MCWG had been requested to respond to a recommendation by the Study Group on Integrated Monitoring of Contaminants (SGIMC) to review the seawater contaminant section of the **ICES database**. This was approached in collaboration with the ICES Data Centre and included comparisons of parameters across monitoring programmes and methods for error identification.

MCWG had asked for reports from the following **ICES expert groups** on the interface to MCWG: IOC/ICES Study Group on Nutrient Standards (SGONS), OSPAR/ICES Study Group on Integrated Monitoring of Contaminants (SGIMC), Working Group

on Marine Sediments in Relation to Pollution (WGMS), Working Group on Biological Effects of Contaminants (WGBEC) and Working Group on Eels (WGEel). Besides the ongoing information and data exchange, MCWG suggested a WGMS/WGBEC/MCWG joint meeting and joint publications. MCWG is also interested in establishing contacts to groups on the interface to MCWG's chemical oceanography work.

Two **guest speakers** had been invited to present their research to MCWG: Clive Trueman (University of Southampton): "Using natural spatio-temporal gradients in stable isotopes to monitor population-scale movements and bottom-up ecosystem effects in pelagic fish" and Alex J. Poulton (NOC Southampton): "Pelagic calcite production in the modern ocean". Further **projects of relevance to MCWG** were presented by MCWG members, about monitoring activities in the Netherlands, research on chemical profiles in fish for characterisation of fish migration (Denmark) and the Belgium project on integrated risk assessment and monitoring of micropollutants in the Belgian coastal zone (INRAM).

Bram Eijgenraam of the **QUASIMEME** project office visited MCWG 2012 to present and discuss new developments at QUASIMEME. This included the feasibility and need for new exercises on carbonate parameters in relation to ocean acidification (OA) monitoring. Quality assurance was also discussed in a broader context, with particular focus on analytical methods for chlorophyll and polyfluorinated alkylated substances (PFAS).

MCWG's work on **ocean acidification** at this meeting included multiple aspects: i) new data in relation to OA, ii) new methods and equipment, iii) data submission to databases, iv) finalisation of the cooperative research report on OA and v) contributions to draft guidelines on OA monitoring provided by OSPAR. MCWG expects its work on OA at this and previous meetings to be of direct relevance to the **OSPAR/ICES study group on OA**. The draft resolution of a **theme session** on ocean acidification at the Annual Science Conference 2013 was confirmed.

Within the area of **organic contaminants**, MCWG received a literature update on the ocean-atmosphere exchange of PFAS, which concluded that pathways for long range atmospheric transport were not fully understood, including the role of sea spray. MCWG also summarised information on monitoring of organochlorines and emerging contaminants in **seabird eggs**, with emphasis on experiences from monitoring programmes in the North Sea, the Baltic Sea and the Arctic. A **TIMES manuscript** on the analysis of polychlorinated biphenyls (PCBs) in sediment and biota was completed at MCWG 2012.

MCWG also summarised the recent literature on the use of **passive samplers** in the marine environment, one of the conclusions being that non-polar passive sampling devices allowed the quantitative determination of aqueous concentrations with a well defined accuracy and precision. Finally, MCWG also discussed new developments in the analysis of **trace metals**.

1 Opening of the meeting

The Marine Chemistry Working Group (MCWG), chaired by Katrin Vorkamp, Denmark, met at the National Oceanography Centre (NOC) in Southampton, England, from 20–24 February 2012. David Hydes was host for MCWG at NOC.

The meeting was opened by Dr. Richard Sanders, head of the Biogeochemistry and Ecosystem Group at NOC. Dr. Sanders welcomed the participants and presented the broad range of activities of his group.

The participants introduced themselves and their affiliations and described their specific interests within the field of marine chemistry. Katrin Vorkamp conveyed regards and messages from MCWG members who were not able to attend MCWG 2012. The chemical oceanography subgroup (COSG) continued from MCWG 2011, consisting of Carlos Borges, David Hydes, David Pearce, Elisabeth Sahlsten, Evin McGovern, Klaus Nagel, Naomi Greenwood, Pamela Walsham and Solveig Olafsdottir.

The list of participants is given in Annex 1.

2 Adoption of the agenda

The agenda was adopted as presented in Annex 2.

3 Report from the Annual Science Conference 2011

3.1 Advice Drafting Group on Monitoring 2011

Katrin Vorkamp had attended the 2011 Advice Drafting Group on Monitoring (ADG MON 2) and presented its work to MCWG, including the comments by the Review Group 2011 (see MCWG 2010 report, Annex 11).

In response to OSPAR request 2011/1, MCWG 2011 had produced a draft version on guidelines for contaminant monitoring in seawater, to be completed at MCWG 2012. ADGMON 2 provided internal advice to MCWG, including comments on the 2011 draft version and a proposed outline of the final guidelines (see section 5.1). Given the 2-year-work period on this OSPAR request, no advice was forwarded to OSPAR in 2011.

MCWG 2010 had produced a piece of advice on the question of atmospheric monitoring of perfluorinated compounds (PFC). Out of scientific interest, MCWG 2011 followed up on this previous piece of advice by reviewing new literature, and reached the same conclusion as MCWG 2010. This information was forwarded to OSPAR as part of the 2011 ICES advice.

Science Steering Group on Human Interactions on Ecosystems (SSGHIE)

Katrin Vorkamp also informed MCWG about a meeting of the Science Steering Group on Human Interactions on Ecosystems (SSGHIE) in June 2011, one of 5 steering groups under the ICES Science Committee (SCICOM). Based on a coding of Terms of References (ToRs) of the SCICOM expert groups in relation to the ICES Science Plan, the coverage of the Science Plan was analysed in terms of cross-cutting issues and poorly covered topics. As the number of ToRs does not necessarily reflect the amount and quality of work behind a particular ToR, this preliminary gap analysis was to be followed up by a more detailed analysis of the actual work. Both poorly covered and cross-cutting areas were discussed in specific sessions at the Annual Science Conference (ASC) 2011.

At the SSGHIE meeting, the SSGHIE chair also informed about SCICOM's plans of an evaluation of expert groups as part of a proposal of multi-annual expert group management. This proposal was also discussed by MCWG, see section 3.3. The SSGHIE chair also asked about proposals of theme sessions for ASC 2012. MCWG had originally submitted a draft resolution for a theme session on ocean acidification. However, realising that the ASC would coincide with a large scientific conference on the same topic, MCWG had decided to postpone its proposal to ASC 2013 (see draft resolution).

Assessment Working Group Chairs (WGCHAIRS)

Furthermore, Katrin Vorkamp informed about the meeting of the Assessment Working Group Chairs (WGCHAIRS) in January 2012. Amongst other topics, ICES activities were presented in relation to the Marine Strategy Framework Directive (MSFD) and progress towards integrated ICES advice was discussed by WGCHAIRS.

3.2 Annual Science Conference 2011

Katrin Vorkamp did not attend ASC 2011, but had prepared a presentation for SSGHIE about MCWG 2011 activities. This presentation was now also shown to MCWG 2012.

3.3 Internal ICES business

ASC 2012 will take place in Bergen, Norway, 17–21 September 2012. The abstract submission is open until 20 April 2012. Session G on the "Implementation of the European Union Marine Strategy Framework Directive (EU MSFD): Implications for science and policy" might be directly relevant for MCWG members. MCWG would be also be interested in regular sessions at ASC on MCWG-related work, for example contaminants, which would also provide a joint forum for MCWG, WGBEC, WGMS and related EGs.

Multi-annual management of expert groups

In July 2011, the ICES Secretariat informed EG chairs about a SCICOM proposal of multi-annual management of EGs and invited EG chairs to comment on this proposal. All MCWG members were consulted and their replies were compiled and forwarded to ICES in due course, expressing concern about reduced continuity and flexibility in the EG work, an uneven workload and difficulties to accommodate MCWG's advisory work.

In January 2012, the ICES Secretariat issued a draft implementation plan, according to which the multi-annual management will be introduced as soon as the EG requests this or at the end of the term of the current chair. EGs are invited to forward comments on this draft document (by 12 March 2012).

MCWG confirmed its concern expressed last year. In general, MCWG is concerned that a long-standing EG like MCWG might be destabilised by the 3-year-working period. ToRs should be kept flexible enough to respond to advisory tasks as well as the members' scientific interest, and the continuity of the MCWG work should be maintained. The uneven workload remains an issue, with the risk of a full report of three years work exceeding the chair's resources. MCWG is in favour of more outcome-oriented work processes, e.g. publications of scientific results.

Action:

Katrin Vorkamp to convey MCWG's comments on the multi-annual management implementation plan to the ICES Secretariat for the 12 March deadline.

4 Plenary presentations

David Hydes and Katrin Vorkamp had invited two guest speakers to present their work at the meeting.

4.1 Alex J Poulton (Directorate of Science and Technology, NOC Southampton): Pelagic calcite production in the modern ocean

Coccolithophores are a unique group of microscopic marine algae that produce small scales of calcium carbonate (coccoliths), which form an outer shell (coccosphere) around the cell. Coccolithophores have important roles in the marine carbon cycle as they convert carbon dioxide into both organic matter (via photosynthesis) and calcium carbonate (via calcification), and coccoliths are effective agents at transferring carbon dioxide as calcium carbonate (calcite) from the surface to deep ocean. Coccoliths are heavier than organic matter and add weight to sinking material so that it also reaches the deep sea. Although coccolithophores have a rich fossil record they face a bleak and uncertain future - increased atmospheric carbon dioxide is causing 'Ocean Acidification' and a chemical environment thought to be unfavourable to calcifying organisms, while global warming may change how the oceans are mixed and the availability of energy (sunlight) and nutrients (nitrogen, phosphorus) needed for growth.

In the modern ocean, coccolithophores are responsible for 50–80% of calcite production and export, and around 1–20% of organic carbon formation through photosynthesis. There are ~200 extant species of coccolithophore living in the world's oceans, from polar seas to the subtropical central gyres. This talk gave information on how coccolithophores form their coccoliths and coccosphere, their diversity in morphology, ecology and physiology, and the impact of diversity within this group on marine calcite production and export. Lastly, the possible fate of coccolithophores in a changing climate was examined and their potential response to 'Ocean Acidification'.

4.2 Clive N Trueman (Ocean and Earth Sciences, University of Southampton): Using natural spatio-temporal gradients in stable isotopes to monitor population-scale movements and bottom-up ecosystem effects in pelagic fish

Highly migratory pelagic fish such as herring, tuna, mackerel and blue whiting are commercially important and highly exploited globally. Successful management of populations and population genetic diversity depends on knowing the distributions of fish stocks and/or populations at sea, but it is difficult to gather these data. Traditional catch and release tagging is expensive and limited by the locations of fishing; genetic analyses are complicated by the relatively high degree of mixing and gene flow within pelagic fish, and data storage tags are limited by cost, size and location of fisheries.

In the last decade the stable isotope composition of terrestrial animal tissues has been used to track origin and migration pathways, but applying these methods to marine environments is complicated by either homogenous (O and H) or extremely dynamic (C and N) isotope distributions.

On the scale of ocean basins, carbon isotopes vary in a relatively predictable fashion, and steep isotope gradients can be used to study large-scale movements, particularly in high latitude environments. On smaller scales, temporal variations in carbon isotope composition linked to climatic variability may overprint the broad spatial isotope gradients. In these cases, models linking tissue isotopes and spatio-temporally explicit environmental data can be used to predict location retrospectively from archived fish tissues.

It was shown how natural spatio-temporal variations in the stable isotope composition of carbon and nitrogen across ocean basins can be used to explore migration pathways, stock structure and climate impacts on nutrient flow in highly migratory pelagic fish, using the Atlantic salmon as a model species.

5 Main agenda

5.1 Development of a JAMP guideline for monitoring of contaminants in seawater

MCWG continued its work on the draft guidelines, taking into account the internal advice given by ADGMON2. The final draft is attached as Annex 5.

5.2 Review of Environmental Assessment Criteria or equivalents (OSPAR request 2012/2)

To review scientific robustness and update, as necessary, EACs or equivalent effects levels calculated for CEMP and pre-CEMP determinants

MCWG was requested to review Environmental Assessment Criteria (EACs) (or equivalents) produced by the Intersessional Correspondence Group on Environmental Assessment Criteria (ICG EAC). Patrick Roose gave an overview of the process to develop EACs through OSPAR and the work of ICG-EAC.

EACs should have been finalised for the 2010 OPAR Quality Status Report (QSR), but this was not possible for all compounds. Therefore, alternative approaches to assessment criteria were developed for the QSR (a document describing this is available: Background Document on CEMP Assessment Criteria for QSR 2010). The available assessment criteria (BACs, EACs, EAC^{passive}, ERLs and food safety levels) were incorporated into a “traffic light” system and this was used to assess contaminant data for the QSR. Some of these assessment criteria were not agreed upon and not all were suitable for environmental monitoring. Therefore, at the OSPAR MIME meeting, ICG-EAC was formed, chaired by Patrick Roose, to take this forward and derive new EACs to be used in future assessments.

An approach to produce new EACs was agreed upon at MIME in 2010, using dose/effect relationships for CEMP and pre-CEMP compounds. A document on this concept was produced by MIME and ICG-EAC. In summary it was proposed that dose/effect relationship data for all CEMP and pre-CEMP compounds would be collated and graphs would be produced. Using an acceptable level of risk (δ) of 10%, and adding confidence levels to the graphs, the EAC would be set as the lower confidence level. No safety factors were used, which is different from the approach used to derive Environmental Quality Standards (EQSs) under the Water Framework Directive (WFD). It was agreed that dose/effect data would be obtained intersessionally for CEMP and pre-CEMP compounds and the approach described above applied to the data at MIME in 2011 to derive new EACs.

However, very little data had been obtained prior to the MIME meeting. Therefore it became clear that this approach could not be applied within the timeframe. Values for endpoints were available but the raw data to produce dose/effect curves could not be easily found. Therefore, an alternative approach was considered, based on WFD EQS values, as illustrated in the decision tree shown as Annex 6. The Marine Strategy Framework Directive requires continuity between implementation of the WFD and coastal waters. Briefly, if an EQS value was available - including existing and proposed EQS values - which was higher than the Background Assessment Concentration (BAC) and considered fit for purpose, this was used as the EAC. If an EQS was available, including proposed EQS values, but less than the BAC then either the BAC needed to be reconsidered or an EAC was calculated. If no EQS value was available EACs would have to be calculated.

The document produced by ICG-EAC included a table of EAC values (Annex 7). Some EACs were unusually high and many above OSPAR BACs.

MCWG pointed out that the EQS might not always be suitable. In some cases, a food safety level is used as the EQS (e.g. PAHs in biota).

MCWG observed that the ratios of the sediment EAC to the biota EAC was highly variable, which is not in agreement with observations in the environment. In addition, some EAC values are very low and might be below limits of detection. This seems to be related to very low proposed EQS values (e.g. for PBDEs in biota), which apparently are based on very few experimental data and lack confirmation.

Some EAC values for biota had been calculated from water EQSs, using a bioconcentration factor (BCF). MCWG was concerned about this approach, given the uncertainty of BCFs and the complexity of the systems. Some of these preliminary EACs, derived in this way, were considerably higher than BACs.

MCWG concluded that EAC values based on very uncertain calculations would be misleading. In this case, no EAC should be given.

MCWG recognised that the right information might be available, but was not readily accessible. Considerable resources and effort would have to be invested to collate suitable dose/effect data, but MCWG considered that this investment of resources was necessary to obtain reliable EACs. Great progress has been made in the area of sensitive and quality assured chemical methods, but the environmental significance of the observed concentrations can still not be adequately assessed. Therefore, it is important that an appropriate group takes this forward and research is directed towards the knowledge and data required to answer these questions.

Actions:

Katrin Vorkamp to provide draft text to the OSPAR HASEC 2012 meeting, via Martin M. Larsen.

Katrin Vorkamp to provide draft text to WGBEC, for the WGBEC 2012 meeting.

5.3 Report of developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME

Katrin Vorkamp had invited a QUASIMEME representative to present and discuss new developments in QUASIMEME to MCWG. Bram Eijgenraam, WEPAL/QUASIMEME manager, kindly agreed to visit MCWG 2011 for one day. In addition to this agenda point, MCWG also discussed agenda item 5.10.4 (Proficiency testing of carbonate parameters) with Bram Eijgenraam.

Furthermore, Denise Smythe-Wright and Stefan van Leeuwen gave presentations on the quality of pigment measurements and analyses of perfluorinated alkylated substances (PFASs), respectively, under this agenda point (see below).

Bram Eijgenraam: The current and future situation at QUASIMEME/WEPAL

1) WEPAL has been accredited since 2000

WEPAL focuses on organic and inorganic parameters in several programs. The programs of WEPAL started as early as 1956 and covers the following programmes: International Plant-analytical Exchange Programme (IPE) (currently 220 participants), International Soil-analytical Exchange Programme (ISE) (since 1988, 280 participants), Sediment Exchange for Tests on Organic Contaminants (SETOC) (since 1992; 90 participants), Manure and Refuse Sample Exchange Programme (MARSEP for compost) (since 1994; 50 participants) and Biomass Exchange Programme (since 2008, 20 participants).

2) Accreditation of QUASIMEME

QUASIMEME is fully integrated into the procedures of the WEPAL QC system. The Dutch accreditation board (RvA) conducted an audit in summer 2011. The main, but not all QUASIMEME programmes are included in the scope of the accreditation.

The choice of programmes to be included in the accreditation was mainly based on the minimum number of participants, costs of test homogeneity and stability, performance in the ring test (coefficient of variance <25%) and a history of a minimum of 3 years.

The RvA visited WEPAL/QUASIMEME again in Nov 2011 and approved the scope. This accreditation is valid through 2016 (with the routine yearly inspection visits).

The following programmes ("Exercices" in QUASIMEME) are now accredited:

- Seawater: AQ-1 (nutrients) AQ-2 (nutrients in estuarine and low salinity water), AQ-11 (chlorophyll),
- Biota: BT-1 (trace metals), BT-2 (chlorinated organics), BT-4 (PAHs),
- Sediment: MS-1 (trace metals), MS-2 (chlorinated organics), MS-3 (PAHs), MS-6 (organotins)

QC procedures are also in place for the other QUASIMEME programmes.

3) Organisation

Administration of WEPAL and QUASIMEME are integrated, this may involve some changes for the current QUASIMEME practice, for example:

- Sample management; barcodes will provide unique code for each sample portion.
- Results are transferred to a new database; the data processing will remain the same, but the reports will be made more uniform between QUASIMEME and WEPAL.
- Sharepoint website; There have been security issues, and the content-user management has to be improved. A new website is being developed and scheduled to be launched in 2012.

4) New developments

Metal rounds (programmes) will be divided into 2 method groups, as different destruction methods result in real totals and in partial digestion.

PFAS and chlorinated paraffins will be incorporated in new programmes. The PFAS exercise will be carried out on a regular basis (BT-10). For chlorinated paraffins, a development exercise is planned (DE-15).

Dispatch dates will be changed to avoid sample dispatch during main holiday periods. April dispatch will be changed to March, and July to August.

Deadlines are fixed from now on, and no extensions will be granted anymore. This means that the QUASIMEME report will be available 1 month after the deadline.

5) New reports

At present, there are still differences between WEPAL and QUASIMEME reports. These will be made more similar in their layout. The following changes will be introduced:

- Permanent lab codes will be assigned. All results will be shown for better comparison between laboratories. Information on analytical methods will be more easily accessible.
- Laboratories are free to choose a lab code or use their own name.

6) Problems and challenges

In round 65, exercise AQ-4 (mercury in seawater), mercury appeared inhomogeneous. In round 67, one bottle was found to be inhomogeneous. The preliminary conclusion is that the cleaning procedure may have caused this inhomogeneity, due to the use of impure SnCl_2 .

In round 66, exercise MS-6 (organotins in sediment), one (natural) sample with a very high concentration was dispatched, but the participants did not report any problems.

7) Announcements

This year, QUASIMEME arranges the following workshops:

- Biotoxins, to be held in Galway, Ireland, 14-15 June 2012.
- Nutrients, in collaboration with MEDPOL.
- Chlorophyll, to be held in Oostende, Belgium, preliminarily scheduled for 24-26 October 2012.

A new participant is required for the scientific assessment group, preferably with an expertise in metals.

QUASIMEME is always interested in possible test materials. QUASIMEME supports a passive sampling project funded by NORMAN.

In the discussion, following Bram Eijgenraam's presentation, MCWG made the following comments:

- Regarding the choice of an anonymous lab code or the use of the laboratory's own name, MCWG members had some doubts about this suggestion. It was stated that laboratories which felt confident of their results, might want to use their own names. As a consequence, the choice of an anonymous code might be perceived as a lack of confidence. It was also mentioned that some laboratories use QUASIMEME for method development and occasionally submit results which are not obtained by fully validated methods. For these cases, anonymity will be preferred.
- Regarding natural samples with very high concentrations (as was the case for MS-6, see above), MCWG wondered about the usefulness of the range

of concentrations which is stated in the protocols. Very high concentrations may result in time-consuming re-analyses, but might also cause technical problems. Too low concentrations may result in no z-score, i.e. no useful result for the participant. MCWG members were of the opinion that analyte concentrations should be within the range given in the protocols.

- MCWG members enquired about tests and analyses prior to sample dispatch. A full target analysis is not done prior to sample dispatch, but for most biota samples, some indicator compounds are analysed. MCWG wondered why this was not the case for sediment samples.
- MCWG members had noted that information on type (species) and origin of sample is no longer provided, nor on approximate lipid content of biota samples. As was explained at MCWG 2011, QUASIMEME chooses not to disclose this kind of information, so previously used samples cannot be identified. However, MCWG felt that information about approximate lipid content and/or levels (which could be derived from the species) should be known by the laboratory, see also comment on ranges in protocols.
- Some MCWG members would be interested in receiving samples during the sampling season of their monitoring programmes. However, others felt that they would not have capacity during the monitoring programmes to accommodate QUASIMEME analyses.
- Norbert Theobald was asked to check PFAS concentrations in marine sediments available at his institute, with regard to suitability as a QUASIMEME test material. Freshwater sediment samples with relatively high PFAS concentrations are available for a potential QUASIMEME exercise on PFAS in sediment.
- MCWG members asked if it was possible to provide the QUASIMEME results in an excel file, so participants can directly use them for their own statistics and calculations. This will be possible in the future.
- Bram Eijgenraam asked about MCWG members' interest in BTEX analyses in seawater.

Denise Smythe-Wright: What do Chlorophyll measurements tell us: best practice for pigment measurements

The determination of chlorophyll as an indicator of primary biomass has underpinned most oceanographic disciplines for many years. In the early 1960s measurements were based on spectrophotometer techniques and these were quickly followed by fluorescence methods. However in the early 1970s the introduction of (High Performance Liquid Chromatography) HPLC showed that chlorophyll degradation products and some carotenoids fluoresce in the same region as the parent chlorophylls. This explained why earlier methods resulted in overestimates due to the presence of pheophytin.

Since the 1970s HPLC technology has moved on and methods improved. This has now resulted in a plethora of chlorophyll data, which unfortunately is not intercomparable. Not only do we have difference between fluorometric and HPLC data, but also experimental studies suggest that acetone extraction can result in only 70% of the pigment being extracted from the detrital material, particularly if extraction time is less than 16 hours and is not accompanied by disruption of the cells and filter paper. Better extraction is achieved with ethanol, but the optimum solvent is 100% methanol, always with extraction time over 16 hours and sonication to macerate the cells.

Other potential pitfalls result from methods of clarification prior to the solute being introduced to the HPLC instrument. Some methods suggest filtration using in line filters attached to a syringe. However evidence suggests that this method also removes some of the pigment signal and that ultra centrifugation is a far superior technique. In addition, the use of different columns can result in the incorrect reporting of allomers. For example, C-18 columns, unlike C-8 columns, do not readily separate divinyl chlorophyll-a from chlorophyll-a and this can lead to large differences in reported values, particularly in the tropics where there is a predominance of the cyanobacteria *Prochlorococcus* which does not contain chlorophyll-a but divinyl chlorophyll-a.

Together all these differences make it difficult to reliably compare chlorophyll and other pigments data and the situation is further compounded when information from fluorescence sensors is included. The latter are calibrated by a variety of methods, often without the necessary metadata

Stefan van Leeuwen: Quality in analysis of PFAS - perspectives from interlaboratory study results

The results of three interlaboratory studies (ILS) on perfluorinated alkylated substances (PFASs) are presented. In addition, a proposal for harmonisation of nomenclature is briefly presented (Buck *et al.*, 2011).

The results of the 1st ILS showed reasonable results for the undisclosed standard, but RSDs up to 250% for fish and a water sample (freshwater). Reasons for these high RSDs are (i) methods were under development and not yet robust, (ii) lack of available good quality standards and internal standards at the time, and the use thereof and (iii) matrix enhancement and suppression in the electrospray ionisation source of the LC-MS instrument.

In a 2nd ILS, two quantification methods were compared, being standard addition and calibration using external standards in solvent. The latter is generally the most applied quantification method, and showed the lowest variance in the results. The RSDs were below 30% for fish but larger for the freshwater sample (up to 70%). This is a substantial improvement compared to the 1st ILS. The main reasons for these improved results were the use of the same standard solution and a wide array of mass labelled internal standards by all laboratories, and the increased knowledge on the behaviour of PFASs in the analytical methods.

Surprisingly, the 3rd ILS showed larger RSDs again in the water sample for several PFASs, which presumably is due to limited use of a wide array of mass labelled internal standards (whereas this was compulsory in the 2nd ILS). Future analytical challenges are the low levels encountered in some marine biota and seawater samples and the analysis of branched isomers. QA/QC tools like certified reference materials, more analytical (internal) standards and frequent interlaboratory studies are needed.

Reference

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S.A., van Leeuwen, S.P.J. 2011. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins, Integrated Environmental Assessment and Management 7 (4), 513–541.

Recommendations:

It is recommended that QUASIMEME includes PFASs in schemes for biota, sediment and seawater in a similar frequency to the brominated flame retardants.

It is recommended that QUASIMEME notes MCWG's comments in this section (5.3) and in section 5.10.4.

Actions:

Norbert Theobald to follow up on QUASIMEME's interest in PFASs in marine sediments.

Katrin Vorkamp to provide MCWG 2012 report to QUASIMEME.

Katrin Vorkamp to add aspects of chlorophyll analysis and related QA/QC to terms of reference for the next meeting.

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

5.4.1 Report on the developments in Water Framework Directive monitoring programmes, including statistical methods for compliance checking of Environmental Quality Standards

Peter Lepom presented an update on a proposed directive amending Directive 2008/105/EC regarding Water Framework Directive priority substances (EC 2011a, 2011b). Key elements of this proposal are:

- 8) The following changes are proposed to existing Environmental Quality Standards (EQS):
 - the water EQS of the following existing priority substances are proposed for update: Anthracene, Fluoranthene, Naphthalene, Polyaromatic hydrocarbons, Polybrominated diphenyl ethers, Lead and Nickel;
 - biota EQS have been developed and are proposed for Fluoranthene, Polyaromatic hydrocarbons and Polybrominated diphenyl ethers, because due to their properties these substances are more easily and reliably measurable in this matrix;
 - existing biota EQS for Hexachlorobenzene, Hexachlorobutadiene and Mercury are maintained, but the water EQS and footnote 9 in Part A of Annex I to Directive 2008/105/EC are deleted because those EQS do not afford adequate protection;
 - Di-(2-ethylhexyl)-phthalate (DEHP) and Trifluralin are proposed to be classified as priority hazardous substances.
- 9) Identification of new priority substances
 - It is proposed to identify the following substances as priority substances: Aclonifen, Bifenox, Cybutryne, Cypermethrin, Dichlorvos, Terbutryn, 17alpha-ethinylestradiol, 17beta-estradiol and Diclofenac, and the following as priority hazardous substances: Dicofol, Perfluorooctane sulfonic acid (PFOS) and its derivatives, Quinoxifen, Dioxins and dioxin-like compounds, Hexabromocyclododecane (HBCDD) and Heptachlor/heptachlor epoxide;
 - Water EQS are being proposed for all the new substances except for Dioxins and dioxin-like compounds. Biota EQS are proposed for Dicofol, PFOS, Dioxins and dioxin-like compounds, HBCDD and Heptachlor/heptachlor epoxide.
- 10) It introduces specific provisions for substances behaving as ubiquitous persistent, bioaccumulative and toxic (PBT) substances whereby chemical

status can be presented separately and monitoring carried out on a less frequent basis than for other priority substances.

- 11) It introduces the concept of a “Watch list” of no more than 25 substance at a time for which member states are obliged to carry out limited monitoring for a 12 month period to provide EU wide data.

In discussion MCWG welcomed the provisions for ubiquitous PBT substances. However, MCWG members expressed concern about the proposed EQS. The group highlighted the comments it had made on EQS proposals in the report of MCWG 2011 and noted that, for the most part, these comments remained valid.

Specifically MCWG 2012 noted that:

- For many substances, the proposed EQS are extremely low and analytical methods are not available to reliably monitor at the required concentrations ($LoQ < 0.3 \times EQS$);
- Many factors affect contaminant concentrations in biota and it is not clear how biota EQS should be applied (e.g. species selection, tissue choice). MCWG noted that the biota EQS in the new proposals refer specifically to fish. For the marine environment mussels are a widely used matrix for monitoring (e.g. shellfish waters directive, OSPAR CEMP) and the proposed EQS should also allow for the monitoring of mussels. While the EQS for mercury is close to mercury levels determined in mussels from unpolluted coastal areas is unlikely to be broadly achievable in fish;
- Some of the proposed EQS values seem to originate from food legislation, e.g. the EQS values for PAH and dioxins in biota, and their relevance in protecting ecological status is unclear;
- Specifically as PAH are readily metabolised in fish, it is generally accepted that PAH monitoring in fish does not provide useful information;
- There are some surprising and questionable outcomes of the EQS derivation process, such as the extremely low biota EQS for brominated flame retardants $0.0085 \text{ ug kg}^{-1} \text{ ww}$.

Additional comments of MCWG 2011 that remain valid are reiterated:

- Dicofol is unstable in water and should not be monitored in this matrix;
- Heptachlor / Heptachlor epoxide are listed with only one EQS instead of two. MCWG also wondered about the scientific basis for this value;
- ΣDDT might be difficult to determine for technical reasons, i.e. low concentrations of o,p'-substituted compounds. Thus, results might be difficult to interpret. It might be more useful to set EQS values for the individual p,p'-substituted DDT and degradation compounds;
- Given the low concentrations in water, EQS should be stated in ng l^{-1} instead of $\mu\text{g l}^{-1}$.

There was discussion in MCWG as to how to ensure that MCWG concerns were reflected back to the relevant EC working group dealing with these issues. It was agreed that individual MCWG members should seek all avenues to highlight concerns on proposed EQS and practical difficulties that are likely to ensue in assessing chemical status under the WFD. MCWG should address these concerns to their national delegates in EC Chemical Monitoring Group and other relevant fora (such as regional sea conventions). The MCWG chair undertook to discuss with ICES secretariat potential other avenues for delivering comments to relevant EC/groups.

References

EC (2011a) COM(2011) 876 final 2011/0429 (COD) Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

EC (2011b) COM(2011) 875 final REPORT FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT AND THE COUNCIL on the outcome of the review of Annex X to Directive 2000/60/EC of the European Parliament and of the Council on priority substances in the field of water policy.

Statistical approaches for compliance checking with Environmental Quality Standards were not discussed as there was no new information.

5.4.2 Report on developments under the Marine Strategy Framework Directive, including information on initial assessments in member states

MCWG members were asked to bring information on developments under the MSFD in their respective country.

In **Germany**, the draft of the initial assessment (IA) report, the description of a good environmental status (GES) as well the definition of the environmental targets were presented on 14 October 2011 and became available for public consultation for a six month period. All reports, both for the North Sea and the Baltic Sea, are in German and can be downloaded from

<http://www.meeresschutz.info/index.php/berichte.html>

The initial assessments according to article 8 of the MSFD are based on recent monitoring information and data, describing the actual status. They include (i) an analysis of the essential physical, chemical and biological properties and characteristics, (ii) an analysis of the main impacts and effects, and (iii) a socio-economic analysis of the actual use and costs of a deterioration of the environment.

Belgium is on schedule both with the IA and the development of GES Descriptors. The draft IA will be available for public consultation in March. Equally, the draft GES Descriptors are being finalised this month. Belgium has opted for a pragmatic, quantifiable approach for its Descriptors, relying as much as possible on existing legislation and approaches (e.g. OSPAR - EcoQOs). For Descriptor 5 (“Eutrophication”) the environmental targets and associated indicators are based on Commission Decision 2008/915/EC for chlorophyll a and *Phaecystis* cells. Nutrient DIN and DIP are based on the OSPAR Common Procedure. For Descriptor 8 (“Contamination”), Belgium will use existing WFD EQS values (in water and biota) for its marine waters and OSPAR EACs (even though they are preliminary) when there are no EQS values available (biota and sediment). For bird eggs, the OSPAR EcoQO will be applied. The contaminants monitored will be the WFD priority substances in the 12-mile zone and OSPAR (JAMP and the Seabird EcoQO) substances in the remaining continental shelf area. For bird eggs, an additional indicator “no difference is measured between Hg concentrations in bird eggs from estuarine and non-industrial zones” has also been defined. Effect measurements have so far been limited to:

- Biota and oil: the average proportion of oiled common guillemots (*Uria aalge*) is below 20 % of the total number found dead or dying on the beaches (OSPAR EcoQO).
- Effects: the average level of imposex is consistent with an exposure to TBT concentration less than the EAC (OSPAR EcoQO).

For Descriptor 9 (“Contaminants in seafood for human consumption”), Belgium intends to check if all measured contaminants in fish and shellfish for human consumption have concentrations below regulatory levels (Commission Regulation 1881/2006 and Directive 2006/113/EC).

It is also worthwhile to note that Descriptors 1, 4 and 6 are dealt with together, due to the strong link and overlap between these Descriptors.

Ireland now has a project in place to deliver the IA and environmental targets. A similar approach to that of Belgium will be taken for the development of GES Descriptors 5, 8 and 9.

United Kingdom has based its IA largely on “Charting Progress 2, The state of the UK Seas” (published in 2010), a comprehensive overview of the state of the marine environment around the UK. In addition, the Marine Scotland Atlas, published in 2011, has contributed to the evidence base of the UK MSFD initial assessment. Several specialised groups for all eleven MSFD Descriptors have developed the GES Descriptors and targets. There are again a lot of similarities with the Belgian approach (WFD EQSs, OSPAR EACs, etc) but the proposed set of indicators is more ambitious. For instance, there is a considerable focus on biological effects measurements and related assessment criteria. As for Belgium, Descriptors 1, 4 and 6 are dealt with together. The document is available for public consultation.

In **Spain**, the law divides the maritime area into five “demarcations” (North Atlantic, South Atlantic, Alboran Sea, Levantino Balear and Canary Islands). Hence, five different IA documents have been prepared, one for each demarcation. They contain the initial assessment, the determination of good environmental status and also, the establishment of environmental targets. Spain used the same approach as in the QSR 2010, to carry out the initial assessment evaluation.

The greatest impacts and problems are found in the coastal zone, particularly in the first miles of the coast. One of the main inconveniences was the lack of information regarding the open sea area, being the largest of the demarcation, but it can be assumed that a good environmental status in coastal water will be reflected in the open sea. All drafts should be completed by March and they will be sent for public consultation in April.

The Netherlands are also developing a very pragmatic approach similar to Belgium and will fit this as much as possible in existing monitoring programmes.

Denmark is currently working on the IA, largely based on information and data of the National Monitoring Programme for Aquatic and Terrestrial Environment. The draft IA is currently being reviewed within the political system and is expected to be available for public hearing in the last week of March.

Sweden will present a draft of the initial assessment report on 19 March 2012, to be available for review.

Katrin Vorkamp informed MCWG about an MSFD-related conference to take place in Copenhagen from 14-16 May 2012. The title of the conference is “The first European Conference on Research and Ecosystem-based Management Strategies in Support of the Marine Strategy Framework Directive” (abbreviated to Marine Strategy 2012). It is organised jointly by ICES, Aarhus University, Danish Hydraulic Institute (DHI) and the University of Copenhagen in collaboration with the Danish Ministry of the Environment. More information is available from <http://marinestrategy2012.dmu.dk>

Katrin Vorkamp also pointed out that the conference co-incided with the 2012 meeting of the Advice Drafting Group on Monitoring to which the chairs of MCWG and WGMS have been invited.

5.4.3 Identify elements of the EGs work that may help determine status for the 11 Descriptors set out in the Commission Decision (MSFDSG request)

MCWG combined this agenda point with the following one (5.4.4 Provide views on what good environmental status (GES) might be for those descriptors, including methods that could be used to determine status (MSFDSG request)).

MCWG initially examined the draft report entitled “DRAFT Overview of ICES work in relation to Marine Strategy Framework Directive” produced by the Marine Strategy Framework Directive Steering Group (MSFDSG). The report compiles comments from expert groups to summarise the ICES expertise in relation to the MSFD. It was suggested that the format of the report might be improved by adding an introduction.

MCWG feels that it has an important role to help determine status for some of the Descriptors. Currently, the draft report includes substantial contributions on Descriptor 3 (“Commercial fish”), while the work and expertise of MCWG can be mentioned under several other descriptors.

Under Descriptor 8 (“Contamination”), MCWG noted that the group – in collaboration with WGMS - had produced a series of guideline documents on contaminant monitoring in the marine environment, such as the JAMP guidelines and several TIMES publications which could also be applied to monitoring under MSFD. MCWG’s expertise in measuring contaminants in water, biota and sediments, in the determination of background concentrations (BCs), and in assessing contaminant levels can be valuable in relation to MSFD, and MCWG can provide advice on these. Furthermore, MCWG has expertise in passive sampling in MCWG. This field of work is an item on the MCWG 2012 Agenda (see section 5.14).

Discussions subsequently progressed to some of the challenges on determining GES. There is a need for targeting analysis to determine what environmental levels mean. The determination of BCs used for assessments is an important and challenging task, and while we have a good handle on BCs in sediment, the task is more difficult for biota. There is a need to establish threshold values, which can be extremely challenging (see section 5.2 on Environmental Assessment Criteria), and will require toxicological expertise.

It was also noted in the discussion that monitoring trends usually focussed on the coast rather than regions, and that there was an issue of scale. In relation to MSFD, there is a need for more data from the open sea. It was suggested that MCWG addressed data from the open sea, including aspects of sampling (e.g. passive samplers) and bioavailability, as a link to the toxicological context.

ICES maintains a substantial database including contaminants and chemical oceanography parameters. MCWG collaborates with the ICES Data Centre (see section 5.6) and has previously worked with the database to extract data for calculations, e.g. developing of BCs. Contaminant data stored in the ICES database can also be used in the future, e.g. for developing and testing tools in relation with MSFD.

For Descriptor 5 (“Eutrophication”), there is currently limited input from other EGs in the draft report, principally contributions from salmon based EGs. Again, the production of guideline documents by MCWG can be included here (See section 5.9 on

JAMP Guidelines on Nutrients and Oxygen). The Group can also provide information on tools for monitoring nutrients and chlorophyll, including Quality Assurance requirements. It can provide advice on phytoplankton, biomass and oxygen.

In terms of challenges under this Descriptor, MCWG discussed that there seemed to be little agreement between countries on setting thresholds.

For Descriptor 9 (“Human consumption”), MCWG can provide advice with regards to contaminants in seafood and seafood safety. There is also an understanding of the geographic origin of seafood and expertise in traceability

Finally, marine litter is a vector for contaminants and an issue that will be taken up by MCWG in the future (Descriptor 10, “Marine litter”).

Actions:

Katrin Vorkamp to contact the chair of MSFDSG to convey MCWG’s input to the MSFDSG draft report.

Katrin Vorkamp to provide draft text to WGBEC, for the WGBEC 2012 meeting.

5.4.4 Provide views on what good environmental status (GES) might be for those descriptors, including methods that could be used to determine status (MSFDSG request)

See section 5.4.3.

5.5 MCWG members to report on projects of interest to MCWG

5.5.1 Stefan van Leeuwen: Monitoring contaminants in (marine) aquatic biota in the Netherlands – RIKILT/IMARES activities

The approach for chemical monitoring of marine biota with respect to food safety by RIKILT/IMARES was presented. The results from this program are evaluated against the applicable legislation (e.g. maximum levels for dioxins and dl-PCBs and heavy metals). The seafood analysed includes popular species like herring, cod, haddock, plaice, sole, mussels and shrimps from the North sea and Atlantic, but also lower volume species like cancer pagurus and imported seafood from Asia. Some freshwater species (mainly eel) are also included in this program. Dioxins, PCBs, PBDEs, OCPs, heavy metals and arsenic are analysed on a yearly basis (monitoring) and PFASs, HBCDDs, TBBP-A, chlorinated paraffins etc are analysed on a survey basis. The program is operated by IMARES (responsible for design, sampling and pre-treatment) and RIKILT (responsible for chemical analysis and reporting).

5.5.2 Katrin Vorkamp: Chemical fingerprinting as a method of tracing fish migration

Little is known about populations of migratory fish at sea, e.g. Atlantic salmon and anadromous brown trout (see also Section 4.2). The main growth of these fish species takes place in the sea and fish take up persistent organic pollutants (POP) while feeding. Therefore, it was hypothesized that the POP profile in the fish, upon return to its natal river, reflects the main feeding grounds of the fish.

This hypothesis was confirmed initially for four populations of Atlantic salmon for which different feeding grounds were known (Lake Vänern and Lake Vättern in Sweden, North Atlantic and Baltic Sea). A case study with Atlantic salmon from the Danish river Gudenå showed that the POP profile in these fish resembled those from the North Atlantic rather than those from the Baltic Sea, suggesting the North Atlantic as their main feeding area.

As a potential confounding factor, the influence of trophic level on the POP profile was studied for a Baltic Sea food chain. Variations in POP profile were similar to those between different locations, confirming that trophic level is an important factor to consider in chemical fingerprinting approaches. It was also studied whether sediment samples could provide a location-specific profile to compare against patterns in fish, but POP concentrations were too low to allow pattern analyses.

Differences in POP profiles were studied for flounders from five locations around Denmark. Although the flounders were not genetically different, they had location-specific POP profiles. Validation data showed correct classification of >90% of the fish to the correct location. This study showed that the chemical fingerprinting approach could also be applied on the relatively small geographical scale of the Danish waters.

Recently, data have been obtained for strontium/calcium ratios in brown trout scales to study their variation in relation to the salinity of the water. Sr variations within a fish scale have been studied as well to establish a temporal gradient, but preliminary results indicate that typically marine and freshwater signals cannot be distinguished.

References

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5.6 ICES Data Centre

5.6.1 Provide expert knowledge and guidance to the ICES Data Centre as may be required

The following task was given to MCWG, following a recommendation of the Study Group on Integrated Monitoring of Contaminants and Biological Effects (SGIMC):

"That the seawater contaminants section of the ICES database should be reviewed, in collaboration with the ICES Data Centre, and updated, giving particular attention to parameter fields, station names/locations, gross errors (e.g. units), uncertainty in identification of contaminants, and the opportunity for improving the QA of data being submitted, for example through automated checking of data at the time of entry, with a view to the seawater data becoming more available for assessment in MSFD and other contexts."

It was discussed with Marilynn Sørensen of the ICES Data Centre prior to the meeting how this recommendation should be approached. Marilynn Sørensen provided a list of parameters and their concentrations in seawater (excel file "sea-

water_ranges_percentiles”) and maps with the geographical data coverage of various compound groups in seawater. It was agreed prior to the meeting that as a starting point, MCWG should focus on the parameter lists and on possibilities to check gross errors in the database.

MCWG has compared the parameter list provided by Marilynn Sørensen with the list of priority substances according to WFD (Directive 200/105/EC), the list of parameters to be measured in seawater according to the HELCOM Combine Programme and OSPAR CEMP. Compounds to be measured in the above programmes have been indicated by “x” in the excel sheet “ICES request” and those not currently included in the excel sheet have been identified (Annex 8). The following compounds are not currently present on the compound list:

Programme	Compounds
WFD	Alachlor, Benzene, SumDDT (p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD)
HELCOM-COMBINE	PAH
OSPAR CEMP	There is no requirement to analyse seawater for any of the hazardous substances except PFOS (OSPAR Pre-CEMP)

The data extracted from the data base contain the column “Basis”. In case of water data this field is an optional field. Normally, “W” is entered, if not, NULL appears automatically. MCWG observed that in extractions from the data base which include the column “Basis”, two data sets might be retrieved for the same population of data (the same matrix).

MCWG suggests automatically entering “W” in column “Basis” instead of “NULL” in case “AF” or “BF” have been entered in the matrix field even if the field “Basis” is left empty by the data submitter, if the field is not made mandatory.

As contaminant concentrations are specific for a certain sampling location, comparing the submitted value at the time of entry, e.g. with the average of the reported concentrations at the relevant station of the last five years might be an option for checking plausibility of reported data and identifying gross errors.

MCWG suggests that any value greater than twice or less than half of the average of the last five years should trigger an alert to the submitter of the data.

Fields to be included in standard extraction of contaminant data in seawater:

NoMeasurements

MinValue

AvgValue

MaxValue

50% percentile

MUNIT

PARAM

MATRX

BASIS

The following columns were included in the data extraction for seawater, but are considered additional information, beyond a standard extraction of contaminant data in seawater:

2xStdev

1% percentile

5% percentile

10% percentile

90% percentile

95% percentile

99% percentile

MCWG further considered that standard unit for contaminant concentrations in seawater should be ng/L instead of µg/L. Standard unit for contaminant concentration in SPM should be ng/g instead of µg/g.

Standard extractions for contaminants concentrations in SPM should include information on organic carbon content (CORG) as well as SPM content in the water sample, if available.

Recommendation:

It is recommended that the ICES Data Centre notes MCWG's suggestions and reports back to MCWG whether the SGIMC recommendation can be closed.

5.6.2 Report on developments in EMODNET, in particular on intersessional MCWG subgroup activities regarding EMODNET

MCWG was not aware of new developments of relevance for MCWG. Katrin Vorkamp had contacted Marilyn Sørensen prior to the meeting who had confirmed that there was no reason to bring in MCWG at the moment.

MCWG confirmed its subgroup for future work on EMODNET: Carlos Borges (expertise: nutrients), David Hydes (expertise: nutrients) and Patrick Roose (expertise: organic contaminants). Katrin Vorkamp asked to be kept informed as well.

MCWG would like to emphasize that the group also is interested in nutrients, besides its expertise in organic contaminants and metals.

5.7 Describe MCWG interests and activities on the interface to other expert groups (e.g. WGMS, WGEel, WGBEC, SGIMC, SGONS)

SGONS

David Hydes gave an update on SGONS activities with regard to MCWG interests. Funding was discontinued after a period of two years, but group members have continued their work on the use of certified reference materials (CRM) for nutrient analyses in seawater. CRMs have been produced by the factory in Japan and have formed the basis for intercalibration studies. Currently, about 80 laboratories participate in a global intercalibration exercise including nitrate, nitrite, silicate, phosphate and ammonia as minimum parameters. The last intercalibration was very successful, but laboratories do not necessarily use CRMs on a routine basis.

As discussed by MCWG 2011, CRMs will be needed to support monitoring in north Atlantic shelf seas. However, currently available CRMs seem to have a bias towards

lower concentrations (e.g. Pacific water) or higher concentrations (e.g. surface waters), while the intermediate concentrations are missing. The Japanese work on this was interrupted by the 2011 earthquake, but MCWG will re-address this issue. David Hydes and Patrick Roose, as members of both EGs, will facilitate links.

MCWG's review and update of the JAMP guidelines on nutrients (see Section 5.9) will ensure consistency with the GO-SHIP manual developed by SGONS.

WGMS

MCWG and WGMS have worked and continue to work closely together. Current joint projects are the TIMES manuscripts for dioxins (in press) and PCBs (see Section 5.16). Following WGMS's request for deep core sediment data, MCWG member Stepan Boitsov had provided data on parent and alkylated PAHs and heavy metals from dated sediment cores in the South-Western Barents Sea and the North-Eastern Norwegian Sea collected by the Institute of Marine Research in Norway and the Norwegian Geological Survey under the Norwegian MAREANO programme.

Patrick Roose gave an update on WGMS activities of relevance for MCWG. WGMS is currently working on an OSPAR request on the spatial design of a regional monitoring programme of contaminants in sediment, which might be interesting for MCWG to review. WGMS is also going to address passive sampling at their forthcoming meeting, which adds to MCWG's discussions of passive sampling (see Section 5.14). It was discussed at MCWG 2011 if passive sampling in the context of a monitoring application, should be addressed in a joint publication by MCWG, WGMS and possibly, WGBEC (see Section 5.14).

Patrick Roose enquired whether a joint meeting of MCWG, WGMS and WGBEC would be of interest to MCWG. This was generally confirmed, provided that there are common agenda points and projects.

SGIMC

Katrin Vorkamp had attended the SGIMC 2011 meeting for one day and presented the SGIMC 2011 report to the group. The study group had dealt with 25 biological effect techniques to be included in marine monitoring in an integrated way.

Background Documents were produced for all parameters and Assessment Criteria were developed, in terms of Background Assessment Concentrations (BACs) for all parameters, and Environmental Assessment Concentrations (EACs) for some. Those parameters for which EACs were available, were considered "Biomarkers of effect", while parameters with only BACs were regarded as "Biomarkers of exposure". A table with an overview of all biological effect techniques and their status with regard to Background Documents, Assessment Criteria and Quality Assurance (QA) is provided in the report as Annex 22 (SGIMC 2011 report).

SGIMC 2011 also produced draft guidelines for the integrated monitoring of contaminants and their effects (Annex 21 of the SGIMC 2011 report). These guidelines describe the simultaneous measurements of contaminant concentrations, biological effect parameters and supporting data. Ideally, biota, sediment and water samples should be collected from the same station and at the same point of time. Several figures illustrate the integration across matrices as well as parameters (e.g. Figure 7, Annex 21 of the SGIMC 2011 report: Sampling strategy for integrated fish monitoring).

The report also includes a technical annex describing an integrated assessment framework for contaminants and their biological effects (Annex 25 of the SGIMC 2011 report). A multi-step approach is suggested, using a “traffic light” system for biological effect parameters in the same way as for contaminant concentrations, i.e. individual parameters are assessed against assessment criteria (BACs or EACs). These can then for example be summarised for a given site, across matrices and parameters.

SGIMC 2011 also considered this approach suitable for determining Good Environmental Status (GES) under the Marine Strategy Framework Directive (MSFD) (Chapters 8 and 12, Annexes 21 and 24 of the SGIMC 2011 report). They suggest using proportions of determinands < EACs to determine GES, e.g. 95% compliance.

In the subsequent discussion, MCWG agreed with the usefulness of this complementary approach: Since only limited numbers of contaminants can be monitored, measurements of biological effects can give an extra indication of potential health impairment of ecosystem health. However, MCWG wondered about the high number of biological effect techniques to be applied on a routine basis. Questions were asked about redundant information and about broad applicability of the biological effect techniques, for example EROD might not be sensitive enough for the low concentrations in the open sea. MCWG assumed that this kind of detailed information was given in the Background Documents which were not discussed at the meeting.

With regard to Descriptor 8 of the MSFD, MCWG did not agree with the statement “It is clear that assessment for Descriptor 8 will require both chemical and biological effect measurements.” (SGIMC 2011 report Chapter 8 and Annex 21). The MSFD text “Concentrations of contaminants are at levels not giving rise to pollution effects” is interpreted by MCWG in a way that concentrations of contaminants and assessment criteria would be sufficient for assessments under Descriptor 8. MCWG considered biological effects measurements relevant for assessments of the general health status of the sea, but not a direct requirement under Descriptor 8. Here, biological effect measurements should be focussed on those parameters that have a direct link to chemicals and their concentrations, i.e. TBT.

WGBEC

WGBEC had largely been involved in SGIMC’s work and prepared a number of the annexes published with the SGIMC 2011 report.

Matt Gubbins, the co-chair of WGBEC, and Katrin Vorkamp met at the WGCHAIRS 2012 meeting and discussed agenda points of mutual interests to WGBEC and MCWG. Several items co-occurred in ToRs of both groups, to be approached from different angles (e.g. EAC review, see section 5.2; MSFD, see section 5.4; Passive sampling, see section 5.14). Matt Gubbins and Katrin Vorkamp discussed to what extent combined outputs could be produced by WGBEC and MCWG, but agreed that the groups lacked a common forum for joint working and discussion of these outputs. Instead, it was agreed that MCWG would provide draft text to WGBEC for the WGBEC 2012 meeting, on those items that WGBEC is going to address as well. These draft texts are forwarded as input for the WGBEC discussions, not as part of a joint MCWG/WGBEC output.

With regard to the EAC review, Patrick Roose informed MCWG that the relevant toxicological data might be available, but were not readily accessible (see section 5.2). MCWG discussed that advice was needed on the toxicological meaning of contaminant concentrations and that this could be a field of collaboration with WGBEC. MCWG also discussed the relevance of a publication on the EAC development and

review process, including a critical data analysis and describing possibilities and limitations. Patrick Roose will take this forward and contact other groups where relevant.

With regard to passive sampling, MCWG discussed the relevance and possibility of a publication on passive sampling in a monitoring context (see Section 5.14), in terms of a joint project with WGMS and WGBEC.

Matt Gubbins had informed Katrin Vorkamp about WGBEC's collaboration with WGEel with regard to effects on contaminants and asked if MCWG would be interested in contributing to this collaboration. MCWG confirmed this interest, but will need more information about the data that are available and the data analyses that WGEel already has conducted. Michiel Kotterman is also a member of WGEel and will provide more information for MCWG (see Action List).

MCWG members expressed interest in discussing marine litter in relation to contaminants at MCWG 2013. As this was on the agenda for WGBEC 2012, MCWG would be interested in seeing WGBEC's work on this topic.

MCWG agreed that a joint meeting with WGBEC (and WGMS) would be beneficial for the work on common projects and publications as well as overlapping agenda items. This could be considered for 2014, provided the groups identify sufficient agenda points of mutual interest and advisory tasks allow for this combined work.

WGEel

Michiel Kotterman presented information from the last meeting and intersessional work of the WGEel. With approximately 45 participants at the meetings, the WGEel is a large expert group. It is divided into several subgroups one of which is the "Eel Quality" group which deals, inter alia, with contaminants in eel. This subgroup runs the Eel Quality Database with European wide coverage of contaminants in eel. If MCWG members are aware of new data, including compounds which are not commonly monitored, this would be of interest to WGEel.

Although contaminants have been monitored extensively in eels, links with biological and ecological effects are not established. Eel stocks have declined over the last few decades, but so have concentrations of persistent organic pollutants. WGEel will collaborate with WGBEC on contaminant effects on eels. WGBEC had also suggested that MCWG contribute to this collaboration, see above. MCWG is interested in working with the eel contaminant data, but will need more information on data availability and accessibility as well as previous data analyses by WGEel or other groups. Michiel Kotterman will provide more information for MCWG (see Action List).

David Hydes suggested contacting further expert groups in the field of hydrography, which might work on the interface to COSG. Katrin Vorkamp will follow up on this.

Actions:

Michiel Kotterman to contact Claude Belpaire (Chair of WGEel subgroup on Eel Quality) about contaminant data on eel.

Katrin Vorkamp to provide draft text of Section 5.2 (Review of Environmental Assessment Criteria) to WGBEC, for the WGBEC 2012 meeting.

Katrin Vorkamp to provide draft text of Sections 5.4.2, 5.4.3 and 5.4.4 (Marine Strategy Framework Directive) to WGBEC, for the WGBEC 2012 meeting.

Katrin Vorkamp to provide draft text on Section 5.14 (Passive sampling) to WGBEC, for the WGBEC 2012 meeting.

Patrick Roose and Katrin Vorkamp to contact WGMS and WGBEC, respectively, to hear about interest in a joint publication on passive sampling in a monitoring context.

Patrick Roose to develop a structure for a publication on the development and review of environmental assessment criteria, including for example a critical data analysis and discussions of possibilities and limitations.

Patrick Roose and Katrin Vorkamp to suggest a joint meeting in 2014 to WGMS and WGBEC, respectively.

Katrin Vorkamp to present WGBEC's work on marine litter at MCWG 2013.

David Hydes to inform SGONS about MCWG's interest in certified reference materials to support monitoring of nutrients in north Atlantic shelf seas.

Katrin Vorkamp to gather information on ICES expert groups on the interface to MCWG's chemical oceanography work and to establish contacts where relevant.

5.8 Evaluate potential for collaboration with other EGs in relation to the ICES Science Plan and report on how such cooperation has been achieved in practical terms (e.g. joint meetings, back-to-back meetings, communication between EG chairs, having representatives from own EG attend other EG meetings).

See 5.7.

5.9 Revision of JAMP guidelines on nutrients and oxygen (OSPAR request 2009/6)

OSPAR made two requests to ICES under the 2006 and 2009 annual ICES Work Programmes relating to the review and as necessary update of the JAMP monitoring guidelines for nutrients, chlorophyll, oxygen and benthos. OSPAR wish to request the completion of the revision of the JAMP monitoring guidelines for nutrients and for oxygen. This should be based on, as deemed relevant:

- **comments on current nutrient and oxygen guidelines as submitted to OSPAR by Contracting Parties;**
- **comments on sampling, storage and pre-treatment submitted by ICES (ICES Advice 2009 Book 1 1.5.5.4);**
- **any pertinent development relating to MSFD Good Environmental Status Descriptor 5 and specifically determination of nutrients and oxygen in the water column;**
- **any other information that ICES may consider of relevance.**

MCWG 2009 revised the JAMP guidelines for nutrient and oxygen monitoring following a request from OSPAR for additional information on specific sections. The Advice Drafting Group (ADG) in 2009 decided, as a consequence of possible changes resulting from the MSFD, that only elements of the MCWG 2009 guidelines should be passed on.

MCWG 2012 was asked to complete the revision of the two guidelines taking into account the comments of the contracting parties. OSPAR contracting parties had commented on the original guidelines and not the MCWG 2009 revised guidelines. After discussion COSG updated the guidelines (Annexes 9 and 10) for both oxygen and nutrients, taking into account the views of contracting parties and whilst also considering implications of MSFD. The group felt that some comments of the contracting parties were already adequately covered in the revised guidelines, and some comments were too specific to be included in the guidelines.

As outlined at MCWG 2011, MCWG also considered the review comments and included information provided by the IOC-ICES Study Group on Nutrients Standards (SGONS) and the recently published GO-SHIP repeat hydrography manual.

5.10 Ocean acidification (OA)

Evin McGovern reported on the status of ICES advice on ocean acidification as drafted by the MCWG 2010 and other working groups in response to an OSPAR request. Advice was submitted to OSPAR in 2010 but due to time constraints and OSPAR restructuring, the report was not considered in detail at technical committee level. A further document from UK, Norway and Sweden was submitted to OSPAR which drew on ICES advice and also included draft OSPAR monitoring guidelines for carbonate parameters. OSPAR's MIME working group has proposed that monitoring for carbonate parameters should be included in the OSPAR monitoring programme (CEMP) and this will be considered at HASEC in February 2012.

Katrin Vorkamp commented that in 2010, MCWG proposed that an OSPAR-ICES study group should be set up for OA. MIME has also proposed an OSPAR-ICES study group on Ocean Acidification with defined terms of reference many of which the COSG could contribute to, such as development of monitoring guidelines. It is hoped that the new study group will maintain close links with the MCWG.

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

Evin McGovern (Ireland) reported on a joint Irish Marine Institute and National University of Ireland, Galway project. Total alkalinity (AT) and dissolved inorganic carbon (CT) were sampled across the Rockall Trough in Feb 2009 (CE0903) and Feb 2010 (CE10002) as part of a baseline study of inorganic carbon chemistry in Irish shelf waters. The results were compared with data from WOCE surveys A01E (Sept 1991), A01 (Dec 1994), AR24 (Nov 1996), and A24 (June 1997). The 2009 and 2010 datasets provide a baseline of inorganic carbon and acidity levels in surface waters of the Rockall Trough in late winter for future comparison. The temporal evolution of anthropogenic carbon (ΔC_{ant}) between the 1990s and 2010 was evaluated using two separate methods; (i) a comparison of the concentrations of CT between surveys, after correcting it for remineralisation and formation and dissolution of calcium carbonate (ΔCT_{-abio}) and (ii) an extended Multiple Linear Regression was used to calculate the ΔC_{ant} between 1991 and 2010 ($\Delta C_{anteMLR}$).

There was an increase in ΔCT_{-abio} and $\Delta C_{anteMLR}$ of $18 \pm 4 \mu\text{mol kg}^{-1}$ and $19 \pm 4 \mu\text{mol kg}^{-1}$, respectively, in the subsurface waters between 1991 and 2010, equivalent to a decrease of 0.040 ± 0.003 pH units over the 19 year period. There was an increase in both ΔCT_{-abio} and $\Delta C_{anteMLR}$ of $8 \pm 4 \mu\text{mol kg}^{-1}$ in Labrador Sea Water (LSW) in the Trough between 1991 and 2010, and LSW has acidified by 0.029 ± 2 pH units over the same time period. Reduced calcite and aragonite saturation states may have implications for calcifying organisms such as cold water corals in the region.

Reference

McGrath, T., Kivimae, C., Tanhua, T., Cave, R. and McGovern, E. Inorganic carbon and pH levels in the Rockall Trough 1991-2010. Deep Sea Research Part-I. In review.

Elisabeth Sahlsten (Sweden) reported that development work on new spectrophotometric and fluorometric methods for pH determination have continued with some method developments together with field studies. The fluorometric method is currently being used together with a $p\text{CO}_2$ -system on a Ferrybox system.

Klaus Nagel (Germany) reported that they have one staff member working on testing different methods for measuring pH but the theory behind the results is not yet clear. The calculations necessary for comparing the results are not established yet.

MCWG remarked that this section and previous work on information available on ocean acidification (MCWG reports 2010 and 2011) could be useful for the ICES/OSPAR study group, in particular regarding its term of reference “**i. collate data and information on ocean acidification in the Convention area**”.

Recommendation:

It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the information given by MCWG 2012 (as well as MCWG 2010 and 2011) with regard to data and information on ocean acidification in the Convention area.

5.10.2 Review new information for determination of pH and carbonate parameters in estuarine and brackish water and the associated calculations

Millero *et al.* (2006) and Millero (2010) have published dissociation constants of carbonic acid in seawater as a function of salinity and temperature which extend over the whole salinity range. They have been included in version 16 of the CO2sys excel version (<http://www.ecy.wa.gov/programs/eap/models.html>). There is also a new program (AquaEnv, Hofmann *et al.*, 2010) which has been used for data collected at low salinities in the Baltic Sea. It includes acid-base systems that are important in anoxic and euxinic systems (with hydrogen sulphide). The latest version (2.3.3) of Seacarb (<http://CRAN.R-project.org/package=seacarb>) may be considered as an alternative to CO2sys in open oceans. Among its benefits, its latest version (2.3.3) includes the most up to date dissociation constants for K1 and K2 of Millero *et al.* (2006) and Millero (2010). Because different pH-scales are in use for pH-determination in marine water, comparability of the results is limited to some extent. To overcome this disadvantage, one topic of the ENV05 OCEAN Project 'Metrology for oceanic salinity and acidification' is the definition of a pH-scale which is retraceable to SI unit system. This EU project will also be relevant for the OSPAR/ICES study group under their term of reference “**ii. liaise with EU projects on Ocean Acidification**”.

References

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- Millero F. J. 2010. Carbonate constant for estuarine waters. *Marine and Freshwater Research* 61: 139-142.

Recommendation:

It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the information given by MCWG 2012 (as well as MCWG 2010 and 2011) with regard to EU projects on Ocean Acidification.

5.10.3 Report on latest developments in *in situ* chemical oceanographic sensor

This was discussed as part of the update of the draft manuscript on OA for publication as a Cooperative Research Report (CRR) (see section 5.10.6). Details of the SeaFET pH sensor were added to the CRR. A new promising fluorometric approach is being developed (Hulth *et al.*, 2002; Hakonen and Hulth, 2008, 2010; Hakonen *et al.*, 2010) to determine pH in a continuous mode. This involves immobilization of a fluorescent dye on a film which is exposed to a continuous flow of seawater, and the resulting fluorescence emission is recorded with a CCD camera. Due to the size of the film a large number of spectra can be recorded per time interval, each of them having an individual calibration. With this system problems of low buffering capacity (and of other confounding factors such as humic substances) are minimized.

References

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5.10.4 Discuss the need for and feasibility of proficiency testing for carbonate parameters (total alkalinity and dissolved inorganic carbon)

Discussions took place with Bram Eijgenraam (QUASIMEME) regarding the feasibility of producing test materials for TA and DIC for proficiency testing within QUASIMEME (see also Section 5.3). It was confirmed by MCWG members that stable test materials can be produced (Prof. Andrew Dickson, Scripps Institution of Oceanography, University of California, San Diego, USA. <http://andrew.ucsd.edu/>).

MCWG proposed that an expert could be provided to advise QUASIMEME after upcoming meetings of international experts (SCOR-ICES working group on nutrients, ICOS Ocean Thematic Centre). QUASIMEME can email potential participants if contacts for potential participating laboratories can be provided and proposed that test materials could be prepared for 2013. There is a need to encourage laboratories across government and research institutions to participate.

Recommendation:

It is recommended that the OSPAR/ICES study group on Ocean Acidification notes this initial discussion with QUASIMEME regarding development of proficiency testing schemes for carbonate parameters.

Action:

Katrin Vorkamp to provide MCWG 2012 report to QUASIMEME.

5.10.5 Review progress on interconnectivity of databases with respect to carbonate system data

MCWG discussed the issue of submission of data to various databases. In a previous international carbon programme, ICES was the data coordinator and therefore may be able to accept carbon data. The project CarboChange has a data manager who may be able to advise. It is felt that institutes would only wish to report their data once i.e. to ICES and that it would then be extracted from ICES to CDIAC. MCWG wondered if the ICES database could take underway type measurements. If not, these would need to be submitted directly to CDIAC.

Action:

Katrin Vorkamp to contact the ICES Data Centre with regard to submission of carbonate system data.

5.10.6 Finalise manuscript on ocean acidification in view of publication as an ICES Cooperative Research Report (CRR)

MCWG updated the draft CRR with new information. The report needs editing by group members; relevant people have been identified for each section and Pamela Walsham will coordinate this to ensure it is complete for July 2012.

Recommendation:

It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the material the CRR draft manuscript submitted to ICES by MCWG.

Action:

COSG members to complete work on respective sections of the CRR draft manuscript and forward input to Pamela Walsham.

Pamela Walsham to submit CRR draft manuscript to ICES by July 2012.

5.10.7 Contribute to OSPAR draft guidelines on ocean acidification

The draft OSPAR guidelines for the monitoring of chemical aspects of ocean acidification were reviewed by MCWG and changes made to the document (Annex 11). This review is directly relevant for the OSPAR/ICES study group and their term of reference “**iii. finalise guidelines for measuring carbonate system**”.

Recommendation:

It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the draft guidelines on ocean acidification in the version reviewed and updated by MCWG 2012.

Action:

Katrin Vorkamp to forward draft guidelines on Ocean Acidification to HASEC 2012, as reviewed and updated by MCWG 2012.

5.11 Contribute, as may be required, to ICES activities on integrated chemical and biological effects monitoring and review new information on effect directed chemical analysis

Patrick Roose: Integrated risk assessment and monitoring of micropollutants in the Belgian coastal zone (INRAM)

Patrick Roose presented the final report of the Belgian INRAM project which had been completed in June 2011 (<http://www.vliz.be/projects/inram>). The project inte-

grated chemical analyses of contaminants in the marine environment with biological effect measurements. It focussed on harbours on the Belgium coast, with additional coastal stations also covered by regular monitoring programmes.

The chemical part included an array of compounds (pharmaceuticals, perfluorinated compounds, pesticides, organotins, PAHs, PCBs etc.) analysed in water, suspended particulate matter and/or sediments. In addition to conventional sampling, passive samplers were used for the determination of time-integrated freely dissolved water concentrations. Examples were shown for PAHs which showed good agreement of both methods at some stations, but not consistently.

Passive samplers were a central element in this project as the same samplers used for time-integrated contaminant collection were also used in ecotoxicity tests ("passive dosing"). Despite similar concentrations of e.g. PCBs at several stations, effects were not repeatable, possibly indicating other influences on study organisms. Experimental results need validation through pure chemical assays, which allow comparisons with responses in the field studies.

An equilibrium partitioning model was developed which linked concentrations in the environmental compartments (sediment, water, biota) with those of the passive sampler and eventually, the effects of contaminants. Thus, the passive sampler works as a reference phase which both environmental compartment concentrations and effects can be referred back to.

It was discussed by MCWG 2012 if equilibrium can always be assumed. This depends on the compound, but it seems possible that equilibrium is not always reached in the toxicity tests. This might lead to an underestimation of effects, due to concentrations in water which are below equilibrium concentrations. Deviations from equilibrium concentrations in biota also occur in cases of biomagnification.

Reference

Janssen, C., Roose, P., De Brabander, H., Vincx, M., Mees, J. 2010. Integrated risk assessment and monitoring of micropollutants in the Belgian coastal zone – INRAM. Final Report Phase 1. Brussels, Belgian Science Policy, Research Programme Science for a Sustainable Development. 53 p.

For discussion of the ICES activities on integrated chemical and biological effects monitoring in terms of outcomes of the Study Group on Integrated Monitoring of Contaminants and Biological Effects (SGIMC), see section 5.7 (Other expert groups).

5.12 Emerging contaminants

5.12.1 Report on new information regarding emerging contaminants in the marine environment

There was no new information to be presented under this agenda point.

5.12.2 Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment

Norbert Theobald and Katrin Vorkamp presented work on perfluorinated compounds (PFCs) on behalf of Zhiyong Xie who was unable to attend MCWG 2012. The presentation was entitled "Atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment" by Ralf Ebinghaus and Zhiyong Xie.

The following text was provided by Zhiyong Xie for MCWG 2012 and includes the literature review presented at MCWG 2011 and new information on this agenda point:

PFCAs and PFSAAs can be transported directly by oceanic currents or indirectly by neutral, volatile precursors, such as fluorotelomer alcohols (FTOHs), fluorinated sulfonamides (FOSAs), and sulfonamido ethanols (FOSEs), that could undergo long-range atmospheric transport and be degraded in remote regions to PFCAs and PFSAAs (e.g. Ellis *et al.*, 2004; Armitage *et al.*, 2006; McMurdo *et al.*, 2008). For example, PFCAs and PFSAAs have been detected in Arctic snow samples, which indicates a direct atmospheric deposition of these compounds or a degradation of their volatile precursors (Young *et al.*, 2007).

Air concentrations of neutral and volatile precursors (FTOHs, FOSAs and FOSEs) were measured in the Pacific and Arctic Oceans in 2010 to 2011. The median concentration of 8:2 FTOH is 123 $\text{pg}\cdot\text{m}^{-3}$ in the Northern Hemisphere and 74 $\text{pg}\cdot\text{m}^{-3}$ in the Southern Hemisphere (Cai *et al.*, 2012), which are ~20 times higher than those present in the Atlantic (8.4 $\text{pg}\cdot\text{m}^{-3}$ in 2008) and East Greenland Sea (2.9 $\text{pg}\cdot\text{m}^{-3}$ in 2009) (Xie, unpublished data), while concentrations of FOSAs and FOSEs are comparable in global oceans. In the Canadian Arctic, Ahrens *et al.* (2011a) reported average concentrations of 40–49 $\text{pg}\cdot\text{m}^{-3}$ for 8:2 FTOHs, 0.1–3 $\text{pg}\cdot\text{m}^{-3}$ for FOSAs and 1.0–13 $\text{pg}\cdot\text{m}^{-3}$ for FOSEs. More recently, relatively high levels of neutral and volatile precursors were measured in air in Asia, with median concentrations range from 48 (India) to 121 pg/m^3 (Japan) for 8:2 FTOH, from 11 (Japan) to 13 $\text{pg}\cdot\text{m}^{-3}$ (China) for FOSAs and 18 (Japan)-37 $\text{pg}\cdot\text{m}^{-3}$ (China) for FOSEs (Li *et al.*, 2011).

Information on environmental levels of PFOS and PFOA in the gas phase of the marine environment is very scarce. Ahrens *et al.* (2011b) studied the water to air transport of PFOA, PFOS and other PFASs over wastewater treatment plants (WWTP) and landfills in Canada. Concentrations over WWTP ranged from 43 to 171 $\text{pg}\cdot\text{m}^{-3}$ for PFOSs and 455–116 $\text{pg}\cdot\text{m}^{-3}$, indicating WWTP is a source to the atmosphere. However, the long-distance atmospheric transport of WWTP related to PFCA and PFSA is uncertain.

Particle phase related PFOS and PFOA have been reported for inland areas, e.g. 0.4–1.6 $\text{pg}\cdot\text{m}^{-3}$ for PFOS and < 0.2–2.6 $\text{pg}\cdot\text{m}^{-3}$ for PFOA in urban aerosols collected in metropolitan Hamburg (Jahnke *et al.*, 2007a), <1.8–46 $\text{pg}\cdot\text{m}^{-3}$ for PFOS and 1.4–552 $\text{pg}\cdot\text{m}^{-3}$ for PFOA in the UK (Barber *et al.*, 2007). In the marine environment, concentrations of PFOS and PFOA in the particle phase were close to method detection limits reported in the literatures (<0.8 $\text{pg}\cdot\text{m}^{-3}$ for PFOA in the Arctic (Ahrens *et al.*, 2011a) and 0.9 $\text{pg}\cdot\text{m}^{-3}$ for PFOS and 1.0 $\text{pg}\cdot\text{m}^{-3}$ for PFOA in the Atlantic Ocean (Jahnke *et al.*, 2007b)), which implies the data are highly uncertain. Although aerosol-mediated transport of PFCAs and PFSAAs has been considered as a potential pathway of long-range transport, knowledge of the importance of long-range atmospheric transport on sea-spray in relation to other potential transport pathways is still very limited (Jahnke *et al.*, 2007; Barber *et al.*, 2007; McMurdo *et al.*, 2008; Webster *et al.*, 2010).

Based on a model exercise, Webster and Ellis (2010) concluded that direct PFOA/PFOS transport in aerosols did not contribute significantly to the occurrence of these compounds in remote regions. However, gas-phase PFOA released from oceans may help to explain observed concentrations in remote regions. This model result is supported by recent experimental data. Chaemfa *et al.* (2010) published evidence of atmospheric transport of PFOS and PFOA based on passive air sampling, in particular for PFOA in samples taken close to the coastline of the North Sea. Furthermore

they concluded that there is reasonable level of agreement between their observed distributions and levels with the few published data from active samplers.

In a very recent study, Reth *et al.* (2011) have published evidence derived from an experimental sea spray simulator, that perfluorinated alkyl acids (such as PFOA and PFOS) are effectively transferred from water to air, indicating that these compounds can have potential for long range atmospheric transport. The authors also point out and conclude that before a semi-quantitative assessment can be undertaken, further research must be conducted to explore the effects of other sea-water constituents on the transfer efficiency and to validate the sea spray simulator experiments under natural marine conditions (Reth *et al.*, 2011).

However, uncertainties in the flux estimates are large and continued laboratory and field studies are required to understand the mechanisms responsible for the fluxes of PFCs between the atmosphere and aqueous systems. Innovatively sampling technologies for determination of PFOS and PFOA and other PFCAs in gas phase should be developed for elucidating gas-particle partitioning of PFCAs (Ahrens *et al.*, 2011c, Cousins *et al.*, 2011).

In summary, pathways for long range atmospheric transport of either PFCs or precursor compounds are not fully understood today, including the role of sea spray.

References

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Evin McGovern informed that Norway had been investigating the role of atmospheric transport and deposition of PFOS and other PFCs to the marine environment since 2008, under their atmospheric monitoring programme. A report has been produced, albeit in Norwegian and currently not translated.

For the last 3 years, MCWG has reviewed information on PFCs in atmosphere. The information reviewed is still not conclusive with regard to a link between atmospheric PFC levels and those in biota and the marine environment. Information on fluxes and deposition is needed. Investigation into transport mechanism would be interesting, and some of this has been done in sea spray studies but more work is required.

MCWG discussed whether or not this item should remain on the agenda and whether the information gathered in the last three years should be compiled in a report. MCWG 2012 decided to keep the item on the agenda and to consider a combined report.

Action:

Katrin Vorkamp to contact Ralf Ebinghaus and Zhiyong Xie with regard to an update at MCWG 2013, with a view of closing this agenda point on atmosphere-ocean exchange of PFCs at MCWG 2013 and preparing a combined report of MCWG 2010–2013 on this topic.

5.13 Report on new information and experiences of using seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants

Michael Haarich and Katrin Vorkamp presented a summary of information on monitoring of organochlorines and emerging compounds in seabird eggs, with focus on the North Sea, the Baltic Sea and the Arctic. Seabird eggs are a suitable monitoring matrix for persistent organic pollutants because they are relatively easy to collect and contain high concentrations, as a consequence of the high trophic level of most seabirds and the biomagnification of the chemicals. Except for the sampling and pre-

treatment step, analytical procedures are identical with those for fish and shellfish and described in guidelines.

In OSPAR, seabird eggs have been included in the JAMP guideline for monitoring of biota since 1998. Results can be assessed against an Ecological Quality Objective (EcoQO) on mercury (100 ng/g) and organochlorines, such as hexachlorobenzene (HCB, 2 ng/g) and Σ PCB (20 ng/g). OSPAR concluded from a pilot study in the North Sea (2008-2010) on eggs of oystercatchers (*Haematopus ostralegus*), Common tern (*Sterna hirundo*) and Arctic tern (*Sterna paradisaea*), that this type of monitoring was suitable for inclusion in the CEMP. The report also includes a list of current monitoring programmes of OSPAR contracting parties, including:

- The Trilateral Monitoring and Assessment Programme (TMAP) in the Wadden Sea (Denmark, Germany, Netherlands), using eggs of oystercatcher and common tern
- Specimen banking of herring gull (*Larus argentus*) eggs (Germany)
- Specimen banking of guillemot (*Uria aalge*) eggs (Sweden)
- The Predatory Bird Monitoring Scheme using gannet (*Morus bassanus*) eggs (UK)

The report does not list the monitoring programmes conducted by contracting parties with relation to the Arctic (see below).

Examples of the results of this pilot study were presented (Dittmann *et al.*, 2011). Furthermore, trends for PCB and Hg were shown in common eggs obtained under the TMAP, generally showing relatively stable concentration since the main concentration decrease (Becker and Dittmann, 2009).

Seabird eggs are also included in HELCOM COMBINE. Examples were shown of the contaminant monitoring in guillemot eggs conducted under the Swedish contaminant monitoring programme since 1969, including different temporal trends for dioxins, BDE-47 and PFOS: While dioxins have decreased throughout the study period, BDE-47 peaked in the late 1980s and PFOS has increased since 1968 (e.g. HELCOM, 2002; Sellström *et al.*, 2003; Holmström *et al.*, 2005; HELCOM, 2010).

In the context of the Arctic Monitoring and Assessment Programme (AMAP), time trends have been established since the mid-1970s for several contaminants and bird species, for example PCBs and DDT in eggs of black-legged kittiwake (*Rissa tridactyla*), thick-billed murre (*Uria lomvia*) and northern fulmar (*Fulmarus glacialis*) from the Canadian Arctic (Braune, 2007). In addition, dioxins and furans were monitored in ivory gull (*Pagophila eburnean*) eggs from Arctic Canada (Braune *et al.*, 2007).

The AMAP also includes time trends for organochlorines in eggs of black guillemot (*Cepphus grylle*) from East Greenland (Vorkamp *et al.*, 2004). Black guillemots overwinter in the Arctic and feed primarily on fish and crustaceans. For the time period from 1999 to 2010, eggs were collected in 8 years. Most compounds did not show any significant trend, presumably because of main contaminant decreases prior to 1999. For HCB, however, a significant increase at an annual rate of 2.3% was found.

Furthermore, time trend monitoring of organochlorines and Hg has been conducted in Northern Norway on eggs of herring gulls, Atlantic puffin (*Fratercula arctica*), black-legged kittiwakes and common guillemots from 1983–2003 (Helgason *et al.*, 2008). The results generally showed decreasing trends for the organochlorines, except for HCB and hexachlorocyclohexane during the 1993–2003 period.

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Peter Lepom added more information on the German Environmental Specimen Bank which has been operating a programme on monitoring metals and organic contaminants in herring gull (*Larus argentus*) eggs for more than 20 years. Samples are collected at one location in the Western Pomeranian Bodden National Park (Baltic Sea) and at two sites at the German Wadden Sea Coast (North Sea). Long time series are available for copper, mercury, lead, arsenic, selenium, dieldrin, octachlorostyrene, HCB, β -HCH, *p,p'*-DDE, *p,p'*-DDD, CB101, CB118, CB138, CB153, CB180, and α -hexabromocyclododecane.

Details on the German Environmental Specimen Bank are available at <http://www.umweltprobenbank.de/en/documents>

5.14 Report on new information on passive sampling of contaminants in the marine environment

The recent literature on measuring aqueous concentrations of organic contaminants using passive sampling devices (PSDs) was summarised by Kees Booij.

A review by Lohmann *et al.* (2012) provides a road map for the selection of PSDs for monitoring non-polar organic compounds. The authors of this article argue that non-polar PSDs allow the quantitative determination of aqueous concentrations with a well defined accuracy and precision. The provided road map allows users of PSDs to

evaluate whether or not these samplers yield results that are accurate and precise enough for spatial and temporal trend monitoring. The authors show that the interlaboratory variability in sampler-water partition coefficients is substantial in some cases (0.18 to 0.45 log units), and that further work will be required to improve the accuracy of this parameter for a number of compounds.

For the sampling of polar contaminants (pharmaceuticals and personal care products), three studies by Li *et al.* (2010a, 2010b, 2011) show that significant progress has been made to further understand the calibration of these PSDs. However, at present these samplers are insufficiently understood for applications in routine monitoring studies.

MCWG noted that the integrated use of PSDs in chemical monitoring and biological effects monitoring offers the potential for a realistic risk assessment of non-polar contaminants in the marine environment, both for water and for sediment. This potential has been demonstrated in the INRAM study (see Section 5.11). MCWG will discuss further steps to be taken with WGMS and WGBEC (see Action List).

MCWG also recognised that further improvement of PSDs for non-polar compounds could be obtained via an interlaboratory development study on the determination of sampler-water partition coefficients of selected PSDs. The NORMAN network could be a suitable platform to organise such a study.

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Actions:

Katrin Vorkamp to provide draft text to WGBEC, for the WGBEC 2012 meeting.

Patrick Roose and Katrin Vorkamp to contact WGMS and WGBEC, respectively, to hear about interest in a joint publication on passive sampling in a monitoring context.

Kees Booij to report from the workshop on “Guidance on Bioavailability/Bioaccessibility Measurements using Passive Sampling Devices and Partitioning-Based Approaches for Management of Contaminated Sediments”, Costa Mesa, California, USA, 7–9 November 2012.

5.15 Discuss recent developments in trace metal analyses

Michael Haarich presented recent developments in trace metals analyses. He informed about a direct method to analyze mercury. The equipment can analyze solid

samples without acid digestion or other wet chemistry sample treatment prior the analysis. The analysis takes less than 5 minutes per sample. The sample is weighed into a quartz or metal boat, without any treatment, mercury is quantitatively measured by atomic absorption. The equipment produces reproducible and accurate results with biological samples and it is very easy to operate.

5.16 Complete guidelines for publication in TIMES series:

5.16.1 Determination of polychlorinated biphenyls in biota and sediment.

Lynda Webster had prepared a draft manuscript for MCWG 2011. Katrin Vorkamp, Michael Haarich, Michiel Kotterman, Patrick Roose and Philippe Bersuder contributed with additions and comments. The manuscript was finalised at the meeting.

Action:

Lynda Webster to submit manuscript to ICES.

6 Plenary discussion of draft report

The draft report was discussed in plenary on Friday 24 February 2012. The final draft version of the report was circulated by e-mail after the meeting, for approval by MCWG.

7 Any other business

MCWG supported extending the tenure of the current chair, Katrin Vorkamp, for another year.

MCWG discussed meetings in autumn instead of spring, for better co-ordination with meetings of OSPAR MIME and HASEC in December and February, respectively. There was no clear preference for either spring or autumn within MCWG. While the ICES Secretariat supported moving MCWG meetings to the autumn, OSPAR was reluctant. Therefore, no change in meeting dates is expected in the near future.

8 Recommendations and action list

For a list of recommendations, see Annex 4.

The following actions have arisen from MCWG 2012:

ACTION	WHO
Convey MCWG's comments on the multi-annual management implementation plan to the ICES Secretariat for the deadline of 12 March 2012.	Katrin Vorkamp
Provide draft text on chapter 5.2 (EAC review) to the OSPAR HASEC 2012 meeting, via Martin M. Larsen.	Katrin Vorkamp
Provide draft text of chapter 5.2 (EAC review) to WGBEC, for the WGBEC 2012 meeting.	Katrin Vorkamp
Follow up on Quasimeme's interest in PFASs in marine sediments.	Norbert Theobald

Provide MCWG 2012 report to QUASIMEME.	Katrin Vorkamp
Discuss with ICES secretariat potential other avenues for delivering comments to relevant EC/groups (see Chapter 5.4.1, Water Framework Directive).	Katrin Vorkamp
Provide draft text of chapters 5.4.2 (MSFD, initial assessments), 5.4.3 (MSFDSG request) and 5.4.4 (MSFDSG request) to WGBEC, for the WGBEC 2012 meeting.	Katrin Vorkamp
Forward MCWG's input to the chair of MSFDSG, for inclusion in the MSFDSG draft report.	Katrin Vorkamp
Contact Claude Belpaire (Chair of WGEel subgroup on Eel Quality) about contaminant data on eel.	Michiel Kotterman
Present new data on eel.	Michael Haarich
Develop a structure for a publication on the development and review of environmental assessment criteria, including for example a critical data analysis and discussions of possibilities and limitations.	Patrick Roose
Provide draft text of chapter 5.14 (Passive sampling) to WGBEC, for the WGBEC 2012 meeting.	Katrin Vorkamp
Suggest to WGMS a joint meeting with WGBEC and MCWG in 2014.	Patrick Roose
Suggest to WGBEC a joint meeting with WGMS and MCWG in 2014.	Katrin Vorkamp
Discuss with WGMS interest in a joint publication (with MCWG and WGBEC) on passive sampling in a monitoring context.	Patrick Roose
Contact WGBEC to inquire about interest in a joint publication on passive sampling in a monitoring context.	Katrin Vorkamp
Present WGBEC's work on marine litter at MCWG 2013.	Katrin Vorkamp
Present information on contaminants in marine litter.	Michiel Kotterman
Inform SGONS about MCWG's interest in certified reference materials to support monitoring of nutrients in north Atlantic shelf seas.	David Hydes
Gather information on ICES expert groups on the interface to MCWG's chemical oceanography work and establish contacts where relevant	Katrin Vorkamp
Contact the ICES Data Centre with regard to submission of carbonate system data (see section 5.10.5).	Katrin Vorkamp
COSG members to complete work on respective sections of the CRR draft	All (COSG)

manuscript and forward input to Pamela Walsham.	
Submit CRR draft manuscript to ICES by July 2012.	Pamela Walsham
Forward draft guidelines on Ocean Acidification to HASEC 2012, as reviewed and updated by MCWG 2012, via Martin M. Larsen.	Katrin Vorkamp
Contact Ralf Ebinghaus and Zhiyong Xie with regard to an update at MCWG 2013, with a view of closing the agenda point on atmosphere-ocean exchange of PFCs at MCWG 2013 and preparing a combined report of MCWG 2010-2013 on this topic.	Katrin Vorkamp
Report from the workshop on "Guidance on Bioavailability/Bioaccessibility Measurements using Passive Sampling Devices and Partitioning-Based Approaches for Management of Contaminated Sediments", Costa Mesa, California, USA, 7-9 November 2012.	Kees Booij
Submit TIMES manuscript on PCB analyses in biota and sediment to ICES.	Lynda Webster

9 Date and venue of the next meeting

Dates and venue of the next meeting (MCWG 2013) have not been settled.

10 Closure of the meeting

The meeting was closed on Friday, 24 February 2012 at 1 p.m.

Annex 1: List of participants

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Annex 2: Agenda

ICES Marine Chemistry Working Group: 34th meeting

National Oceanography Centre
Southampton, UK

20–24 February 2012

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

3 REPORT FROM THE ANNUAL SCIENCE CONFERENCE 2011

- i) 2011 Advice Drafting Group
- ii) 2011 Annual Science Conference
- iii) Internal ICES information

4 PLENARY PRESENTATIONS

- 4.a Alex J Poulton (Directorate of Science and Technology, National Oceanography Centre, Southampton): *Pelagic calcite production in the modern ocean*
- 4.b Clive N Trueman (Ocean and Earth Sciences, University of Southampton): *Using natural spatio-temporal gradients in stable isotopes to monitor population-scale movements and bottom-up ecosystem effects in pelagic fish*

5 MAIN AGENDA

General

- 5.a **Development of a JAMP guideline on monitoring of contaminants in seawater:** Develop the general text for a JAMP guideline on monitoring contaminants in seawater, which could act as the overarching chapeau to technical annexes concerning specific substances. The technical annex on analysis of PFC compounds in seawater developed by ICES in 2009 is the first such document. The development of the overarching text should take into account the need to address the following issues: purposes; quantitative objectives; sampling strategy; sampling equipment; storage and pre-treatment of samples; analytical procedures; analytical quality assurance; reporting requirements (OSPAR request 2011/1).
- 5.b Review of **Environmental Assessment Criteria** or equivalents (OSPAR request 2012/2).
To review scientific robustness and update, as necessary, EACs or equivalent effects levels calculated for CEMP and pre-CEMP determinands.

- 5.c** Report on developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME.

Bram Eijgenraam to present developments in QUASIMEME.

Denise Smythe-Wright: Best practise for chlorophyll and other pigment measurements.

Stefan van Leeuwen: Quality in analysis of PFAS - perspectives from interlaboratory study results

- 5.d** Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD):

- i) Report on the developments in Water Framework Directive monitoring programmes, including statistical methods for compliance checking of Environmental Quality Standards;
- ii) Report on developments under the Marine Strategy Framework Directive, including information on initial assessments in member states;
- iii) Identify elements of the EGs work that may help determine status for the 11 Descriptors set out in the Commission Decision (MSFDSG request);
- iv) Provide views on what good environmental status (GES) might be for those descriptors, including methods that could be used to determine status (MSFDSG request).

- 5.e** MCWG members to report information on projects of relevance to MCWG activities.

Stefan van Leeuwen: Monitoring contaminants in (marine) aquatic biota in the Netherlands. RIKILT/IMARES activities

Katrin Vorkamp: Chemical fingerprinting as a method of tracing fish migration.

- 5.f** ICES Data Centre

- i) Provide expert knowledge and guidance to the ICES Data Centre, as may be requested

That the seawater contaminants section of the ICES database should be reviewed, in collaboration with the ICES DataCentre, and updated, giving particular attention to parameter fields, station names/locations, gross errors (e.g. units), uncertainty in identification of contaminants, and the opportunity for improving the QA of data being submitted, for example through automated checking of data at the time of entry, with a view to the seawater data becoming more available for assessment in MSFD and other contexts.

- ii) Report on developments in EMODNET, in particular on intersessional MCWG subgroup activities regarding EMODNET.

- 5.g** Report on activities in other expert groups on the interface to MCWG (e.g. WGMS, WGEel, WGBEC, SGIMC, SGONS).

Patrick Roose to report on activities in WGMS.

Michiel Kottermann to report on activities in WGEel.

David Hydes to report on activities group in SGONS.

- 5.h** Evaluate potential for collaboration with other EGs in relation to the ICES Science Plan and report on how such cooperation has been achieved in practical terms (e.g. joint meetings, back-to-back meetings, communication between EG chairs, having representatives from own EG attend other EG meetings).

Chemical Oceanography

- 5.i** Revision of JAMP guidelines on nutrients and oxygen (OSPAR request 2009/6).

OSPAR made two requests to ICES under the 2006 and 2009 annual ICES Work Programmes relating to the review and as necessary update of the JAMP monitoring guidelines for nutrients, chlorophyll, oxygen and benthos. OSPAR wish to request the completion of the revision of the JAMP monitoring guidelines for nutrients and for oxygen. This should be based on, as deemed relevant:

- comments on current nutrient and oxygen guidelines as submitted to OSPAR by Contracting Parties;
- comments on sampling, storage and pre-treatment submitted by ICES (ICES Advice 2009 Book 1 1.5.5.4);
- any pertinent development relating to MSFD Good Environmental Status Descriptor 5 and specifically determination of nutrients and oxygen in the water column.
- any other information that ICES may consider of relevance.

- 5.j** Ocean acidification:

- i) Present and discuss new chemical oceanographic data relating to ocean acidification;
- ii) Review new information for determination of pH and carbonate parameters in estuarine and brackish water and the associated calculations;
- iii) Report on latest developments in *in situ* chemical oceanographic sensor;
- iv) Discuss the need for and feasibility of proficiency testing for carbonate parameters (total alkalinity and dissolved inorganic carbon);
- v) Review progress on interconnectivity of databases with respect to carbonate system data;
- vi) Finalise manuscript on ocean acidification in view of publication as an ICES Cooperative Research Report (CRR);
- vii) Contribute to OSPAR draft guidelines on ocean acidification.

Contaminants

- 5.k** Contribute, as may be required, to ICES activities on integrated chemical and biological effects monitoring and review new information on effect directed chemical analysis.
- 5.l** Emerging contaminants:
 - i) Report on new information regarding emerging contaminants in the marine environment;
 - ii) Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment;
- 5.m** Report on new information and experiences of using seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants.
- 5.n** Report on new information on passive sampling of contaminants in the marine environment.
- 5.o** Discuss recent developments in trace metal analyses.
- 5.p** Complete guidelines for publication in TIMES series:
 - i) PCBs in biota and sediment

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 resolutions

MCWG draft terms of reference for the next meeting

The **Marine Chemistry Working Group** (MCWG), chaired by Katrin Vorkamp, Denmark, will meet in **VENUE** (TBA), in **spring** 2013 (TBA) to:

- a) Report on developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME;
- b) Water Framework Directive and Marine Strategy Framework Directive:
 - i) Report on the developments in Water Framework Directive monitoring programmes;
 - ii) Report on developments under the Marine Strategy Framework Directive, including information on initial assessments in member states;
- c) Report on information on projects of relevance to MCWG activities;
- d) ICES Data Centre:
 - i) Provide expert knowledge and guidance to the ICES Data Centre, as may be requested;
 - ii) Report on developments in EMODNET;
- e) Report on activities in other expert groups on the interface to MCWG (e.g. WGMS, WGEel, WGBEC, SGONS);
- f) Ocean Acidification:
 - i) Present and discuss new chemical oceanographic data relating to ocean acidification;
 - ii) Report on activities in the OSPAR/ICES study group on Ocean Acidification and provide comments and input as may be requested;
 - iii) Review progress on interconnectivity of databases with respect to carbonate system data;
- g) Discuss aspects of chlorophyll analysis and related QA/QC;
- h) Contribute, as may be required, to ICES activities on integrated chemical and biological effects monitoring and review new information on effect directed chemical analysis;
- i) Emerging contaminants:
 - i) Report on new information regarding emerging contaminants in the marine environment;
 - ii) Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment;
- j) Update information on using seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants;
- k) Report on new information on passive sampling of contaminants in the marine environment;
- l) Discuss the role of marine litter as a potential source of contaminants;
- m) Follow up on discussions of publications on e.g.:
 - i) the development and review of environmental assessment criteria;

- ii) passive sampling in a monitoring context.

MCWG will report by 15 April 2013 (via SSGHIE) for the attention of ACOM and SCICOM.

Supporting Information

Priority	<p>This group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. The activities are considered to have a high priority.</p> <p>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.</p>
Scientific justification	<ol style="list-style-type: none"> a) MCWG has a particular interest in quality assurance and maintains strong links with QUASIMEME with a view to supporting quality assurance activities in this field. b) This work was initiated by MCWG and will be of interest to EU/OSPAR/HELCOM. It will also tie into internal ICES initiatives, e.g. MSFD SG. c) MCWG members are interested in receiving reports on relevant projects and activities from other members. d) This is in direct response to possible requests by the ICES Data Centre. An EMODNET subgroup with potential intersessional tasks was requested by the ICES Data Centre at MCWG 2011. e) Collaboration between expert groups, as highlighted by SSGHIE at ASC 2010. f) These items will support the OSPAR/ICES study group on Ocean Acidification. g) This item was identified by MCWG 2012 as a relevant area for more in-depth discussions. h) Given activities within OSPAR on integrated monitoring of contaminants and biological effects, MCWG wishes to stay updated with developments in this field. i) This was initiated by MCWG members on the basis of concerns regarding emerging contaminants in the marine environment and is an ongoing area of interest to the group. The review of PFC-related research follows up on OSPAR request 2010/6 and is expected to be closed at MCWG 2013. j) This was initiated by MCWG 2011 as an item of general interest to the group. k) This follows up on previous MCWG work on guidelines on passive sampling. Being a promising technique of potentially wide applicability, MCWG wishes to be kept informed about new developments. l) This was initiated by MCWG 2011 as an item of general interest to the group. m) Following several TIMES publications and one CRR manuscript, MCWG has discussed other areas of MCWG work which might be of interest for a larger scientific community, i.e. relevant for publication beyond the annual report.
Resource requirements:	<p>The research programmes which provide the main input to this group are already underway, and resources are already committed. The additional resource required to undertake additional activities in the framework of this group is negligible.</p>
Participants:	<p>The Group is normally attended by some 20–25 members and guests.</p>
Secretariat facilities:	<p>None.</p>

Financial:	No financial implications.
Linkages to advisory committees:	ACOM
Linkages to other committees or groups:	SCICOM MSFDSG WGMS, WGBEC, WGEeI, SGONS OSPAR/ICES study group on Ocean Acidification ICES Data Centre
Linkages to other organizations:	The work of this group is closely aligned with EU Working Groups under the Water Framework Directive. Specific agenda points will be directly relevant for QUASIMEME. The group provides the basis for some advice to OSPAR.

Draft resolution for a Publication

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

PUBLICATION TITLE	MCWG LEAD	ESTIMATED PAGE NUMBERS
Determination of polychlorinated biphenyls (PCBs) in sediment and biota	Lynda Webster	18

Supporting Information

Priority	Monitoring guidelines are required to support monitoring under the regional sea conventions (e.g. OSPAR) and under activities (e.g. EC directives). This analytical guideline supports general monitoring activities by providing best practice for monitoring these specific substances in marine biota and sediment. It updates the previous TIMES publication on determination of polychlorinated biphenyls (PCBs) in sediment (Smedes and de Boer, 1998. TIMES no. 21).
Scientific justification	These products are based on technical annexes for monitoring contaminant in biota and in sediment produced by MCWG and WGMS in response to OSPAR requests. For relatively little additional effort, publication in the TIMES series would make the information more widely available to, for example, scientists engaged with other regional sea conventions and EC directives such as the WFD and MSFD.
Resource requirements	Cost of production and publication.
Participants	External reviewers.
Secretariat facilities	Help with document preparation/publication. Final editing.
Financial	Publication costs.
Linkages to advisory committees	
Linkages to other committees or groups	The work has been coordinated with WGMS.
Linkages to other organizations	This manuscript is based on guidelines produced by MCWG on request for OSPAR. It will also support monitoring activities of other regional conventions and under the EU WFD.

Theme session proposal for the 2013 ASC

The Marine Chemistry Working Group (MCWG) proposes a Theme Session for the 2013 Annual Science Conference:

Title: Physico-chemical aspects of ocean acidification in the ICES area

Conveners: David Hydes (UK)

Further suggestions: Marta Alvarez (Spain), Alberto Borges (Belgium), Jan Olafsson (Iceland).

Marta Alvarez and Alberto Borges principally agreed to act as conveners, subject to availability.

Annex 4: Recommendations

RECOMMENDATION	FOR FOLLOW UP BY:
1. It is recommended that QUASIMEME includes PFASs in schemes for biota, sediment and seawater in a similar frequency to the brominated flame retardants.	QUASIMEME
2. It is recommended that QUASIMEME notes MCWG's comments in sections 5.3 and 5.10.4.	QUASIMEME
3. It is recommended that the ICES Data Centre notes MCWG's suggestions and reports back to MCWG whether the SGIMC recommendation can be closed.	ICES Data Centre
4. It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the information given by MCWG 2012 (as well as MCWG 2010 and 2011) with regard to data and information on ocean acidification in the Convention area.	OSPAR/ICES study group on Ocean Acidification
5. It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the information given by MCWG 2012 (as well as MCWG 2010 and 2011) with regard to EU projects on Ocean Acidification.	OSPAR/ICES study group on Ocean Acidification
6. It is recommended that the OSPAR/ICES study group on Ocean Acidification notes this initial discussion with QUASIMEME regarding development of proficiency testing schemes for carbonate parameters.	OSPAR/ICES study group on Ocean Acidification
7. It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the material the CRR draft manuscript submitted to ICES by MCWG.	OSPAR/ICES study group on Ocean Acidification
8. It is recommended that the OSPAR/ICES study group on Ocean Acidification notes the draft guidelines on ocean acidification in the version reviewed and updated by MCWG 2012.	OSPAR/ICES study group on Ocean Acidification

Annex 5: Guidelines for Monitoring Contaminants in Seawater (draft)

1. Introduction

These guidelines provide advice on the sampling and analysis of seawater, for determination of trace metals and organic contaminants in environmental monitoring. Seawater covers oceanic, coastal and estuarine waters. Its analysis is a complex task which requires carefully designed and conducted sampling campaigns, appropriate equipment and its correct handling as well as suitable pre-treatment and storage methods for the analysis in question, i.e. numerous steps which will affect data quality prior to the chemical analysis itself.

The present guidelines are general recommendations on contaminant monitoring in seawater. The techniques selected in this guideline are useful for routine monitoring and ship/campaign based work. However, this guideline is not intended as a complete laboratory manual. Requirements for specific contaminants or contaminant groups should be further specified by expert groups, in order to meet the objectives of the monitoring programme and to ensure consistent and comparable data sets.

2. Purposes

Monitoring of contaminants in seawater of the North-east Atlantic Ocean is performed within the framework of OSPAR as the regional convention for the protection of the marine environment of this area. One of the aims of OSPAR's Hazardous Substances Strategy is that concentrations of naturally occurring chemicals should approach background concentrations, and concentrations of man-made chemicals should be zero. This strategy provides the basis for the Joint Monitoring and Assessment Programme (JAMP) of chemicals for priority action and hazardous substances in general, with the following objectives:

1. Identification of temporal and geographic trends of hazardous substances in relation to their background levels and toxic effects levels,
2. Assessment of the sources and discharges of these substances, and
3. Improvement of OSPAR's monitoring framework and its link with understanding biological effects and ecological impacts of these substances

The JAMP also describes the objectives of monitoring in relation to the EU Marine Strategy Framework Directive (OSPAR, 2010).

Compared with the analysis of trace metals and organic contaminants in marine sediments and biota, the water phase can be considered a "primary" compartment where compound concentrations are less affected by interactions with the matrix. In sediments and biota, enrichment and other factors have to be considered which may depend on intrinsic parameters of the matrices themselves. The choice of water based monitoring, as opposed to monitoring of sediment and biota, might also be pre-defined in the monitoring programme and/or be the consequence of the target analytes' physical-chemical properties (see also section 3). OSPAR Background Documents on chemicals for priority action may provide valuable information with regard to the preferred monitoring matrix.

The monitoring of contaminants in seawater may be carried out in relation to i) the temporal development of pollution, ii) its spatial variation or iii) as an element of integrated monitoring and assessment of contaminants and biological effects. Furthermore, beyond the objectives of the JAMP, it can provide information on the fate of

contaminants in the environment, e.g. transformation, partitioning and transport processes.

i) Performing time trend monitoring can assess the effectiveness of measures taken to reduce contamination of the marine environment. The statistical assessment of a trend over a longer period also supplies a more reliable assessment for the environmental status within a certain period. The fitted value of the last year measured is a more optimum value for comparing against assessment criteria and hence assessment of the actual environmental status. In such a way, the within and between year variability is taken into account.

ii) Spatial distribution monitoring can assess the existing level of marine contamination throughout the convention area. The measured levels can be compared to background or close to background concentrations, as well as to levels describing thresholds below which no chronic effects are expected to occur in marine species, i.e. environmental assessment criteria (OSPAR, 2009).

iii) Contaminant analysis of seawater can be an element of an integrated approach, where chemical and biological effect measurements are combined, in order to assess potential harm to living resources and marine life (OSPAR, 2012). The role of chemical measurements in integrated chemical and biological effects monitoring programmes is to identify sites where contaminant-specific biological effects programmes should be applied and to investigate the chemical cause of observed biological effects. In general, chemical measurements in seawater should contribute to improve and extend OSPAR's monitoring framework and better link it with the understanding of biological effects and ecological impacts of individual substances and the cumulative impacts of mixtures of substances.

OSPAR monitoring can assist member states of the European Union to fulfil their obligations under the relevant EU directives, such as the Marine Strategy Framework Directive (MSFD) (EU, 2008) and the Water Framework Directive (WFD) (EU, 2000) with its related directives such as the daughter directive on Environmental Quality Standards in the field of water policy (2008/105/EC).

3. Quantitative objectives

Seawater monitoring should provide concentrations of target analytes in water, which are representative of the location and time of sampling. General considerations regarding quantitative objectives are given in the JAMP (OSPAR, 2010). More specifically, the following issues should be considered prior to water monitoring: 1. Contaminant speciation; 2. Detection limits; 3. Detectability of temporal and spatial trends; 4. Costs.

3.1. Contaminant speciation

Trace metals and organic contaminants can exist as freely dissolved species in water or bound to colloids and suspended particulate matter (SPM). Trace metals can also exist as inorganic and organic complexes. The targeted contaminant fraction determines which sampling and/or pre-treatment method to use:

- Unfiltered batch water samples yield the sum of the concentrations of contaminants that are freely dissolved, complexed, and bound to colloids and SPM. These samples are also referred to as total water or whole water samples;

- Filtered batch water samples yield the concentrations in SPM (residue on the filter) and the concentrations of contaminants that are freely dissolved, complexed, and bound to colloids (filtrate);
- Passive sampling yields the concentrations of freely dissolved contaminants (organics) or freely dissolved + complexed contaminants (trace metals).

The choice of the targeted contaminant fraction may be pre-defined by legal obligations. For example, monitoring under the Water Framework Directive requires the monitoring of metal concentrations in filtered water, and of organic contaminants in total (i.e. unfiltered) water.

3.2. Detection limits

The sampling methods should have detection limits that are sufficiently low to monitor spatial and temporal trends for the contaminants of interest. For example, 1 L batch water samples may be sufficient for time trend monitoring of PAHs in contaminated harbours, but may be insufficient for monitoring programmes in the open sea or the open ocean. For consistency with Commission Directive 2009/90/EC, a limit of quantification (LOQ) should be equal or below a value of 30% of the relevant assessment criteria, e.g. the Environmental Quality Standard.

3.3. Statistical significance and power

In the context of temporal trend monitoring, it is important to know the power of a time series to detect significant changes, i.e. the chances of revealing true trends in concentration instead of “random” variation. The necessary or possible power of a monitoring programme will vary with the contaminant and area being investigated. One approach would be to estimate the power of the time series based on the “random” between-year variation. Alternatively, the lowest detectable trend could be estimated at a fixed power. A quantifiable objective could be to detect an annual change of 5% within a time period of 10 years with a power of 90% at a significance level (α) of 5%. In the case of an expected decrease, the null hypothesis would be chosen as $dC/dt=0$ and the alternative hypothesis as $dC/dt < 0$.

A spatial distribution monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in contaminant concentrations. This would include a definition of the monitoring area and some knowledge of the spatial variability in this area. A preliminary/exploratory sampling programme will provide useful information for designing the final programme. Statistical procedures must be taken into account to estimate the number of samples and sampling sites needed to meet the required confidence level (avoid Type I errors) and statistical power (avoid Type II errors).

3.4. Costs

The cost of replicate water samples should be carefully considered prior to a water based monitoring program. It should be noted that concentrations in water as determined by batch water sampling may be quite variable, both in space and time, and that meeting the quantitative objectives may require extensive replication, which increases the costs of the programme. In addition, seawater sampling for contaminant analysis often requires equipment that is expensive to buy and maintain. Furthermore, keeping the process blanks for this equipment at low levels also adds to the costs of the monitoring programme.

4. Sampling strategy

The sampling strategy should reflect the purpose of the monitoring programme according to the JAMP (OSPAR, 2010), in relation to the OSPAR Hazardous Substances Strategy. Where applicable, the sampling strategy should consider requirements of the EU WFD (EU, 2000) and MSFD (EU, 2008). Furthermore, the sampling strategy should meet the quantitative objectives of the monitoring programme (see section 3). In accordance with the JAMP Guideline on Integrated Monitoring of Contaminants and Their Effects, seawater sampling should be carried out at the same time and locations as the sampling of other matrices (sediment, biota) and biological effect measurements (OSPAR, 2012).

The expected temporal variability of the analyte concentrations will have to be considered in a strategy for sampling times (i.e. at what time of year) and frequencies. Analyte concentrations will also vary between locations and with water depth. The analyte in question (its physical-chemical characteristics and expected concentration) as well as environmental conditions will further determine how samples are taken, e.g. what equipment is used and what volumes are required. However, sampling strategies also include compromises between scientifically advisable approaches and the economical and logistical frames of the sampling effort (see section 3).

4.1. Temporal trend monitoring

The ability of the program to identify temporal trends strongly depends on the extent to which unwanted sources of variability can be controlled. The short term (< 1 year) temporal variability of contaminant concentrations in water is potentially very large, due to the limited buffering capacity of the water phase. Concentrations may be subject to day-night variations in input and removal processes (Jaward *et al.*, 2004). In addition, concentrations at a fixed geographical position may vary over the tidal cycle (e.g., in estuaries). Further temporal variability may arise from variation in local inputs, such as discharges from ships, seasonality in the riverine input, changes in atmospheric deposition during rainfall events, and seasonal differences in seawater stratification. Some precautionary measures can be taken to reduce short time temporal variability. These include sampling at pre-described times of the year and at the same phase of the tidal cycle (e.g., always as high tide), although for ship based batch sampling it should be recognized that logistic constraints do not always allow for these measures to be taken.

4.2. Spatial trend monitoring

Analyte concentrations in seawater will vary between locations and with water depth, due to various physical and biogeochemical processes. The expected spatial variability is an important factor in the development of an adequate geographical sampling scheme, i.e. the outline of the station grid and its vertical resolution (Brügman and Kremling, 1999). It should be recognised that the identification of spatial trends may be obscured by temporal variability (see section 3.1), and that the same measures to reduce this source of variability also apply here. If the aim of the program is to identify local sources of contaminants, then the sampling grid should be denser in the vicinity of these suspected sources. Often, the variability of salinity or SPM content of the water can give an indication on the variability of pollutants and even may act as "normalisation" factors.

4.3. Sampling method considerations

With increasing polarity of the pollutants, the portion which is freely dissolved in the water phase increases (see section 3). On the other hand, non-polar pollutants sorb to SPM and sediments and thereby are removed from the water column by sedimentation. For these contaminants, additional factors that should be taken into account when filtration-extraction methods are used are the SPM content and the volume of water that is sampled (see section 3). These factors are important in filtration-extraction methods because the particle bound and colloiddally bound contaminant fraction that escapes phase separation depends on the extent of filter clogging (Hermans *et al.*, 1992). The measurement of SPM concentrations is even more important for monitoring contaminants in total water. The required water volume should be estimated before the sampling campaign, taking into account the method detection limits (see section 3).

4.4. Supporting data

Additional data might be needed to properly interpret contaminant concentrations. Important co-factors to be recorded are salinity, total organic carbon content, SPM concentrations and temperature. These data should be obtained at the same time and locations as sampling for contaminant analysis takes place.

4.5. Statistical considerations

Prior to starting a full scale monitoring study, the available information on temporal variability should be carefully evaluated, possibly amended by a small-scale pilot programme. This evaluation should include a statistical assessment that certifies that the objectives of the monitoring study can be met (see section 3).

If no previous information exists, the sampling strategy can be based on a combination of general statistical principles and expert knowledge about sources and fate of the studied substances in the investigated sea basin. The statistical approach could include the principles of stratified sampling: First the sampling area under consideration is partitioned into smaller more homogeneous areas, so-called strata, and then the allocation of samples to these strata is optimised. The partitioning of the study area into homogeneous strata can be based on simple information, such as depth, distance to land, or measured or modelled salinity. A successful stratification is characterized by a small variation of the measured concentrations within each stratum and a substantial variation between strata.

The target variable might be correlated to a covariate which can be analysed more easily or modelled at a grid of points (Figure 1), e.g. the salinity of the sample. Then this covariate can be used to define suitable strata. Furthermore, the estimated relationship between the target variable and the covariate (the dotted line in Figure 1) can be used to estimate the target variable at an arbitrary grid point.

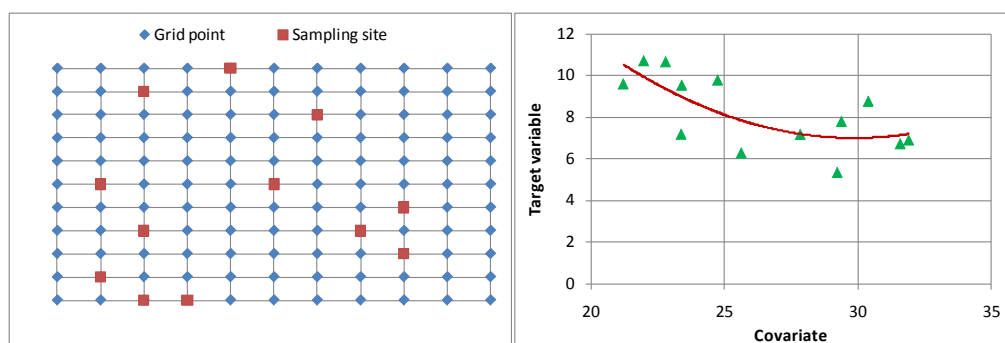


Figure 1. Location of sampling sites (left panel) and scatter chart of the measured target variable versus a covariate.

4.6. Batch sampling versus time-integrated sampling

The water phase, unlike sediments and biota, has a short response time, and there is hardly any time integration. This may be of advantage in detecting peak events but, on the other hand, it may yield higher natural variability which has drawbacks in long-term monitoring and may require high sampling frequencies causing high costs.

The extent of temporal variability may be reduced by time-integrated sampling. Continuous water intake over a prolonged time period followed by filtration and extraction may often prove to be impractical and costly, particularly for ship based sampling programs. Passive samplers (PSDs) also yield a time-integrated concentration if the necessary calibration parameters are available for the target analytes and if suitable deployment sites can be selected, such as jetties, buoys, bottom landers, long-term moorings, among others. It should be noted that these deployment sites always have to be visited twice and that bottom landers may be lost due to fisheries. Furthermore, if the monitoring programme requires sampling of total water this will limit the applicability of PSDs.

Considerations for evaluating if the necessary PSD calibration parameters are available for the target analytes, are given by Lohmann *et al.* (2012) for the case of non-polar organic contaminants. PSDs for polar contaminants (pharmaceuticals, detergents, and personal care products) presently are insufficiently mature for quantitative spatial and temporal trend monitoring, but may be useful in initial surveys. Diffusive gradients in thin films (DGT) is a mature PSD technique for trace metals, but its application in the marine environment has been quite limited so far (Mills *et al.*, 2011).

5. Sampling equipment

The choice of sampling equipment depends on the physical-chemical properties and expected concentrations of the analytes, on the depth and location of the sampling site, and on the available infrastructure. All materials used for the sampling equipment (sample containers, tubing, connectors, valves, pumps, filters) should neither absorb nor release the target analytes, or any non-target substance that interferes with the chemical analysis.

Since concentrations of organic contaminants and metals in seawater are usually very low, large volumes of water must be sampled. Still, contamination of the sample by compounds that leach out of the sampling equipment as well as analyte loss due to wall sorption are serious issues that in addition may give rise to memory effects.

Sample contamination from the atmosphere should be avoided (e.g., paint and rust particles, engine exhausts, atmospheric background). To minimise contamination

from the atmosphere, the surfaces of the sampling equipment in contact with the sample should be isolated from the atmosphere before and after the sampling, including storage of the equipment. These surfaces should be cleaned using appropriate solvents prior to sampling. Equipment blanks and recovery samples yield important quality control information that can be used to assess sample contamination and analyte losses.

Local water mass contamination by the sampling platform should also be carefully evaluated. Concentrations of target analytes in the water may be elevated because of leaching from the sampling platform itself (e.g. polyaromatic hydrocarbons, organotin, polychlorinated biphenyls, iron, chlorofluoroalkanes can be released from the ship during ship based sampling). The ship's length axis should be at an angle of 20 to 40 degrees to the current coming from the front at the sampling side (typically starboard side), to minimise any influence from the ship's hull. Repeated sample intake at increasing distance from the sampling platform can provide evidence on the significance of this source of contamination.

Since the sampling equipment passes through the air-water interface, sample contamination from the sea surface microlayer is a significant risk. Concentrations of dissolved and particulate matter are elevated in this microlayer, and the associated analytes may therefore contaminate samples that are taken at larger depth. Sample contamination from the microlayer can be avoided by closing the sampling equipment during passage through the sea surface and only allowing sample intake at the intended depth.

5.1. Trace metals (including MeHg)

Contamination from the ship has to be avoided at all times. For analyses of trace metals, all contact between the seawater sample and metal must be avoided. Approaching a station, the sampling for trace metals has to be performed immediately.

For sampling, discrete samplers should be used that are specially designed for trace metal analysis, e.g. GO-FLO (from General Oceanic), available in sizes from 1.7 to 100 liters, or MERCOS samplers (from Hydrobios; or modified version, size 0.5 liter). They are typically operated on a Teflon, polymer or Kevlar jacketed inox hydrographic wire and burdened by a coated bottom weight for tensioning the wire. The messengers should also be free of metals; any parts made of metals for construction reasons should be of seawater resistant stainless steel (V4A). The disadvantage of operating on a hydrographic wire is that samples can only be taken from pre-determined depths, typically including 10 m and close above bottom, generally depending on the water depth and characteristics of the water column. Therefore, hydrographical information about water depth and the stratification of the water column has to be available in advance.

For ship-based sampling, samples should be taken from at least 5 m downwards, depending on the draught of the vessel, to avoid contamination by the hull of the ship. Sampling bottles should be made of plastic with low metal content, e.g. special LDPE. For mercury, glass should be preferred if the samples are stored for a longer period. Teflon bottles may also be used, but they are relatively expensive, and depending on the manufacturing process, may have a relatively rough inner surface (e.g. the original sampling bottles of the MERCOS sampler).

Pumping using metal free devices may be an alternative to discrete sampling, e.g. for separating SPM by subsequent centrifugation, but not preferable when sampling

from a ship at distinct sampling depths or in the open sea where concentrations are very low. More details on sampler types are described in the Technical Annex.

After sampling, the sampler should immediately be placed in a plastic bag or box or an aluminium container (if aluminium is not determined), followed by transport to a clean-room or laboratory with a clean-air bench. These measures are particularly critical for open sea samples.

5.2. Organic contaminants

Concentrations of organic contaminants in seawater are usually very low. In order to reach the projected LOQs in the low pg L⁻¹ range, large water volumes (10 to 100 L or more) have to be sampled and extracted. With modern analytical equipment, these LOQs are often not limited by the signal intensity in the instrumental analysis, but by blank levels and interferences from the matrix background.

Blank problems can often only be overcome by increasing the sample size. However, the maximum sample size may be limited by operational constraints, such as container size for discrete samplers, pumping time, and the ability to process large water volumes. Blank levels can be reduced by minimising the size of the sampling equipment (e.g. short inlet tubings) and by using sampler designs that minimise exposure to the atmosphere (short assembly/disassembly times). The use of *in situ* filtration/extraction equipment that is both compact and easy to operate combines the advantages of small size and short exposure to the atmosphere. This holds even stronger for passive samplers (see section 4.6), provided that the sampling phase is sufficiently clean and that times of exposure to the atmosphere during deployment and retrieval are sufficiently short.

Hydrophobic compounds occur in a continuum of dissolved, colloidal and particulate-bound forms (see section 3.1). Unless a total concentration is to be determined, the compound partitioning should not be altered during sampling and subsequent treatment, which is very challenging. The separation process must be both contamination-free and should not change the concentration distribution. It should be applied during or immediately after sampling. For details, see section 6.2.

The materials used for the sampling equipment depend on the target contaminants. Sampling equipment for organic contaminants in seawater is preferably made of glass or stainless steel. Teflon parts are often used for legacy persistent organic pollutants (POPs), while they cannot be used for sampling of fluorinated compounds. Before use, the equipment has to be cleaned, e.g. rinsed with appropriate organic solvents. Examples of sampling equipment suitable for organic contaminants are given in the Technical Annex.

6. Storage and pre-treatment of samples

The storage and pre-treatment of samples should be carried out by trained personnel being aware of the risk of contamination or analyte loss if samples are handled incorrectly. Appropriate measures should be taken to avoid contamination, such as wearing clean gloves, pre-cleaning equipment etc. All storage and pre-treatment steps should be fully documented on a per sample basis. Field control samples (for assessing sample contamination) and surrogate spikes (for assessing analyte losses) should be processed on a regular basis, as part of the quality assurance and control procedures (see section 8). All storage and pre-treatment steps should be fully validated prior to the start of a monitoring programme.

6.1. Storage

It is advisable to process samples as soon as possible rather than store them for a longer period of time. Storage of samples bears the risk of changing concentrations, by microbial degradation or sorption processes. However, appropriate laboratory facilities for handling of samples for trace analyses need to be available. If this is not the case, samples may have to be conserved. Water samples for metal analysis are typically acidified for conservation purposes. Sub-sampling of seawater, if required, should preferably be performed immediately after sampling.

Water samples for organic pollutants can generally not be stored because of their large volumes. Instead, they are extracted onboard by liquid-liquid-extraction (LLE) or solid-phase-extraction (SPE) and the extracts or adsorbent cartridges are stored under cool ($< 4^{\circ}\text{C}$) and dark conditions. If water samples must be stored, this should also be in the dark and in a refrigerator (4°C). Preferably, internal standards (e.g. isotopically labelled analogues) should be added before extraction or/and storage. Storage times should be kept as short as possible and the stability of all compounds during storage must be checked.

For storage, either short or long term, only appropriate (pre-cleaned) containers should be used. The analyte of interest determines the container material (plastic, glass, metal), the need for acidification, and the optimal storage temperature. All storage conditions should be fully validated by the laboratory that carries out the monitoring, since sample contamination and loss of analyte may be affected by subtle changes in the materials and procedures for sample storage. SPM samples should always be stored frozen until further analysis.

6.2. Sample pre-treatment

Whether or not samples are filtered, is mainly determined by the monitoring programme which typically requires the analysis of either filtered or unfiltered water (total water, whole water) (see section 3.1). For the analysis of whole water, no pre-treatment is required, although acidification may be necessary as part of the extraction procedure, depending on the analyte, and on the extraction method that is used.

For small sample volumes (e.g. metal analysis) filtration is the preferred technique to separate the dissolved phase from the SPM. For the analysis of trace metals, polycarbonate or cellulose acetate filters with a pore size of $0.45\ \mu\text{m}$ are frequently used, whereas glass fibre filters ($0.7\ \mu\text{m}$ or $1.2\ \mu\text{m}$ pore size) are commonly used in the analysis of dissolved non-polar and polar organic contaminants. It should be noted that the efficiency of the separation between dissolved and particulate contaminants depends on the pore size of the filters, and may also depend on SPM content of the water and on the sample intake (see section 4). In addition, adsorption of dissolved analytes to the filter may be an issue for some compounds.

For separation of larger volumes a flow-through centrifuge is suitable for obtaining larger amounts of solids but less suitable for obtaining particle free water (less separation). In general, the efficiency of the separation depends on the geometry of the centrifugation equipment (residence time, effective gravity force), as well as on the density and size of the SPM. Filtration is more effective in this respect, but also more susceptible to artefacts and more time consuming. Ideally, filtration should occur online while sampling or immediately after sampling.

7. Analytical procedures

Analytical methods should be specific to the target analytes and sufficiently sensitive to allow analyses of seawater samples which generally have low concentrations of contaminants. They should meet minimum performance criteria consistent with Commission Directive 2009/90/EC, including an uncertainty on measurements < 50%, estimated at the level of the relevant Environmental Quality Standard, and an LOQ \leq 30% of the Environmental Quality Standard. When no method applies to the minimal performance criteria, the best available analytical method, not entailing excessive costs should be used. All analytical methods should be capable of being brought under statistical control to ensure adequate quality assurance and quality control. It should be noted that analyses at such low concentration require extensive experience.

7.1. Trace metals

Analysis of trace metals in seawater generally includes pre-treatment and pre-concentration steps (depending on the method, separation from the salt may be necessary), followed by detection using element-specific spectrometric instrumental procedures, e.g. graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS), anodic stripping voltammetry (ASV) and total reflection x-ray fluorescence (TXRF). For mercury, further methods and instruments are used, such as cold vapour atomic absorption spectrometry (CVAAS) and cold vapour atomic fluorescence spectrometry (CVAFS). These techniques are usually combined with a pre-concentration by amalgamation. ICP-MS is used for mercury analysis as well.

7.2. Organic contaminants

Organic contaminants are usually found in the water phase at low concentrations, entailing the need for an extraction and enrichment step (e.g. SPE, LLE, SPME) and a selective chromatographic/detection step (e.g. GC-MS⁽ⁿ⁾, GC-ECD, LC-MS⁽ⁿ⁾, LC-FL.) within every analytical procedure. Depending on the analytes chosen, the water body studied and expected pollutant concentration, clean-up may be necessary. Although GC-MS/MS and HPLC-MS/MS are very selective techniques, it is good practice to use a second MS transition as a qualifier.

8. Quality assurance (QA)

The quality assurance programme should ensure that the data conform to the quantitative objectives of the programme (see section 3). All procedures including laboratory, field and on-line methods must be validated and controlled on a regular basis.

The laboratory must establish a quality assurance / quality control system, consistent with requirements of Commission Directive 2009/90/EC. The laboratory should also participate in intercalibration exercises and proficiency testing to provide external verification of results. The quality assurance procedures should cover sampling design, sampling, sample storage, analytical procedures (including field controls, analytical blanks and recoveries), equipment maintenance and handling, training of personnel, data management, and an audit trail.

The use of a second (and different) sampling method, carried out simultaneously to the routine procedure, is recommended for validation. All QA and QC data should be fully documented.

Because of the extremely low concentrations of pollutants in seawater, blank problems are generally more relevant and more difficult to control than in other matrices.

Even ultra-pure chemicals and solvents used sometimes have to be purified before use. Concentrations often are close to the LOQs, which means difficult calibration and integration, and reduced analytical precision.

In addition, the following problems are encountered specifically in seawater analyses of organic pollutants:

- Because of the large sample volumes, it is not possible to analyse replicate samples on a routine basis to take samples for back-up analysis. However, it is often possible to make a plausibility check by comparing the results with those of samples taken from a homogeneous water body at adjacent stations. Homogeneity can be derived from oceanographic parameters like salinity.
- No certified reference materials are available for organic contaminants in seawater. Therefore, laboratory reference materials have to be used, which should preferably be a natural or spiked extract from a typical monitoring station. Extraction efficiencies should be checked by standard addition tests.
- Laboratory performance studies (e.g. by QUASIMEME) are difficult to perform and to evaluate because sample volumes in these studies (max. 1 L) differ from those used in real analysis (> 10 L). Thus, concentration ranges in the tests are often higher than in real-life samples.

For temporal trend monitoring in particular it is extremely important to perform reliable and reproducible high-quality analyses over decades. Therefore, such analyses require well-documented procedures and experienced analysts (see section 7).

9. Reporting requirements

Secure data storage and appropriate access to the data should be ensured by submission of data to national databases and the ICES database. Reporting requirements will depend on the database. For entry of OSPAR data into the ICES database, data of trace metals and organic contaminants should be reported in accordance with the latest ICES reporting formats, i.e. ICES Integrated Environmental Reporting Format, version 3.2.3.

The calculation of results and the reporting of data can represent major sources of error. Control procedures should be established in order to ensure that data are correct and to avoid transcription errors. This could include comparisons with independently obtained results for the same area or with typical concentration intervals. Data stored on databases should be checked and validated, and checks are also necessary when data are transferred between databases.

Concentrations of trace metals and organic contaminants in seawater should be given in weight per volume (e.g. ng/L). To ensure correct interpretation, reporting should include information on the sampling method, filtration (filter type and pore size), storage / conservation and analytical method. Minimum performance criteria such as LOQ and uncertainty measurement along with relevant QA/QC data such as reference materials should be included in the report.

Purpose of monitoring, geographical coordinates and the name of the sampling stations should be reported in the data as well as being defined in the OSPAR Station Dictionary (<http://www.ices.dk/datacentre/accessions/>). Sample depth, suspended particulate matter concentration, total organic carbon content and physicochemical

parameters at the time of sampling, such as air and water temperatures, salinity, pH and weather conditions should also be reported.

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Acknowledgements

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Technical Annex: Sampling equipment for analysis of trace metals and organic contaminants in seawater

1. Trace metals

1.1. Discrete sampling

An example of a discrete sampler is the GO-FLO sampler (by General Oceanics) (Figure 1). This sampler consists of a cylinder with inward Teflon-coating which can be closed and lowered into the water column and opens automatically at a certain depth (ca.10 m) by hydrographic pressure. This avoids contact of the sample with the water surface. At the desired depth, a messenger is sent on the hydrographic wire (in teflonized inox, polymer or better Kevlar) to release the closing valves in both ends of the sampler. Each bottle can be equipped with a second messenger that is released when

the valves close. Water samples can thus be taken by mounting a series of bottles along the cable at increasing depth.

A variety of the GO-FLO sampler is the reversing water sampler. The messenger releases the sampler from the upper attachment, it rotates, and closes the two valves. If a special thermometer type is attached to the sampler, it fixes the actual temperature at the sampling depth, which can be determined later on board. This accessory can be used when no CTD-sensor is used to record the temperature profile.

Generally, all samplers have to be cleaned before the first use by rinsing the inner surfaces with diluted hydrochloric acid. In the open sea, this may not be necessary between sampling where rinsing with deionised water is sufficient in most cases, for the outer surface at open sea the sea water is sufficiently clean for this purpose. Therefore, a Niskin sampler appears less suitable, due to rubber parts which cannot be acid-cleaned, moreover, it cannot be closed before deployment. The contact with the water surface increases the risk of contamination or at least unrepresentative sampling.



Figure 1. Picture of a GO-FLO sampler (General Oceanics) (photo courtesy of IFREMER, France).

The MERCOS sampler (Hydrobios Kiel) is designed for two 500 mL thick-walled cylindrical or ball-shaped Teflon bottles, which are closed by two silicone tubes of different diameters in the water. As the bottles are filled with air, the operating depth is restricted to about 50 m for the cylindrical and about 200 m for the globular type. However, this sampler is not any longer offered by the manufacturer (<http://www.hydrobios.de>, 2012).

A modified version for four bottles was developed by the Bundesamt für Seeschifffahrt und Hydrographie (BSH, Germany), maintaining the triggering device, but using LDPE bottles of low metal content material (NALGENE) that are protected against the water pressure by a polyacryl mantle. The LDPE bottles are cheaper and easier to clean due to the smooth inner surface compared to the relatively rough one of the thick-walled Teflon bottles. Therefore, they usually show much lower blank values.



Figure 2. Modified MERCOS water sampler of the first (above) and second generation (below) for four bottles, manufactured by BSH, Germany (photos by courtesy of M. Haarich, vTI, and S. Schmolke, BSH, Germany).

1.2. Sampling by pumping

For depths down to 100 m, perhaps even 200 m, seawater can be pumped up through silicone or Teflon tubing, optionally including in-line filtration. The tubing should be cleaned by pumping acid (e.g. 10% hydrochloric acid) prior to sampling. The first litres of seawater sampled subsequently should be discarded. Peristaltic pump or Teflon piston pumps are suitable. The peristaltic pump can be placed between the sampling tube and the filter. The outflow from the in-line filter can then be collected in polyethylene bottles, Teflon bottles, or for mercury analyses in glass or quartz bottles.

2. Organic contaminants

Usually large volumes of seawater samples are needed for the analysis of organic contaminants. Sampling devices depend on the amount of sample to be processed and the method of extraction (liquid/liquid extraction (LLE) or solid phase extraction (SPE)).

LLE and SPE do not yield exactly the same concentrations as they use different extraction principles. While SPE effectively extracts only freely dissolved compounds, LLE extracts freely dissolved humic acids complexed and – in part - particle bound pollutants (Sturm *et al.*, 1989). Non-polar compounds can be extracted by either LLE or SPE, whereas the extraction of polar compounds generally requires SPE.

Volumes of 1 to 100 L can be sampled by discrete sampling and/or pumping and are usually extracted either by LLE or SPE. Sample volumes > 100 L are generally sampled by pumping and extracted by SPE.

2.1. Discrete sampling

Several different sampling devices have been designed for discrete sampling depending on the volumes needed and the extraction techniques to be applied.

All-glass bottle samplers for volumes of 10 L and 100 L are shown in Figure 3. They are fixed on a stainless steel cage and lowered on a hydrographic wire down to the desired sampling depth and opened under water. After filling, the sampler is brought on deck of the ship and the sample can be extracted by LLE directly in the glass bowl (using a non-polar solvent) or by SPE. For example, non-polar pollutants like organohalogen pesticides (e.g. DDX, HCH, HCB, dieldrin, endrin) can be extracted and enriched from sea water by means of LLE using hexane or pentane.

Gaul *et al.* (1983) described a 10 L glass bowl sampler allowing extraction in the sampling bowl itself, thus minimising problems with sample handling, blanks, and adsorption. Later, the same principle was expanded to a 100 L bowl, thus increasing the sample volume and lowering the limit of quantification (LOQ) by a factor of 10 (Theobald *et al.*, 1990). Figure 3 shows pictures of 10 L and 100 L sampling bowls. Extraction is done by agitating the samplers with 0.2 and 1 litre, respectively, of pentane using a stirrer. The glass sampler can be used to a depth of 2000 m (10 L) and 100 m (100 L).

Collecting samples at greater depth can be done with stainless steel bottles (Figure 4) holding about 30 litres. This type of sampler was developed following the models of Niskin and GoFlo type bottles, and has been used for analyzing dissolved herbicides in water samples collected down to 3000 m depth.

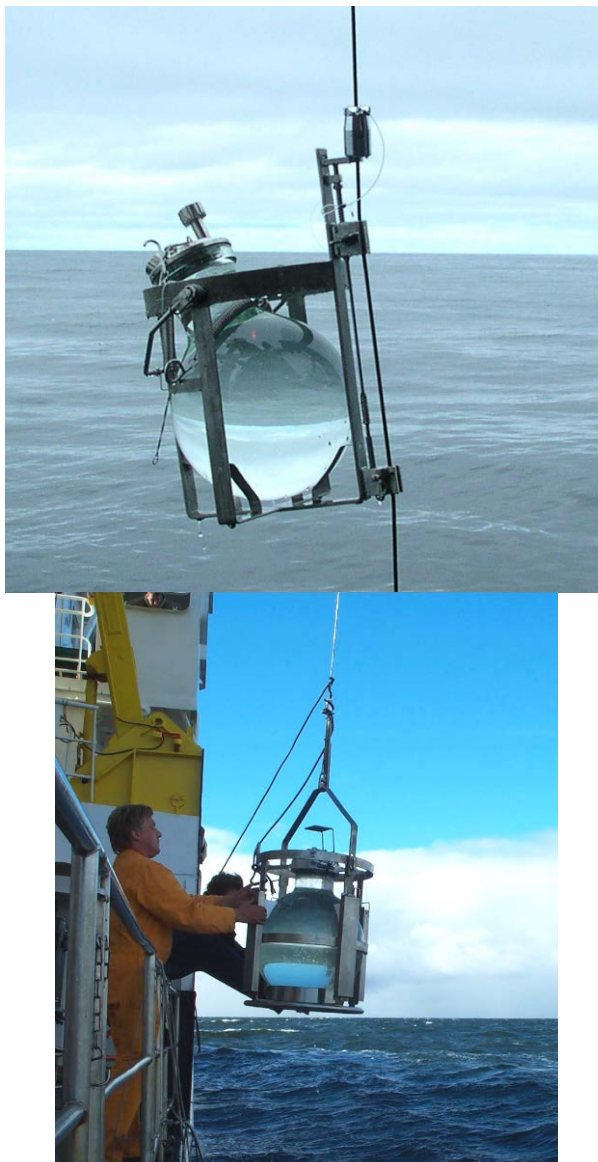


Figure 3. Left: BSH all-glass bottle water sampler (10 L). Right: 100 L glass bowl sampler for sampling seawater for organic pollutant analysis.

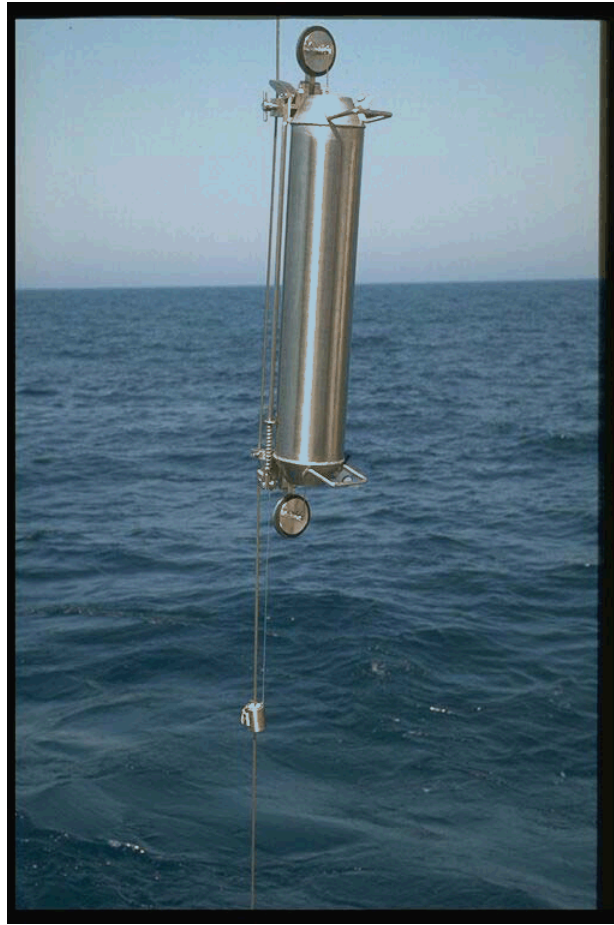


Figure 4. A stainless steel sampling bottle, for subsequent analysis of organic contaminants in seawater.

2.2. Sampling by pumping - *In situ* filtration and extraction

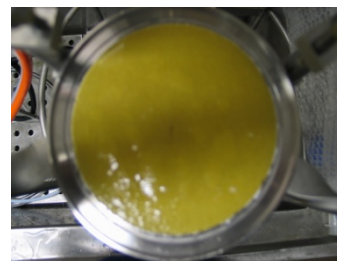
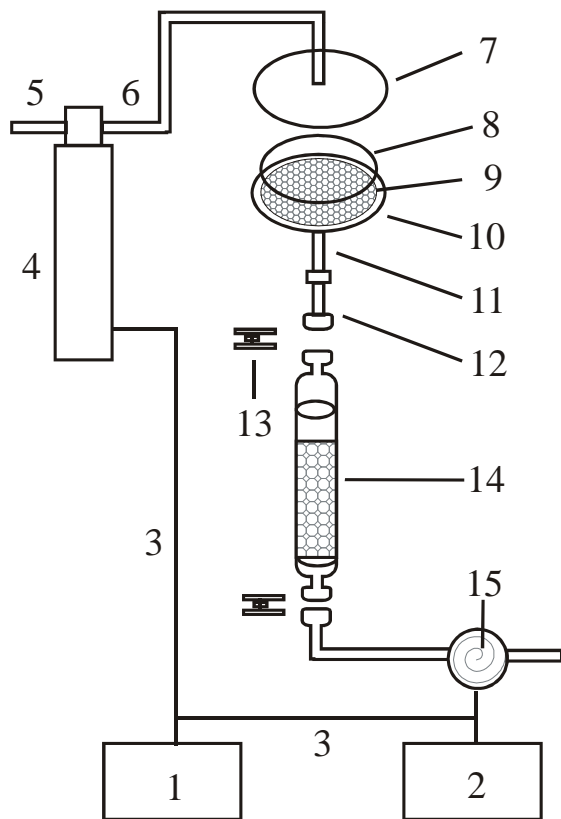
For larger volumes of 200 to 1000 L, Schulz-Bull *et al.* (1995) described an SPE procedure using large extraction cartridges filled with XAD resins. With this adsorbent, they obtained good extraction results for PCBs, DDT and PAHs, but not for HCH.

Sampling by pumping can be performed with compressed air Teflon pumps (not suitable for subsequent analysis of perfluorinated compounds). In order to equilibrate the system with the sampling water, the water is pumped for about ten minutes, before the actual sampling begins. Then the sampling bottles are thoroughly rinsed with the sample, before beginning the sampling itself. During the rinsing stages of the system and during the collection of the sub-surface samples, the hose is kept away from the ship's hull.

In situ filtration and solid-phase extraction sampling devices may minimize the risk of sample contamination during sampling. A typical *in situ* pump system, Kiel In-Situ Pump (KISP), has been widely applied to the extraction of organic contaminants in seawater (Petrick *et al.*, 1996). A modified KISP has been described for seawater sampling on board research vessels (Ebinghaus and Xie, 2006). Briefly, as shown in Figure 5, KISP includes a filter holder, a polymeric resin column, a pump and a flowmeter. A glass fibre filter (pore size 0.7 μm) is used for the particulate phase and a glass column packed with polymeric resin for the dissolved phase. The KISP can be easily operated onboard by connecting it to the ship seawater-intake system for sampling seawater at certain depths. The pump system assembly with batteries can be

deployed at different depths on a hydrographic wire, and the pumping can be started and ended by remote control.

The original KISP contains some plastic parts and connections, which may present a contamination risk for some organic contaminants, such as brominated flame retardants, alkylphenols and plasticizers. Although low blanks and detection limits have been obtained from KISP samples for legacy persistent organic pollutants (POPs), such as PCBs, DDTs and HCHs (Lakaschus *et al.*, 2002; Sobek and Gustafsson, 2004), it is recommended to replace these parts by stainless steel or glass if KISP is applied for sampling seawater for the determination of emerging organic contaminants. Surrogate standards can be added to the resin column before sampling to control the extraction recoveries and storage. It should be noted, that the validation of the *in situ* pump sampling method is difficult, and extraction efficiency may depend on dissolved organic matter and humic substances.



GF filter after sampling of 300 L seawater

Figure 5. Schematic presentation of the Kiel In-Situ Pump (KISP). 1: flow meter controller; 2: flow meter; 3: cable connections; 4: pump; 5: pump inlet; 6: pump outlet; 7: stainless steel deck of filter holder; 8: GF 52 filter; 9: glass plate; 10: filter holder; 11: stainless steel tubing; 12: glass connect; 13: adjustable clip; 14: resins column; 15: counter of flow meter.

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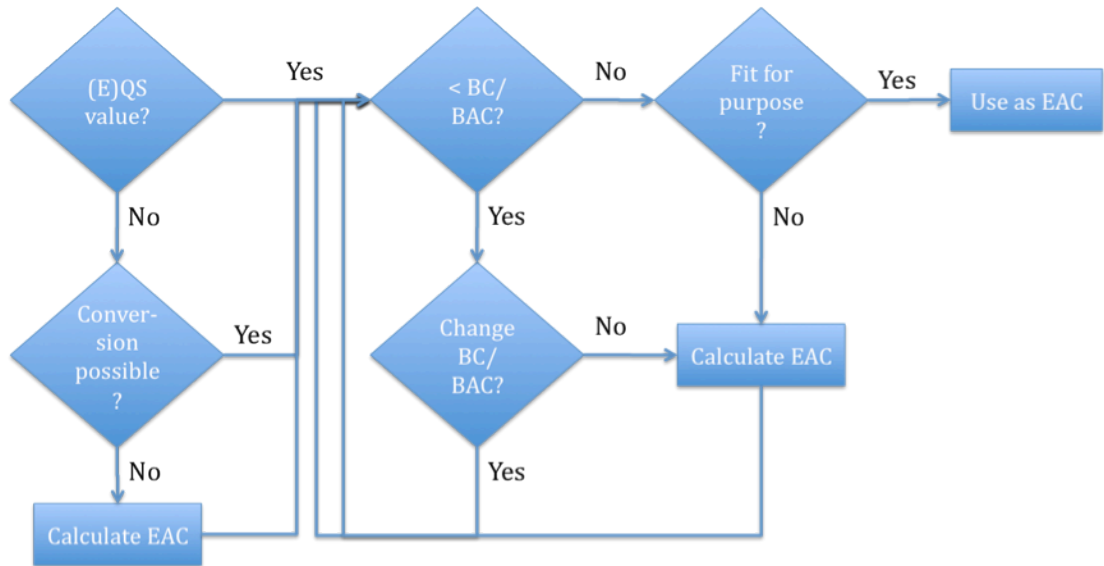
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Annex 6: Decision tree for the production of EAC values by ICG-EAC

(copied from document HASEC 12/2/6-E: Report of the Intersessional Correspondence Group on Environmental Assessment Criteria)



Annex 7: Preliminary EAC values produced by ICG-EAC

(copied from document HASEC 12/2/6-E: Report of the Intersessional Correspondence Group on Environmental Assessment Criteria)

Parameter	EAC	
	Sediment	Biota
CEMP		
Metals (mg/kg d.w.)		
Hg	BC+0.47	0.1
Cd	-	0.8
Pb	123	5.00
Organics (µg/kg d.w.)		
PAHs		
<i>Naphthalene</i>	2.8	61350
Phenanthrene	3.8	-
Anthracene	4.8	12174
Fluoranthene	2000	150
Pyrene	-	-
Chrysene	-	-
Benz[a]anthracene	-	-
<i>Benzo[b]fluoranthene</i>	70.7	10
<i>Benzo[k]fluoranthene</i>	67.5	10
Benzo[a]pyrene	91.5	10
Benzo[ghi]perylene	4.2	10
Indeno[1,2,3-cd]pyrene	-	10
PCBs		
CB 28		
CB 52		
CB101		
CB 118	0.014	0.015
CB 138		
CB 153		
CB 180		

PBDEs		
BDE 28		
BDE 47		
BDE 66		
BDE 85		
BDE 99		
BDE 100		
BDE 153		
BDE 154		
BDE 183		
BDE 209	310	4.25 10 ⁻²
TBT	0.01	76
Pesticides		
<i>g</i> -HCH (<i>lindane</i>)	1.1	165
<i>a</i> -HCH		
<i>DDE</i> (<i>p,p'</i>)		
<i>Hexachlorobenzene</i>	16.9	50
<i>Dieldrin</i>		
Pre-CEMP		
Alkylated PAHs		
C1-, C2- and C3-naphthalenes,		
C1-, C2- and C3-phenanthrenes,		
C1-, C2- and C3-dibenzothiophenes		
Dibenzothiophene		
PFOs		
PFOs related substances		45.5
<hr/>		
Non-ortho and Mono-ortho PCBs		
PCB 77		
PCB 81		

PCB 105		
PCB 114		
PCB 118		
PCB 123		4.25 10 ⁻² *
PCB 126		
PCB 156		
PCB 157		
PCB 167		
PCB 169		
PCB 189		
Dioxins and Furans		4.25 10 ⁻² *

* Proposed AA-EQS in biota for sum of dioxins and DL compounds [fresh and marine] [$\mu\text{gWHO98-TEQ.kg-1ww}$ converted to dw]



Annex 8: Parameters to be measured in seawater according to WFD, OSPAR-CEMP and HELCOM-COMBINE, and comparisons with the current parameter list of the ICES database

The list of parameters was taken from the excel file (seawater ranges) provided by the ICES Data Centre, i.e. data exists in the ICES database for these parameters in seawater.

This list was then compared to the compounds to be measured according to the Water Framework Directive (WFD), OSPAR CEMP and HELCOM-COMBINE. The following compounds are not currently present on the parameter list of the ICES database:

PROGRAMME	COMPOUNDS
WFD	Alachlor, Benzene, SumDDT (p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD)
HELCOM-COMBINE	PAH
OSPAR CEMP	There is no requirement to analyse seawater for any of the hazardous substances except PFOS (OSPAR Pre-CEMP)

In the table below, “x” indicates the parameters of the ICES database which are included in one of the three programmes (WFD, OSPAR CEMP, HELCOM-COMBINE) for seawater analysis.

PARAM	MATRIX	WFD	OSPAR CEMP	HELCOM COMBINE
24D	Before filtration			
ACNE	After filtration			
ACNE	Before filtration			
ACNE	Suspended particulate matter			
ACNLE	After filtration			
ACNLE	Before filtration			
ACNLE	Suspended particulate matter			
ALACL	Before filtration			
ALCANC12	Before filtration			
ALCANC13	Before filtration			
ALCANC14	Before filtration			
ALCANC15	Before filtration			
ALCANC16	Before filtration			
ALCANC17	Before filtration			
ALCANC18	Before filtration			
ALCANC19	Before filtration			
ALCANC20	Before filtration			
ALCANC21	Before filtration			
ALCANC22	Before filtration			
ALCANC23	Before filtration			
ALCANC24	Before filtration			
ALCANC25	Before filtration			
ALCANC26	Before filtration			
ALCANC27	Before filtration			
ALCANC28	Before filtration			

ALCANC29	Before filtration	
ALCANC30	Before filtration	
ALD	After filtration	
ALD	Before filtration	
AMTR	Before filtration	
ANT	After filtration	x
ANT	Before filtration	x
ANT	Suspended particulate matter	
AS	After filtration	
AS	Before filtration	
ATRZ	Before filtration	x
AZM	Before filtration	
B	After filtration	
B	Before filtration	
BAA	After filtration	
BAA	Before filtration	
BAA	Suspended particulate matter	
BAP	After filtration	x
BAP	Before filtration	x
BAP	Suspended particulate matter	x
BBF	After filtration	x
BBF	Before filtration	x
BBF	Suspended particulate matter	x
BD100	After filtration	x
BD100	Suspended particulate matter	x
BD119	After filtration	
BD119	Suspended particulate matter	
BD138	After filtration	
BD138	Suspended particulate matter	
BD153	After filtration	x
BD153	Suspended particulate matter	x
BD154	After filtration	x
BD154	Suspended particulate matter	x
BD183	After filtration	
BD183	Suspended particulate matter	
BD190	After filtration	
BD190	Suspended particulate matter	
BD209	After filtration	
BD209	Suspended particulate matter	
BDE28	After filtration	x
BDE28	Suspended particulate matter	x
BDE47	After filtration	x
BDE47	Suspended particulate matter	x
BDE66	After filtration	
BDE66	Suspended particulate matter	
BDE71	After filtration	

BDE71	Suspended particulate matter		
BDE75	After filtration		
BDE75	Suspended particulate matter		
BDE77	After filtration		
BDE77	Suspended particulate matter		
BDE85	After filtration		
BDE85	Suspended particulate matter		
BDE99	After filtration	x	
BDE99	Suspended particulate matter	x	
BENTZN	Before filtration		
BENZ	Before filtration		
BEP	After filtration		
BEP	Before filtration		
BEP	Suspended particulate matter		
BGHIP	After filtration	x	
BGHIP	Before filtration	x	
BGHIP	Suspended particulate matter	x	
BIPN	After filtration		
BIPN	Before filtration		
BIPN	Suspended particulate matter		
BKF	After filtration	x	
BKF	Before filtration	x	
BKF	Suspended particulate matter	x	
CB101	After filtration		
CB101	Before filtration		x
CB105	Before filtration		
CB118	After filtration		
CB118	Before filtration		x
CB138	After filtration		
CB138	Before filtration		x
CB153	After filtration		
CB153	Before filtration		x
CB156	Before filtration		
CB180	After filtration		
CB180	Before filtration		x
CB194	Before filtration		
CB28	After filtration		
CB28	Before filtration		x
CB52	After filtration		
CB52	Before filtration		x
CCDAN	Before filtration		
CCL4	After filtration	x	
CCL4	Before filtration	x	
CD	After filtration	x	x
CD	Before filtration	x	
CD	Suspended particulate matter	x	x

CHCL3	After filtration	x	
CHCL3	Before filtration	x	
CHR	After filtration		
CHR	Before filtration		
CHR	Suspended particulate matter		
CHRTR	After filtration		
CHRTR	Before filtration		
CL	Before filtration		
CMNB123	Before filtration		
CMNB124	Before filtration		
CMNB142	Before filtration		
CMNB214	Before filtration		
CMNB412	Before filtration		
CNONC	Before filtration		
Co	Before filtration		
CORG	Before filtration		
Cr	After filtration		
Cr	Before filtration		
CS134	Before filtration		
CS137	Before filtration		
CU	After filtration		x
CU	Before filtration		
CU	Suspended particulate matter		x
CVP	Before filtration		
DBACA	Before filtration		
DBAHA	After filtration		
DBAHA	Before filtration		
DBAHA	Suspended particulate matter		
DBT	Before filtration		
DBTIN	After filtration		
DBTIN	Suspended particulate matter		
DCE	After filtration	x	
DCE	Before filtration	x	
DCM	Before filtration	x	
DCV	Before filtration		
DDEOP	Before filtration	x	x
DDEPP	After filtration	x	
DDEPP	Before filtration	x	x
DDEPP	Suspended particulate matter	x	
DDTOP	After filtration	x	
DDTOP	Before filtration	x	x
DDTPP	After filtration	x	
DDTPP	Before filtration	x	x
DDTPP	Suspended particulate matter	x	
DIAZN	Before filtration		
DIELD	After filtration	x	

DIELD	Before filtration	x	
DIURN	Before filtration	x	
DMT	Before filtration		
DOC	After filtration		
DPTIN	After filtration		
DPTIN	Suspended particulate matter		
END	After filtration	x	
END	Before filtration	x	
ENDA	Before filtration	x	
ENDB	Before filtration	x	
ENDOS	Before filtration		
Fe	After filtration		
Fe	Before filtration		
FENT	Before filtration		
FLE	After filtration		
FLE	Before filtration		
FLE	Suspended particulate matter		
FLU	After filtration	x	
FLU	Before filtration	x	
FLU	Suspended particulate matter	x	
HCB	After filtration	x	
HCB	Before filtration	x	x
HCBD	After filtration	x	
HCBD	Before filtration	x	
HCEPX	Before filtration		
HCHA	After filtration	x	
HCHA	Before filtration	x	x
HCHA	Suspended particulate matter	x	
HCHB	After filtration	x	x
HCHB	Before filtration	x	
HCHB	Suspended particulate matter	x	
HCHD	Before filtration	x	
HCHG	After filtration	x	
HCHG	Before filtration	x	x
HCHG	Suspended particulate matter	x	
HEPC	Before filtration		
HEXZ	Before filtration		
HG	After filtration	x	
HG	Before filtration	x	x
HG	Suspended particulate matter	x	
HSUL	Before filtration		
ICDP	After filtration	x	
ICDP	Before filtration	x	
ICDP	Suspended particulate matter	x	
IOPRTN	Before filtration	x	
IRGA	Before filtration		

ISOD	After filtration	x	
ISOD	Before filtration	x	
LINRN	Before filtration		
LOIGN	Before filtration		
MAL	Before filtration		
MBTIN	After filtration		
MBTIN	Suspended particulate matter		
MCPA	Before filtration		
MCPP	Before filtration		
METHG	After filtration		
METHG	Suspended particulate matter		
MIREX	Before filtration		
MLCL	Before filtration		
Mn	After filtration		
Mn	Before filtration		
MPTIN	After filtration		
MPTIN	Suspended particulate matter		
MZCL	Before filtration		
NAP	After filtration	x	
NAP	Before filtration	x	
NAP	Suspended particulate matter	x	
NAP1M	After filtration		
NAP1M	Before filtration		
NAP1M	Suspended particulate matter		
NAP2M	Before filtration		
NAPDI	After filtration		
NAPDI	Before filtration		
NAPDI	Suspended particulate matter		
NAPTM	After filtration		
NAPTM	Before filtration		
NI	After filtration	x	
NI	Before filtration	x	
NI	Suspended particulate matter	x	
NOPHE4	Before filtration	x	
NORG	Suspended particulate matter		
OCPHE4	Before filtration	x	
OCPHEpt	Before filtration	x	
OCS	Before filtration		
PA	After filtration		
PA	Before filtration		
PA	Suspended particulate matter		
PAM1	After filtration		
PAM1	Before filtration		
PAM1	Suspended particulate matter		
PB	After filtration	x	x
PB	Before filtration	x	

PB	Suspended particulate matter	x	x
PCB	Before filtration		
PCP	After filtration	x	
PCP	Before filtration	x	
PER	After filtration		
PER	Before filtration		
PER	Suspended particulate matter		
PFOS	Before filtration		
PHYT	Before filtration		
PMTR	Before filtration		
POC	Suspended particulate matter		
PRIS	Before filtration		
PROZ	Before filtration		
PSAL	After filtration		
PSAL	Before filtration		
PSALA	Before filtration		
PSALD	Before filtration		
PSALF	Before filtration		
PYR	After filtration		
PYR	Before filtration		
PYR	Suspended particulate matter		
QCB	Before filtration	x	
Se	After filtration		
SIMZ	Before filtration	x	
SN	Before filtration		
SR90	Before filtration		
SUSP	After filtration		
SUSP	Before filtration		
SUSP	Suspended particulate matter		
TBSN+	Before filtration	x	
TBTIN	After filtration	x	
TBTIN	Before filtration	x	
TBTIN	Suspended particulate matter	x	
TBUAZ	Before filtration		
TCDAN	Before filtration		
TCE	After filtration		
TCE	Before filtration		
TCE2	After filtration		
TCE2	Before filtration		
TDEOP	Before filtration		
TDEPP	After filtration		
TDEPP	Before filtration		
TDEPP	Suspended particulate matter		
TECE	After filtration	x	
TECE	Before filtration	x	
THCUV	Before filtration		x

TI	Before filtration	
TNONC	Before filtration	
TOL	Before filtration	
TPTIN	After filtration	
TPTIN	Suspended particulate matter	
TRCB	After filtration	x
TRCB	Before filtration	x
TRCB1	Before filtration	x
TRCB1	Before filtration	x
TRCB2	Before filtration	x
TRCE	After filtration	x
TRCE	Before filtration	x
TRF	After filtration	x
TRF	Before filtration	x
TRIAZP	Before filtration	
TURB	Before filtration	
U	After filtration	
V	After filtration	
V	Before filtration	
XYLMP	Before filtration	
XYLO	Before filtration	
ZN	After filtration	x
ZN	Before filtration	
ZN	Suspended particulate matter	x

Annex 9: Revised JAMP Eutrophication Monitoring Guideline: Oxygen

1. Introduction

Biological activity and hydrodynamic processes are the main causes of change in the oxygen concentration in seawater. Nutrient enrichment/eutrophication may give rise to decreased oxygen concentrations and saturation percentages, increased frequency of low oxygen concentrations and increased rate of oxygen consumption, mainly in deeper layers of stratified waters. Dissolved oxygen concentration is used as an indicator of ecosystem health. The use of dissolved oxygen concentration as an Ecological Quality Objective (EcoQO) has been established within an Ecological Quality Framework for an eco-system based approach to the management of the North Sea. It is also used within the Water Framework Directive and European Marine Strategy Framework Directive. These guidelines are intended to support the minimum monitoring requirements of the OSPAR Eutrophication Monitoring Programme and will also support monitoring in accordance with the above directives. The reader should refer to detailed guidance on sampling and measurement of dissolved oxygen in marine waters provided in Aminot, 1997.

2. Purposes

The measurement of oxygen concentrations in water is carried out for, *inter alia*, the following purposes:

- 1) to establish the spatial distribution and frequency of low oxygen concentrations;
- 2) to establish temporal trends in oxygen concentration over periods of several years;
- 3) as a component of the Eutrophication Monitoring Programme.

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) of the marine areas concerned.

It is intended that the region-specific temporal trend monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 50%) over a selected period (e.g. 10 years). To clarify the situation and to help define objectives Contracting Parties should undertake statistical analyses of their existing data sets. This would help to determine the representativeness of the monitoring stations and thus the selection of suitable sampling stations and sampling frequencies.

The spatial distribution monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in oxygen concentrations. This would include a definition of the extent of the monitoring area and some understanding of the randomness of the monitoring stations.

4. Sampling strategy

Oxygen deficits tend to occur in the deeper layers of stratified water, including semi-enclosed basins and in some specific environments such as light limited deep channels and dredged estuaries. Low oxygen concentrations can be found at times of increased oxygen consumption following maximum primary production and are concomitant with certain meteorological and hydrographic conditions (including

temperature and wind speed). Oxygen concentrations may vary considerably from year to year as a result of many influences and therefore trends may be difficult to establish. However, it may be possible to establish trends in some semi-enclosed basins.

Frequent measurement during and after the production season should take place in relation to phytoplankton bloom events, at stations suitable for this purpose, e.g. at stations characterised by vertical stratification or sited in semi-enclosed basins. Sampling should be conducted so that oxygen concentration gradients are resolved, especially those near to the seabed. In order to assess oxygen consumption rates, time-series measurements are required covering appropriate periods of time with high oxygen consumption. If hydrogen sulphide occurs, the concentration should be determined using the methylene blue method (Fonselius *et al.*, 1999). Concentrations of hydrogen sulphide should be given in $\mu\text{mol l}^{-1}$ rather than in negative oxygen equivalents.

For the interpretation of oxygen measurements it is essential to have corresponding measurements of temperature and salinity in order to calculate oxygen saturation which is needed for the assessments of effects on the biota. For some areas additional information including nutrients, organic matter, chlorophyll, pigments, turbidity, hydrographic characteristics of the water column such as stratification at the sampling site may be necessary.

5. Sampling equipment

Many different water samplers may be used to collect discrete samples for oxygen determination. It is essential however, that the water sampler used completely isolates the sample from the surroundings so that no leakage or exchange occurs. In particular circumstances it may be necessary to use a special bottom water sampler.

Immediately after taking the water sample, an aliquot has to be transferred into a calibrated Winkler bottle. Care must be taken to minimize contact between the water sample and atmosphere, especially in samples with low oxygen concentrations. This includes the process of transferring the water from the sample bottle into the Winkler bottle as well as by introducing air into the sample bottle due to leakage. As this transfer of the sample is one of the steps in the whole determination procedure which is responsible for the greatest error, only well trained personnel should be allowed to take the samples.

Oxygen may also be determined using sensors. These sensors may be used attached to a CTD system, as part of an autonomous system on moored platforms or installed on ships for continuous measurements. The advantage of sensor measurements is the provision of high resolution data in space or time, depending on the instrumentation used. Sensors can be particularly useful, compared with conventional discrete sampling techniques, for determining temporal and spatial variability and for capturing short term oxygen deficiency or supersaturation events. On a commercial basis Clark type and Optode type sensors are widely available (Moore *et al.*, 2009).

As all sensors have limitations in their performance, no type of sensor can be generally recommended. These limitations may include the sensitivity, the precision of measurement, low response time, instability of measured results, instability due to varying environmental conditions, poisoning in anoxic waters, etc. Therefore it is necessary to test different sensors and select the one most suitable for measurements in the area to be observed.

Apart from a proper selection of a sensor, the calibration and handling of any sensor has to be validated. Furthermore, regular control, using the Winkler method as reference, is essential. Intervals of calibration, control of measurements and maintenance depend on the type of sensor and the environmental conditions in which the sensor is used. These intervals have to be evaluated and controlled as one element in the validation process of the sensor. The validation process also includes a description of the handling of the sensor in order to obtain the specified precision of the sensor.

6. Storage and pre-treatment of samples

Oxygen in discrete samples must be fixed immediately after collection to bind the oxygen in the sample. The precautions mentioned above must be maintained. After fixation, samples have to be kept in a dark place at a constant temperature - if possible the same as the *in situ* temperature - for at least one hour. The fixed sample should be titrated within 24 hours of collection. In some cases longer storage of the fixed sample may be necessary. Although not recommended, longer storage is possible, provided that storage conditions and handling procedures are validated and clearly documented. Zhang *et al.* (2002) noted that storage under seawater is advisable in such circumstances. Sensors for oxygen determination are designed for *in situ* measurements and should not be used for analysis of discrete samples.

7. Analytical procedures

Standard procedures for the determination of oxygen in discrete water samples are based on the Winkler method. Modifications of this method, which have been verified in intercalibration exercises, are described elsewhere (e.g. Carpenter, 1965; Grasshoff *et al.*, 1999; Strickland and Parsons, 1968). Modifications mainly concern composition of the reagents, titration devices (manual titration, automatic systems) and the method used for detecting the end point of the titration step (e.g. visible colour change of indicator dyes, conductivity measurement, photometric detection). As verified by intercalibration exercises, reliable results can be obtained with all methods, if validated procedures are used by well trained personnel.

Oxygen sensors should only be used if their calibration, handling and maintenance is properly validated (see section 5), including procedures for regular checks of calibration and correct functioning of the sensor (stability, reproducibility, precision of results). The Winkler method should be used as reference method for this purpose. Care should also be taken to avoid unreliable results caused by ignoring the technical limitations of the sensor used for the measurements (see section 5) or by calibrating over an inappropriate range.

8. Analytical quality assurance

At present there is no Certified Reference Material available for oxygen in water. For the Winkler method it is therefore recommended to use internal laboratory procedures according to Grasshoff *et al.* (1999). In order to demonstrate reliable results, each laboratory must establish, validate and document a quality assurance system, which is adequate for the samples to be analysed. Specific technical information on quality assurance is to be found in Carpenter (1965b), Vijverber and Cofino (1987), Aminot (1997), and in the Nordtest report (2006). It is recommended that the laboratory has a quality system in place such as under EN ISO/IEC 17025. The effectiveness of the quality assurance system should be verified by participation in appropriate intercalibration exercises, where available, as often as possible.

9. Reporting requirements

Oxygen must be reported in $\mu\text{mol l}^{-1}$ together with in situ salinity, temperature and sample depth data. Data reporting should be in accordance with the requirements of the latest ICES reporting formats, together with QA information on methods used, detection limits, reference values and any other comments or information relevant to an assessment of the data (e.g. participation in intercalibration exercises).

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Annex 10: Revised JAMP Eutrophication Monitoring Guideline: Nutrients

1. Introduction

Nutrient enrichment may give rise to eutrophication if other conditions are favourable. Nutrient concentrations may be used to help assess the trophic status of marine waters and to determine the cause of eutrophication problems. These guidelines are intended to support the minimum monitoring requirements of the Eutrophication Monitoring Programme. In addition they will support the Water Framework Directive and the European Marine Strategy Framework Directive.

2. Purposes

The measurement of nutrients in seawater is carried out for, *inter alia*, the following purposes:

- a) to monitor the spatial distribution of nutrient concentrations within the maritime area which are influenced by anthropogenic nutrient inputs, taking into account the minimum monitoring requirements of the Eutrophication Monitoring Programme;
- b) to monitor temporal trends in nutrient concentrations over periods of several years (in areas identified under purpose a) in order to assess whether there are increasing or decreasing trends in concentrations as a result of changes in inputs, taking into account the minimum monitoring requirements of the Eutrophication Monitoring Programme;
- c) to support an assessment of the degree of nutrient enrichment within the maritime area, within the context of the work on the development and implementation of a Common Procedure for the Identification of the Eutrophication Status of the Maritime Area;
- d) to further the work on understanding the relationship between nutrient concentrations and/or fluxes and the eutrophication effect parameters specified in the minimum monitoring requirements of the Eutrophication Monitoring Programme.

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) of the marine areas concerned.

It is intended that the region-specific temporal trend monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 50%) over a selected period (e.g. 10 years). To clarify the situation and to help define objectives Contracting Parties should undertake statistical analyses of their existing data sets. This would help to determine the representativeness of the monitoring stations and would also help to determine the selection of suitable sampling stations and sampling frequencies.

The spatial distribution monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in nutrient concentrations. This would include a definition of the extent of the monitoring area and some understanding of the randomness of the monitoring stations.

4. Sampling strategy

Monitoring should consider the following nutrient species¹:

- ammonia, nitrate, nitrite, particulate nitrogen, total nitrogen;
- phosphate, total phosphorus, particulate phosphorus;
- silicate;

From these parameters the dissolved organic fractions of nitrogen (DON) and phosphorus (DOP) can be calculated.

Apart from station information, temperature and salinity are essential supporting parameters. Additional parameters, including chlorophyll pigments, Secchi depth, turbidity, suspended particulate matter, current speed or information about tides, may be needed depending on site and purpose of the investigation.

The most important inorganic nutrients with respect to eutrophication problems are phosphate and the sum of nitrite plus nitrate. Silicate and ammonia are important mainly in relation to particular events and situations. Ammonia is often present in high concentrations in low oxygen waters, e.g. anoxic stagnant bottom waters. Total phosphorus, total nitrogen and particulate nitrogen and phosphorus are important in relation to temporal trends, ecosystem analysis and nutrient budgets. The dissolved organic fractions should also be recognized as a significant source of matter for the recycling of inorganic nutrient species within the system. Dissolved organic carbon concentration is necessary for the interpretation of organic nutrient concentrations.

4.1. Monitoring for purposes a), b) and c)

Monitoring for purposes a), b) and c) (see section 2) should take place at the time of lowest algal activity, which is usually winter. This is because surface waters become progressively depleted in inorganic nutrients during spring, summer and autumn due to their removal by phytoplankton. Therefore, for the maritime area as a whole, the sampling period and the sampling frequency cannot be specified in terms of months or dates; the period is dependent on regional and interannual differences.

Monitoring for nutrients should take place along salinity gradients in order to account for freshwater run-off from land to sea and as a measure to improve consistency. Monitoring for nutrients should take account of inputs, including terrestrial and atmospheric inputs, and the oceanographic characteristics of each region.

A nutrient-salinity relationship for a coastal area can provide information about processes affecting nutrient concentrations and total amounts of nutrients. A linear relationship indicates that physical mixing is the dominant process regulating the nutrient concentration, while non-linearity indicates the additional influence of chemical and/or biological processes. Several sources of freshwater or offshore water may add complexity to nutrient-salinity mixing diagrams, and temporal variability in the nutrient concentrations of the sources may contribute additional scatter and variability to the relationship.

The temporal trend monitoring strategy should ensure that sufficient data are collected in order to confirm that maximum winter nutrient concentrations are covered

¹ The nutrient species specified in the minimum monitoring requirements of the Eutrophication Monitoring Programme are as follows: ammonia, nitrite, nitrate and phosphate. Silicate is a required parameter in problem and potential problem areas.

and that a nutrient-salinity curve can be constructed from which an adequate concentration normalised to a specified salinity (e.g. 30) can be calculated.

In most cases it will be possible to decide only after sampling with suitable temporal and spatial resolution, and with the assistance of supporting parameters which prove lowest algal activity (e.g. chlorophyll a) that the data are suitable for temporal trend studies.

4.2. Monitoring for purpose d)

For purpose d), the sampling strategy for nutrients should be in accordance with the sampling strategy for the eutrophication effect parameters i.e. phytoplankton and benthos.

5. Sampling equipment

5.1. Equipment

A variety of sampling bottles can be used for the collection of nutrient samples. These are deployed on either a CTD-rosette or are clamped to a hydrowire and lowered to the prescribed depth. Reliability of CTD and depth measurements should be ensured and documented.

Working in (shallow) estuaries and coastal areas sometimes requires special equipment and sampling, e.g. samples collected by pumping water through a flexible plastic hose deployed over the side of the ship. It is however essential to validate that the equipment used is demonstrated as adequate for the desired purpose.

It is important to use suitable bottles to collect and store samples, i.e. glass bottles may leach silicate and phosphate into samples. Polyethylene or polypropylene bottles may be used. The sample bottles and containers should always be rinsed with sample water before filling.

5.2. Contamination

Sampling activities always include the risk of contamination, which may have various sources depending on specific sampling situations. Care should be taken to ensure good laboratory practice during sampling procedure (e.g. avoidance of contamination from ship, cleaning of instrumentation and bottles, etc.). It is recommended that laboratories performing measurements check contamination risks and document how they minimize and control potential contamination during sampling. Among the common nutrients ammonia is usually the most challenging to determine due to airborne contamination, both onboard ship and onshore. Contact with cigarette smoke has to be avoided (both in the air and on workers' fingers). At all times the exposure of samples to the atmosphere should be minimised.

6. Storage and pre-treatment of samples

6.1. Storage

Nutrient determinations should be carried out as soon as possible after sampling. Ammonia should be determined immediately after sampling, while nitrate, phosphate and silicate should be determined within a few hours after sampling with samples protected from light and stored in a refrigerator between sampling and analysis.

If immediate analysis is not possible samples must be preserved. Commonly used preservation methods are freezing the samples or adding a preservative, e.g. HgCl₂. If

the sample contains amounts of particulate matter which may compromise the analysis, it should be filtered to remove the particles before freezing (see section 6.2). Samples for the determination of silicate, which have been frozen, should be defrosted for sufficient time for de-polymerisation to occur. This is particularly important for water with high silicate concentrations.

Since no preservation method for nutrients can, at present, be recommended for general use, each laboratory must validate, and document, its storage methods for each nutrient before they are used routinely. The validation should be done over the whole seasonal cycle to investigate varying conditions e.g. during high and low nutrient concentrations and during high and low primary productivity. The QUASH (Quality Assurance of Sampling and Sample Handling) project (1996–2000) carried out an intercomparison of sampling handling and preservation methods for nutrients in seawater for a number of laboratories. The outcome demonstrated the need for laboratories to validate and document their procedures and highlighted the particular challenges of preserving samples for subsequent ammonia analysis (QUASH, 2000).

6.2. Pre-treatment

Unnecessary manipulation of the samples should be avoided, however, filtration at constant pressure or centrifugation may become necessary in particle-rich waters (i.e. in coastal zones, estuaries, or during phytoplankton blooms). Filtration with glass fibre filters (e.g. Whatman GF/F) or hydrophilic cellulose acetate filters (e.g. Sartorius Minisart 0.45 µm pore size) should generally be adequate. Each laboratory should validate the filtration methodology on test samples, including the pressure at which filtration is carried out and for potential contamination from filters, before using them routinely. If unfiltered samples are analysed the need for a correction for turbidity should be assessed.

7. Analytical procedures

The determination of nutrients is largely based on colorimetric methods (e.g. Grasshoff *et al.*, 1999). There are also fluorometric methods available, e.g. for the analysis of ammonia in seawater (Holmes *et al.*, 1999; Aminot *et al.*, 2001) and UV spectrophotometric methods for the direct determination of nitrate (Johnson & Coletti, 2002).

Most methods commonly used are manual methods or manual methods adjusted to automated analytical equipment (continuous flow analysis or flow injection analysis) (Kirkwood, 1996). In addition to the validation of the chemical method itself, the validation of the handling procedures and maintenance of the automatic equipment is important.

Manuals are available, which detail what to consider especially when working at sea with continuous flow analysis of nutrients (Aminot & Kerouel, 2007; Hydes *et al.*, 2010).

8. Analytical quality assurance

For monitoring in off shore environments

The quality assurance programme should ensure that the data are fit for the purpose for which they have been collected, i.e. that they satisfy detection limits and levels of accuracy compatible with the objectives of the monitoring programme. The quality assurance procedures must cover all steps of the nutrient determinations, including sampling, storage of samples, analytical procedures, maintenance and handling of

the equipment, training of the personnel, as well as an audit trail. It is recommended that the laboratory is accredited to EN ISO/IEC 17025. The laboratory should also take part in intercalibration exercises and proficiency testing, as provided by e.g. QUA-SIMEME, to provide external verification of results.

Specific technical information on quality assurance is to be found in Kirkwood (1996) and Vijverber & Cofino (1987) and in the Nordtest report (Nordtest, 2006). In the laboratory performance tests described in these references a “Z score” ≤ 2 (i.e. from -2 to +2) is considered a minimum requirement for a satisfactory analysis. The standard score (Z) is: $Z = (x-u)/\sigma$ where: x is the individual result to be converted to standardised score ; μ is the mean of the population; σ is the standard deviation of the population.

Certified Reference Materials (CRMs) for nutrients in seawater are commercially available from:

- KANSO Technos in Japan (<http://www.kanso.co.jp/eng/production/index.html>), currently for nitrate plus nitrite, nitrite, phosphate and silicate.
- National Research Council of Canada (http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_files_e/MOOS-1_e.pdf) for nitrate plus nitrite, nitrite, phosphate and silicate.
- Eurofins, Denmark (<http://www.eurofins.dk/dk/milj0/reference-materialer/certified-reference-materials.aspx>) for ammonia, total nitrogen, total phosphorous, nitrate plus nitrite, nitrite, phosphate and silicate.

Use of these materials should enable comparability of data to be achieved to within a few percent for silicate and approaching 1 % for nitrate and phosphate for samples with concentrations greater than 100 times the detection limit of the method.

Performance requirements for the methods applied in individual laboratories will depend on the concentrations they are required to measure in their samples. Laboratories should determine their limits of detection and also limits of quantification at which they can reliably quantify nutrient parameters and these should be appropriate for the specific monitoring requirement and target waters. For determining temporal trends of winter nutrients in European Atlantic shelf waters (to S-35), laboratories should aim at the following limits of quantification: Approximately 0.2 μM for TOxN; 0.03 μM for nitrite; 0.06 μM for phosphate; 0.2 μM for silicate and 0.3 μM for ammonia.

9. The use of in situ nutrient analysers

9.1. Platform types

Autonomous nutrient analysers have been increasingly used for providing *in situ* semi-continuous measurements of nutrient concentrations. Where a static platform is used (such as on a mooring), high frequency measurements of nutrient concentrations at a single point may be obtained. When used with a ships pumped seawater supply (such as Ferrybox), a map of nutrient concentrations over a wide area may be obtained. A Ferrybox system allows samples from a fixed depth to be obtained. A mooring may allow deployment of analysers at multiple depths. These techniques are especially useful in environments where there is a substantial temporal and spatial variability of nutrient concentrations. Such platforms should be considered to be part of a wider monitoring programme which includes ship based observations providing a wide spatial coverage as required within section 3.

9.2. Instrument selection

Sensors for *in-situ* applications are based on wet chemistry colorimetric methods or a direct optical UV spectrophotometric measurement (nitrate only). Reviews by Moore *et al.* (2009) and Johnson *et al.* (2007) discuss different types of sensor. Potential problems faced with *in situ* sensors are biofouling, and power constraints. Biofouling may be more readily overcome on a Ferrybox system where cleaning of the measurement system may be programmed into the routine cycle. Controls implemented on some *in situ* optical sensors include wiped sensors, guarding with copper mesh and chlorination. Power constraints on a Ferrybox system will not usually be a problem but may be a consideration on a mooring. The extent of biofouling and power considerations will contribute to determining the length of time sensors can be left *in situ*. Coloured dissolved organic matter (CDOM) has a spectral component to its absorption curve and thus appreciable CDOM may interfere with nitrate measurement when using optical sensors, although in general this is unlikely to be an issue in many marine applications.

9.3. Quality assurance

Appropriate calibration and ongoing quality control must be implemented to ensure that data collected are fit for purpose. Routine laboratory testing and validation of results against discrete samples analysed in the laboratory must be undertaken to ensure that comparable results of known and acceptable quality are obtained.

10. Reporting requirements

Data collected as part of the Eutrophication Monitoring Programme should be reported to the ICES database using the latest ICES reporting formats (currently ERF 3.2 http://www.ices.dk/env/submitting_data.asp).

Table 1 in Appendix 1 presents the ICES field codes recommended for reporting. These include comprehensive metadata regarding analytical method and quality control data. It is recommended that Uncertainty of Measurement (UCM) is reported. Guidance on calculating UCM is available from OSPAR (2011) and Nordtest (2006).

In addition to the ICES field codes Table 1 of Appendix 1 also identifies further information recommended for reporting by the GO-SHIP manual (Hydes *et al.*, 2010). A standard electronic form is being developed and will be made available via the GO-SHIP web portal to enable efficient and consistent reporting of metadata across the global marine nutrient measurement community.

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Acknowledgements

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Appendix 1. Data reporting requirements.

Table 1. Recommended data and metadata field codes (ICES ERF 3.2 http://www.ices.dk/env/submitting_data.asp) for reporting OSPAR nutrients monitoring data to ICES. Right hand column contains additional information to achieve consistent reporting of metadata across the global marine nutrient measurement community as recommended by the Go-Ship manual (Hydes *et al.*, 2010).

ICES Field Codes	Definition	Mandatory Field	Additional Information Identified for reporting in GO-SHIP Manual
RLABO	Reporting laboratory	Y	
CNTRY	IOC Country Codes	Y	
MYEAR	Monitoring year	Y	
OWNER	Owner of data		
PRDAT	Public release date		
Sampling Information			
SHIPC	SeaDataNet Ship and Platform Codes	Y	<ul style="list-style-type: none"> • Date / port of departure and arrival • Name of experiment • Cruise leg • Geographical coverage • Number of CTD stations
CRUIS	Cruise identifier	Y	
STNNO	Station number	Y	
LATIT	Latitude	Y	
LONGI	Longitude	Y	
POSYS	Positioning System Codes		
SDATE	Sample date	Y	
STIME	Sample time		
WADEP	Water depth (sounding in m)		
DEPHU	Sampling depth (upper)		
DEPHL	Sampling depth (lower) (i.e. for flow rated sample)		
SLABO	Sampling lab		
SMTYP	Sampler type		
Station Information			
STATN	Station name		
MPROG	Monitoring programmes & activities (e.g. JAMP)	Y	
WLTYP	Water and land station types (e.g. WFD water bodies)		
MSTAT	Type of monitoring station (e.g. WFD baseline station)		
PURPM	Purpose of Monitoring (e.g. trend)		
Sample / Measurement Information			
SMPNO	Sample number	Y	<ul style="list-style-type: none"> • Sampling container details • Raw and track / RMNS results • Date and time sample was measured • Use of WOCE qualifier flags
SUBNO	Subsample		
NOAGG	Number of aggregated samples		
FINFL	Factors potentially influencing guideline compliance and interpretation of data		
MATRX	Matrix code (WT or SPM)	Y	

PARAM	Parameters Codes	Y	
MUNIT	Measurement unit	Y	
BASIS	Basis of determination		
VFLAG	Data Validity Codes		
QFLAG	Qualifier flag (i.e. "<")		
VALUE	Value	Y	
PERCR	Percentage recovery (%)		
SIGND	Significant digits		
UNCRT	Uncertainty value		
METCU	Method of calculating uncertainty		
Method and Quality Control Information			
ALABO	Analysis lab		<ul style="list-style-type: none"> • Deviations / modifications from standard method or instrument configuration • Instruments settings (e.g. rinse cycles, temperature, gas bubbles) • Lab temperature • Thawing procedure if sample was frozen • Brand and sock info of reagents / salts used • Temperature of preparations of standards • Additional standard preparation details (temp of preparation, dilution sequence, pipettes used) • Quantification procedures (software details for peak picking & calibration, # of points in calibration curve) • Correction procedures (blank correcting, matrix correcting) • Method used to round off results to the number of significant digits • Proportion of samples measured in duplicate
METDC	Method documentation		
REFSK	Reference source or key		
METST	Method of storage		
METFP	Methods of Chemical Fixation/Preservation of Samples		
METPT	Method of pretreatment		
METCX	Method of chemical extraction		
METPS	Method of purification/separation		
METOA	Method of analysis/assay type		
SREFW	Source of reference sea water		
FORML	Formulas used in calculations		
DETLI	Detection limit		
LMQNT	Limit of quantification		
PRFLG	Pressure Flag (if depths are by pressure, "Y")		
CONCH	Reference material type used as control chart basis		
CRMCO	Reference material codes	Y	
Method and Quality Control Information <i>continued</i>			
CRMMB	Reference material control chart measurement basis		
CRMMV	Reference material control chart mean measured value		
MUNIT	Reference material control chart measurement unit		
CRMSD	Reference material control chart standard deviation		
CRMNM	Reference material control chart number of measurements		
CRMPE	Reference material control chart period in weeks		
ICCOD	Intercomparison exercise code		
ICLAB	Intercomparison: lab participation code		

Annex 11: Monitoring Guidelines for Chemical Aspects of Ocean Acidification

1. Introduction

Ocean acidification is an unavoidable consequence of the increased atmospheric concentrations of CO₂ and the partitioning of CO₂ into seawater. CO₂ reacts with seawater to produce carbonate, bicarbonate and hydrogen ions. Since the industrial revolution the concentration of hydrogen ions in seawater has increased by 30%. Ecosystems in certain seas such as Arctic waters are potentially more vulnerable to these changes as they will tend to become undersaturated with respect to the carbonate minerals forming the shells of many organisms earlier than other areas (Gattuso and Hansson, 2011). Elsewhere it is important to consider that hydrogen ions affect many biogeochemical processes such as the ratio of available ammonia to ammonium supporting primary production and the solubility of trace metals. Eutrophication may be closely linked to ocean acidification through the production of organic matter from CO₂ during primary production (Borges and Gypens, 2010; Provoorst *et al.*, 2010; Cai *et al.*, 2011). The degree of ocean acidification is assessed through the measurement of carbonate species in solution and the calculation of the saturation states of the shell forming carbonate mineral aragonite and calcite and monitoring of pH during late winter immediately prior to the spring bloom (as with nutrients). At present data of sufficient accuracy and precision for the assessment of acidification status is generally absent. We are at a stage where the collection of baseline data to look at regional and temporal difference through the year should be encouraged and has to be carried out before a minimum set of monitoring observations can be prescribed. It should be noted that work on Ocean Acidification complements any the study and budgeting of marine CO₂ inventories and air-sea fluxes. Planning of these two activities should not be done in isolation.

2. Purposes

The measurement of carbonate species in seawater is carried out for the following purposes:

- i) To monitor the spatial distribution of carbonate species concentrations within the maritime area to determine the anthropogenic influence on their distribution. High quality marine observations should be coupled to regular monitoring of major river inputs².
- ii) To assess trends in degree of ocean acidification by monitoring pH, other carbonate system parameters and carbonate mineral saturation, over periods of several years.
- iii) To provide information of sufficient spatial and temporal resolution to underpin the identification of biological impacts and future ecological risks.

² River monitoring is needed for (1) understanding of the variability in river inputs and the drivers of this variability (2) to give better parameterisation of river inputs in numerical models of marine acidification (e.g. Blackford *et al.*, 2006).

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) of the marine areas concerned.

It is intended that the region-specific temporal trend monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 0.02 pH) over a selected period (e.g. 10 years). To clarify the situation and to help define objectives Contracting Parties should collect and undertake statistical analyses of new baseline data sets collected (collection of new data should meet the quality criteria required for the monitoring of ocean acidification). The representative monitoring stations chosen for this should be selected on the basis of numerical modelling results and cover the range of environments from nutrient rich estuaries to deep ocean water and around cold water corals.

The spatial distribution of the monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in carbonate parameter concentrations. This would include a definition of the extent of the monitoring area and understanding of how monitoring by different Parties is complementary. This should be done to allowing a full assessment to be integrated across the whole OSPAR area.

4. Sampling strategy

Monitoring should consider all four carbonate species (Dickson, 2010) measured as Total Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), Partial Pressure (of dissolved) Carbon Dioxide ($p\text{CO}_2$), and hydrogen ion concentration measured as pH³ (Dickson *et al.*, 2007). The following supporting parameters are required for calculation of final concentrations: temperature, salinity, silicate and phosphate.

The equilibrium chemistry of the carbonate system has been studied extensively (Dickson, 2010) and the equilibria have been precisely quantified so that if two components of the system are measured the other two can be calculated with known level of error that varies with the choice of the pair and the concentration levels being worked at (Hydes *et al.*, 2010). Well-tested software (e.g. CO2SYS and SEACARB⁴) is available for carrying out the required calculation.

At the present state of development of analytical methods and supporting reference materials, the most reliable methods for work with samples are measurements of DIC and TA, which are supported by Reference Materials⁵. For underway sampling high frequency (<5 minutes) measurements with high precision and accuracy (< 1 ppm) can be achieved for the measurement of $p\text{CO}_2$ (measurements can be referenced

³ Confusion can arise due to the existence of several different pH scales. pH is an operationally defined concept and there are four different scales (U.S. National Bureau of Standards (NBS), free scale, total hydrogen ion scale, seawater scale), which result in significantly different numerical values. The recommended scale for use in seawater related calculation is the total hydrogen ion scale. It is critical that the scale used is reported as part of the meta-data when data is included in a data base.

⁴ CO₂ system calculation software can be down loaded from (1) <http://cdiac.ornl.gov/ftp/co2sys/> (2) Lavigne H. & Gattuso J.-P., 2011. seacarb: seawater carbonate chemistry with R. R package version 2.4. <http://CRAN.R-project.org/package=seacarb> (3) http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/

⁵ Dickson Lab <http://andrew.ucsd.edu/co2qc/>

against WMO approved gas standards⁶). For assessment of ocean acidification, in some areas where only measurements of pCO₂ are available they can be coupled to estimates of TA from salinity (Lee *et al.*, 2006) to give a reliable calculation of pH.

Prior to establishing long term monitoring Parties should undertake wide ranging measurements to define the levels of variability across their marine areas before defining a minimum effective programme for observations in their areas. This should take into account and be coordinated with the plans of other Parties and their own existing programmes for monitoring other parameters (eutrophication being the likely most complementary activity).

Guidelines for monitoring are set out below in line with existing guidelines for the monitoring of eutrophication. For the parallel assessment of air-sea fluxes for the establishment of annual air-sea fluxes, year round monitoring of pCO₂ needs to be done with repeat visits sites on at least a monthly basis in representative areas (to be defined from numerical models).

4.1. Minimum monitoring for purposes i) and ii)

In the mature phase monitoring for purposes 1 and 2 in surface waters should take place in late winter prior to the spring bloom. This is because this is the period of least rapid change in concentrations resulting from biological activity.

Monitoring of carbonate parameters should take place along salinity gradients in order to account for freshwater run-off from land to sea and as a measure to ensure consistency in treatment of the data for assessment. Monitoring in shelf seawaters should be sufficiently extensive take account of inputs and the oceanographic characteristics of each region, particularly the in-flow of ocean water across the shelf break.

TA-salinity relationships for a coastal area can provide information about processes involved in regulating TA concentrations and the levels and variability of riverine inputs. A linear relationship indicates that physical mixing is the dominant process regulating the nutrient concentration, while non-linearity indicates the additional influence of chemical and/or biological processes. Several sources of freshwater or offshore water may add complexity to TA-salinity mixing diagrams, and temporal variability in the TA concentrations of the sources may contribute additional scatter and variability to the relationship. The temporal trend monitoring strategy should ensure that sufficient data are collected in order to confirm that maximum winter DIC concentrations are covered.

Sufficient data should be collected so that a normalisation of the carbonate parameters to salinity (e.g. 34.5 for the North Sea) can be carried and the precision of the normalisation defined statistically. pH and pCO₂ vary significantly with temperature therefore for assessments their values should be reported at agreed common temperature (e.g. 15.00° C).

After sampling, the supporting parameters should be inspected to check that algal activity was likely to have been low at the time of sampling (e.g. chlorophyll a) to assess that the data are suitable for inclusion in temporal trend studies.

⁶ NOAA Carbon Cycle Greenhouse Gases Group (CCGG <http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html>) is presently responsible for maintaining the World Meteorological Organization mole fraction scales for CO₂, CH₄, and CO.

For Ocean Acidification monitoring in off shelf waters key areas include Arctic Seas and around cold-water corals because of their vulnerability to change. Measurements are required in subsurface waters as these can be used for calculation of the accumulation anthropogenic carbon in the water.

4.2. Monitoring for purpose iii)

Monitoring for purpose 3 is intended to address issue of where do decreased pH conditions affect ecosystem function such as the formation of shells in plankton and macrofauna. For purpose 3, the sampling strategy for the carbonate system should be linked to e.g. studies of effects on coccolithophores, molluscs and embryonic life stages of certain groups of organisms. From a biological perspective there is need to capture data on the spatial and temporal variation in the acidity of ecosystems. Consideration needs to be given to the linkage of observations of chemical changes to those assessing biological impacts of chemical changes.

5. Sampling equipment

5.1. Equipment

Water samples for analysis of DIC/TA can be collected using a rosette frame or hydro-bottles clamped to a hydro-wire and lowered to the prescribed depth. Use of a rosette sampler combined with a profiling probe for measurement of temperature and salinity (a "CTD" profiler) is preferred. Additional sub-samples should be taken from water bottles and analysed for salinity and nutrients and chlorophyll-a. Sampling from an underway water supply may also be possible but the procedure should be validated.

Samples for DIC/TA should be collected directly into Pyrex glass bottles with gas tight stoppers and the samples poisoned by the addition of Mercuric Chloride. For rosette sampling the priority for the order of drawing samples is - samples for DIC/TA should be taken after CFC and oxygen samples but before nutrient and salinity samples, to minimise the CO₂ exchange across the free surface that forms in the hydro-bottle as it drains.

5.2. Contamination

Sampling should be undertaken in such a way that any ship's discharges are avoided. Sample bottles should remain closed when not in use.

Sample bottles should be thoroughly rinsed with sample before filling. A tube attached to hydro-bottle running to the base of the sample bottle should be used to minimise the possibility of gas exchange during sampling.

6. Storage and pre-treatment of samples

6.1. Storage

Bottles that are gas tight should be used for sample storage. Normally Pyrex bottles of 250 or 500 ml capacity are used and sealed with a greased ground glass stopper held in with a retaining band. Samples poisoned with Mercuric Chloride (Dickson *et al.*, 2007; SOP 1) can stable for at least one year if collected carefully.

It is recommended that laboratories should conduct systematic studies of the stability of their samples. As part of these tests exchange samples between laboratories should be done to separate errors due to degradation of samples from measuring errors.

6.2. Pre-treatment

Unnecessary manipulation of the samples should be avoided, however filtration with GF-F filters may be used for TA samples from turbid waters. No recommendation can be given for DIC samples. An accepted filtration method that minimises the gas exchange for DIC samples has not been published.

7. Analytical procedures

The methods for the determination of the four carbonate species are described in detail in Dickson *et al.* (2007). The preferred methods are (1) TA - acid base titration with the end point calculated by Gran fit (2) DIC - addition of phosphoric acid with quantification of the evolved CO₂ by Coulometry (3) pCO₂ underway samples - equilibration of gas stream with the surface water and determination of the equilibrated mole fraction of CO₂ in the gas stream by infra-red spectrometry at a known gas pressure (4) No recommendation can presently (2012) be given on a technique for direct measurements of pH because both the equipment and methods of calibration are not at a mature stage of development.

8. Analytical quality assurance

The quality assurance programme should ensure that the data are fit for the purpose for which they have been collected, i.e. that they satisfy levels of precision and accuracy compatible with the objectives of the monitoring programme.

Regular collection of duplicate samples should be undertaken. Specific technical information on QA and QC is provided by Dickson *et al.* (2007, SOPs 21, 22 and 23). Reference Materials (RM) are available for TA and DIC and reference gasses for pCO₂ (see above). Recommendations and Matlab tools for pCO₂ QC procedures were developed as part of the Surface Ocean CO₂ Atlas (SOCAT) project and are available at <http://www.socat.info/publications.html>. Quality assurance information should be reported as specified in Section 9.

When possible in addition to routine use of RMs, the data should be checked for cruise-to-cruise consistency by comparing samples from the deep ocean with near-steady CO₂ chemistry (>2000 meters for instance), by comparing DIC-Salinity relationships, and/or relationships between DIC and nitrate, phosphate and oxygen (Tanhua *et al.*, 2010).

A system of regular inter-comparisons between the concerned laboratories should be organised.

Table 1. Summary tables of total errors and biases for individual methods.

Table 8.1. Generally accepted levels of error associated with each method based on Dickson (2010).				
		Ref Method	State of art	Other
	Total dissolved inorganic carbon (μmol kg ⁻¹)			
(A)	Acidification / vacuum extraction / manometric determination	1.0		
(B)	Acidification / gas stripping / coulometric determination		2-3	
(C)	Acidification / gas stripping / infrared detection			4
(D)	Closed-cell acidimetric titration			10+
(E)	Auto-analyser colorimetric			5+

	Total alkalinity $\mu\text{mol/kg}$			
(F)	Closed-cell acidimetric titration		2-3	
(G)	Open-cell acidimetric titration	1.2		
(H)	Other titration systems			2-10
	pH			
(I)	Electrometric determination with standard TRIS buffer.		0.005	0.01-0.03
(J)	Spectrophotometric determination using I. <i>m</i> -cresol purple	0.003		
	$x\text{CO}_2 / p\text{CO}_2 \mu\text{atm}$			
(K)	Direct - equilibrator infrared determination of $x\text{CO}_2$		2	
(M)	Indirect - membrane colorimetric determination of $x\text{CO}_2$			2-10
(L)	Direct - membrane infrared determination of $x\text{CO}_2$			1-10

Analytical Measurement	Desired Accuracy ¹	Uncertainty ²	Availability
DIC	$\pm 1 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$	since 1991 ³
TA	$\pm 1 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$	since 1996 ⁴
pH	± 0.002	± 0.003	since 2009 ⁵
Mole fraction of CO ₂ in dry air	$0.5 \mu\text{mol mole}^{-1}$	$\pm 0.1 \mu\text{mol mole}^{-1}$	since 1995 ⁶

¹ Based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the CO₂ content of sea water that allow the increases due to the burning of fossil fuels to be observed. (SCOR, 1985. Oceanic CO₂ measurements. Report of the third meeting of the Working Group 75, Les Houches, France, October 1985.)

² Estimated standard uncertainties for the Dickson SIO reference materials.

³ Sterilised natural seawater, certificated using a definitive method based on acidification, vacuum extraction, and manometric determination of the CO₂ released. Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

⁴ Certificated using a definitive method based on an open-cell acidimetric titration technique (Dickson *et al.*, 2003). Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

⁵ Standard buffer solutions based on TRIS in synthetic seawater (Nemzer & Dickson, 2005; DeVallis & Dickson, 1998). Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>). These now available, in at present limited quantities, from Dickson's laboratory for the validation of locally prepared buffers. Dickson *et al.*, 2007 - SOP 6a describes the preparation of buffers using 2-amino-2-hydroxy-1,3-propanediol (TRIS) and 2-aminopyridine (AMP) in synthetic sea water.

⁶ For calibration of continuous pCO₂ measurement systems, cylinders of air certificated on the basis of non-dispersive infrared spectrometry are available from NOAA/ESRL, (<http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html>).

9. Reporting requirements

Data reporting should be in accordance with the latest ICES reporting formats, together with information on methods used, detection limits, reference values and any other comments or information relevant to an ultimate assessment of the data. In order to establish the acceptability of the data, they should be reported together with and summary information from recent control charts, including dates, sample sizes, means and standard deviations. Only directly measured data can be reported.

Data for TA and DIC should be reported in units of $\mu\text{mol kg}^{-1}$ and accompanied by a measurement of the in-situ temperature recorded with an error of less than ± 0.01 °C, salinity $<\pm 0.1$, phosphate $<\pm 0.1 \mu\text{mol kg}^{-1}$, silicate $<\pm 1.5 \mu\text{mol kg}^{-1}$.

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Annex 12: Technical minutes by RGLYSAC

Ketil Hylland (Chair), Michelle Giltrap, Thomas Lang

Ecotoxicological assessment criteria

This review is based on documents from OSPAR (HASEC 2011, MIME 2010) and reports from MCWG 2012 and WGMS 2012, as well as the draft report from WGBEC 2012.

Background

The intention of ecotoxicological assessment criteria (EAC) is to predict the concentration of a chemical in the tissues of marine organisms, in water or in sediment that will cause effect in the actual organism, in organisms higher in the food chain (such as humans) or in organisms present in the relevant habitat (water, sediment). As was commented by WGBEC 15 years ago during the first efforts to develop EACs, the concept is problematic since other factors will modulate effects in ways that cannot be easily predicted, be for EACs in biota or sediment. This means that any management system using EACs will have to take into account large uncertainties.

EACs for biota

Lipophilic substances will not exercise any effects while stored in fatty depots, but if and when they are released, e.g. during starvation or other mobilization of fat. A fraction of a substance may be associated with membrane lipids and interact directly with cellular processes, so the above is not necessarily the entire truth, but serves to illustrate the problem of attempting to relate levels of chemicals in tissues to effects. Similarly, metals in tissues may be in a form which is not readily available for tissues, e.g. as granules.

EACs for sediment

It is also problematic to predict the toxicity of chemicals in natural sediments from its concentration, as commented by WGMS 2012. As for biota there are many modulating factors that will affect the toxicity and extrapolation from lab-based studies with spiked sediments is not really appropriate (spiked sediments will be more toxic than the same concentration in natural sediments). At WGMS it was indicated that a way forward could be the use of passive samplers combined with in vitro assays or effect-directed assessment. Such approaches should clearly be investigated, but there is no data available at present.

General considerations

Conceptually, the lowest value available should be used to provide protection for both human consumers and aquatic organisms. It should always be specified which "trophic chain" has been the basis for the EAC – whether human/top predator, fish or invertebrate. It is not necessarily so that human/top predator will be the most sensitive (organotins is an example of this).

It is important not to oversimplify the calculation of EACs even if it could be tempting due to scarcity of data. As commented by WGBEC (2012) it is crucial to separate between different organisms for EACs, both due to different metabolism and trophic chains. At the very least, fish and mussel need to be separated. Another major organism group for which there will be data is crustaceans, which should also be treated separately to the other two. It is to be expected that other taxonomic groups in marine

ecosystems, e.g. echinoderms and tunicates, will have different sensitivity to the above, and it should be considered whether a general application factor should be applied to make the EAC more conservative, reflecting the data availability (as is done in general risk assessment of chemicals, EU TGD).

Each estimated factor, as compared to a measurement, used to derive an EAC will clearly increase the uncertainty of the final value. Any EAC should only at most include one estimated value.

The documents are using the term “dose-effect” for the relationship between the chemical and effects on aquatic organisms, but the correct term in this context is “dose-response”. In toxicology and ecotoxicology, “dose-effect” is generally used to describe the relationship between the concentration of a substance in an organism and response in a single endpoint, e.g. activity of an enzyme or respiration.

Recommendations

There are fundamental chemical and biological issues with estimating coefficients in the derivation of EACs, simply because it requires impossible assumptions on processes in the environment and within organisms. Within organisms the main issue is a lack of knowledge of internal bioavailability and of interactions with other chemicals, and for sediment a lack of knowledge of bioavailability.

In addition to ensuring that the uncertainty in any given EACs is included with the value itself, it should be accepted that there may not be sufficient data to establish values for all chemicals. It is better not to have an EAC for a chemical than a highly uncertain (and probably erroneous) EAC.

Updating guidelines (biological effects)

A number of guidelines currently exist within OSPAR concerning biological effects of contaminants, all of which have been developed at different times during the last 15 years. They include JAMP Guidelines for general biological effects monitoring (1997), JAMP Guidelines for contaminant-specific biological effects monitoring (1997) and OSPAR Guidelines of offshore monitoring (2004), Background document of biological effects of contaminants (2007). In addition, recent work within ICES/OSPAR SGIMC (SGIMC, 2011) has addressed methods and assessment criteria for biological effects.

As in any other research area there has been a development of methods and techniques, as well as increased experience, with biological effects methods. There is therefore be a more or less continuous need to update and revise existing guidelines. The two JAMP guidelines from 1997 will be superseded by the framework resulting from SGIMC processes and should be made redundant. The part of the guideline on offshore monitoring concerning water column monitoring need to be updated taking the outcome from SGIMC into account.

Recommendation

Efforts should be made to find an appropriate channel for regular updates to existing guidelines. ICES WGBEC would presumably be the most appropriate forum.

Annex 13: Technical minutes by RGMON 2012

RGMON was convened to review the material prepared by 2 ICES Working Groups in response to 4 requests from OSPAR as detailed below. The RGMON worked by correspondence. The 2 members (see Annex III) prepared initial individual reviews to the draft responses. These individual reviews were collated by the chair and then reviewed and approved by all RG members by 10 May 2012.

The 4 requests were:

1. Revise the JAMP guidelines on nutrients,
2. Revise the JAMP guidelines on oxygen,
3. Develop JAMP guidelines on monitoring of contaminants in seawater, and
4. Develop guidance for the spatial design of a regional monitoring programme for contaminants in sediments.

Details of the requests are provided in Annex 1.

Two of the OSPAR requests, guidelines for sampling seawater for contaminants and the spatial design of a sediment monitoring program had been reviewed in 2011 but the advice at that time was preliminary and comments from the RG and ADG were internal advice to the respective working groups. This year's reviews of those two documents will focus on the WG's response to the advice from 2011 and the technical details of the advice.

1. Revised JAMP Eutrophication Monitoring Guideline: Nutrients

This request was originally received from OSPAR in 2009 and MCWG drafted an initial response. ICES advised OSPAR that it would delay its response until there was time to consider the potential impact of requirements under the MSFD, specifically for Descriptor 5. MCWG has considered developments under the MSFD in this draft response.

The document has been substantially revised to incorporate advances since the guidelines were last revised. There have been changes in the purpose of nutrient sampling programs and changes in the techniques used to collect samples. There have also been some advances in quality assurance.

The document seems to be complete in the identification of significant changes however the document requires substantial editing to make the document more readable. Specific suggestions are made in Annex "Nutrients" attached to this document.

2. Revised JAMP Eutrophication Monitoring Guideline: Oxygen

The background for this revision is the same as for the nutrient guidelines; an initial revision was made in 2009 and then updated in 2012 to take into account developments with the MSFD.

This revision is very substantial. The sections on "Sampling Strategy", "Sampling Equipment", and "Storage and Pre-treatment of Samples" have been expanded to include detailed information that is of importance to any laboratory involved in this type of work. The draft would benefit from substantial editing to make the text clearer and easier to read. Specific recommendations are made in the Annex "Oxygen" attached to this document.

3. JAMP guidelines on monitoring of contaminants in seawater

An initial draft response by MCWG in 2011 was reviewed by ADGMON2. The internal advice provided by ADGMON2 focussed mostly on the scope and organization of the document. This review is largely an evaluation of the MCWG response to the internal advice of 2011. Comments are organized under the headings of the draft document from MCWG with the heading numbers at one lower level, i.e. a level 1 heading is a level 2 heading in the following text.

3.1 Introduction

See marked up text of draft document from MCWG for specific editing recommendations.

3.2 Purposes

In 2012 ADGMON2 commented –

“There needs to be an introductory piece that describes seawater, contaminants, and their dynamics. Some of the aspects of seawater composition that need to be considered are its salinity and its dissolved and particulate components. The particulate component needs to be described in terms of its biotic and abiotic components and how these might affect sampling strategy and procedures, and also how they might affect the distribution of contaminants in a seawater sample. There also needs to be some discussion of the boundary layers; the water-air and water-sediment interfaces. Sampling of the surface layer seems to belong in this document. Sampling of the benthic boundary layer probably belongs in a similar document on sediment sampling.”

The present text does not deal with this in any substantive manner. This description is important because it establishes the rationale for sampling strategy and the details of sampling procedures.

“There also needs to be a discussion of the importance of collecting and recording observations that describe the ecosystem context of the sample; e.g. salinity, temperature, depth of thermocline, halocline, etc. Whether this information is here or in the section on sampling strategy the case needs to be made for collecting contextual information along with the seawater sample.”

There is no discussion of water body structure and how this might impact the distribution of contaminants, the text as written appears to assume that the water column is well mixed and vertical structure does not have to be considered. There needs to be a statement to the effect that sampling design should include the consideration of advice from physical oceanographers on water column dynamics and structure.

“The general purpose for monitoring contaminants in seawater also needs to be discussed, i.e. to protect the health of marine organisms. This should then lead to the need for integrated monitoring and the role that measuring of contaminants in seawater has.”

There is a detailed discussion of how monitoring of contaminants in seawater responds to the overall goals of the OSPAR hazardous substance strategy etc.

3.3 Quantitative objectives

This section has been substantially expanded with the addition of subsections on

1. Contaminant speciation
2. Detection limits

3. Detectability of temporal and spatial trends
4. Costs

The expanded text covers all of the points identified in the ADGMON2 advice. Some specific recommendations regarding wording and organization are provided in the marked up text.

3.4 Sampling strategy

The ADGMON2 advice and this revised draft document refer to the “JAMP Guideline on Integrated Monitoring of Contaminants and Their Effects.” To our knowledge this document has not been finalised and therefore needs to be referred to appropriately. The revised and greatly expanded section includes subsections on specific considerations for temporal trend and spatial monitoring.

The section on “sampling method considerations” responds to the ADGMON2 comments about describing “seawater.” The points raised here are good but would benefit from an earlier discussion about the composition and structure of seawater.

The section on “supporting data” needs to be more inclusive. If the seawater sampling is not being done in cooperation with other biological and physical oceanographic data and sample collection then the co-factors could be a minimum requirement for “open ocean” sampling but in near shore areas it would be desirable to include parameters that provide some measure of the human impact in the sampling area.

The section on “statistical considerations” is good but could use some additional information; see the marked up text for specific comments. The revised draft deleted the equations and detailed calculations found in the earlier draft. The value of this detail should be considered by the ADGMON.

Section 4.6: Batch sampling versus time integrated sampling” is a welcome addition. Some specific recommendations regarding wording are provided in the marked up text.

3.5 Sampling equipment

The revised text responds to the recommendation of ADGMON. Some specific recommendations regarding wording are provided in the marked up text.

3.6 Storage and pre-treatment of samples

The initial draft text was amended as suggested by ADGMON2.

3.7 Analytical procedures

The initial draft text was amended as suggested by ADGMON2.

3.8 Quality assurance (QA)

The initial draft text was amended as suggested by ADGMON2.

3.9 Reporting requirements

The initial draft text was amended as suggested by ADGMON2.

4. Guidance on the design of a regional monitoring programme for contaminants in sediments

This report provides technical comments on the draft advice from the 2012 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS) on the request from OSPAR to provide advice on the spatial design of a regional monitoring programme for contaminants in sediments. Specifically:

“to develop guidance on the design of a regional monitoring programme for contaminants in sediments which can explain whether good environmental status has been achieved on a larger regional scale (e.g. sub-Regions of the OSPAR Regions) within the period 2010–2020, with the major effort in 2014–2020. The guidance should address:

- a. the selection of areas where monitoring makes most sense, i.a.
 - (i) depths that are sensible to monitor (does it make sense to monitor below 1000 m? 500 m? 200 m? 100 m?)
 - (ii) sediment types that are sensible to use and the implication for possible spatial coverage
 - (iii) ship time considerations;
 - (iv) time from changes in inputs to response in the sediment can be detected
- b. the required spatial resolution of sampling within these areas

The guidance should be divided into coastal and open water (i.e. beyond 12 nautical mile limit) and take into account the need to distinguish between point source monitoring and diffuse sources”

In 2011 RGMON2 reviewed material from the WGMS 2011 report that was very preliminary in nature, the intention being to provide the requested advice to OSPAR in June of 2012. The comments of RGMON2 were therefore focused on the general content of the WGMS 2011 report rather than the detailed content. The review of the material provided by WGMS in its 2012 report focuses on the response of the WG to the comments provided by ADGMON2 in 2011.

5. RGMON comments

The response from WGMS suggests that the request from OSPAR has perhaps been unofficially modified or expanded. The OSPAR request is for advice on sampling design for the purpose of interregional comparisons as per the requirement of the MSFD. However another aspect of the MSFD is that where GES has not been met that member states must show that they are making progress toward achieving GES, i.e. an appropriate temporal trend. According to the WGMS text a decision has already been made that the spatial comparison and the test of whether or not GES is made will be based on the analysis of whole sediments. We presume that there is no reason to argue this point further even if it severely compromises the ability to detect interregional differences or to reasonably assess whether or not GES is met.

WGMS is however continuing to make the argument that it is futile to try to determine temporal trends in sediment contamination by analysing whole sediments. As we understand the WGMS text a pilot study is being undertaken in the southern

North Sea to determine the practicality of identifying strata based on sediment type and sediment dynamics. It is not clear what properties of sediment dynamics will be used, perhaps some measure of shear strength to express sediment mobility? Presumably the purpose of this exercise is to provide member states and OSPAR with a stronger basis for arguing the need to explicitly sample fine sediments or else sieve sediments to obtain the fine grain component for analyses.

Given that the information contained in the WGMS report will have already been informally communicated to OSPAR the ADGMON will have to consider what information needs to be formally communicated. The text from the WGMS report lacks clarity and will need to be amended if it will be the basis for the ICES response. We have provided numerous comments in the WGMS text that hopefully assist with the editing.

Annex Nutrients

Revised JAMP Eutrophication Monitoring Guideline: Nutrients

1. Introduction

Nutrient enrichment may give rise to eutrophication if other conditions are favourable. Nutrient concentrations may be used to help assess the trophic status of marine waters and to determine the cause of eutrophication problems. These guidelines are intended to support the minimum monitoring requirements of the Eutrophication Monitoring Programme. In addition they will support monitoring and assessment requirements the Water Framework Directive and the European Marine Strategy Framework Directive.

2. Purposes

The measurement of nutrients in seawater is carried out for, *inter alia*, the following purposes:

- a) to monitor the spatial distribution of nutrient concentrations within the maritime area where nutrient levels are influenced by anthropogenic inputs, taking into account the minimum monitoring requirements of the Eutrophication Monitoring Programme;
- b) to monitor temporal trends in nutrient concentrations over periods of several years (in areas identified under purpose a) in order to assess whether there are increasing or decreasing trends in concentrations as a result of changes in inputs, taking into account the minimum monitoring requirements of the Eutrophication Monitoring Programme;
- c) to support an assessment of the degree of nutrient enrichment within the maritime area, within the context of the work on the development and implementation of a Common Procedure for the Identification of the Eutrophication Status of the Maritime Area;
- d) to further the work on understanding the relationship between nutrient concentrations and/or fluxes and the eutrophication effect parameters specified in the minimum monitoring requirements of the Eutrophication Monitoring Programme. (Add a comment regarding requirements under Descriptor 5 of the MSFD)

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) of the marine areas concerned.

It is intended that the region-specific temporal trend monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 50%) over a selected period (e.g. 6 years). To clarify the situation and to help define objectives Contracting Parties should undertake statistical analyses of their existing data sets. This would help to determine the representativeness of the monitoring stations and would also help to determine the selection of suitable sampling stations and sampling frequencies.

The spatial distribution monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in nutrient concentrations. This would include a definition of the extent of

the monitoring area and some understanding of the randomness of the monitoring stations.

4. Sampling strategy

Monitoring should consider the following nutrient species⁷:

- ammonia, nitrate, nitrite, particulate nitrogen, total nitrogen;
- phosphate, total phosphorus, particulate phosphorus;
- silicate;

From these parameters the dissolved organic fractions of nitrogen (DON) and phosphorus (DOP) can be calculated.

Apart from station information, temperature and salinity are essential supporting parameters. Additional parameters, including chlorophyll pigments, Secchi depth, turbidity, suspended particulate matter, current speed or information about tides, may be needed depending on site and purpose of the investigation. (See next par. – it seems that data for DOC is also needed)

The most important inorganic nutrients with respect to eutrophication problems are phosphate and the sum of nitrite plus nitrate. Silicate and ammonia are important mainly in relation to particular events and situations. Ammonia is often present in high concentrations in low oxygen waters, e.g. anoxic stagnant bottom waters. Total phosphorus, total nitrogen and particulate nitrogen and phosphorus are important in relation to temporal trends, ecosystem analysis and nutrient budgets. The dissolved organic fractions should also be recognized as a significant source of matter for the recycling of inorganic nutrient species within the system. Dissolved organic carbon concentration is necessary for the interpretation of organic nutrient concentrations.

There needs to be an explanation given of the different sampling requirements for non-problem, potential problem, and problem areas as defined by OSPAR.

4.1 Monitoring for purposes a), b) and c)

Monitoring for purposes a), b) and c) (see section 2) should take place at the time of lowest algal activity, which is usually winter. This is because surface waters become progressively depleted in inorganic nutrients during spring, summer and autumn due to their removal by phytoplankton. Therefore, for the maritime area as a whole, the sampling period and the sampling frequency cannot be specified in terms of months or dates; the period is dependent on regional and interannual differences. (Due to these inter-regional differences the concept of winter nutrients should be re-visited. The first and second parts of this paragraph are contradictory)

Monitoring for nutrients should take account of inputs, including terrestrial and atmospheric inputs, and the oceanographic characteristics of each region. For example, monitoring for nutrients should take place along salinity gradients in order to account for freshwater run-off from land to sea.

A nutrient-salinity relationship for a coastal area can provide information about processes affecting nutrient concentrations and total amounts of nutrients. A linear

⁷ The nutrient species specified in the minimum monitoring requirements of the Eutrophication Monitoring Programme are as follows: ammonia, nitrite, nitrate and phosphate. Silicate is a required parameter in problem and potential problem areas.

relationship indicates that physical mixing is the dominant process regulating the nutrient concentration, while non-linearity indicates the additional influence of chemical and/or biological processes. Several sources of freshwater or offshore water may add complexity to nutrient-salinity mixing diagrams, and temporal variability in the nutrient concentrations of the sources may contribute additional scatter and variability to the relationship.

The temporal trend monitoring strategy should ensure that sufficient data are collected in order to confirm that maximum winter nutrient concentrations are covered and that a nutrient-salinity curve can be constructed from which an adequate concentration normalised to a specified salinity (e.g. 30) can be calculated.

In most cases it will be possible to decide only after sampling with suitable temporal and spatial resolution, and with the assistance of supporting parameters which prove lowest algal activity (e.g. chlorophyll a) that the data are suitable for temporal trend studies.

(Is it true for all OSPAR areas that maximum nutrient levels are present in the winter?

Nutrients are normally not homogeneously distributed with depth (specially during the stratification annual period). This vertical variability could be more important than the seasonal one. Therefore, it is necessary to emphasize that the samplings cover this vertical variability adequately.)

4.2 Monitoring for purpose d)

For purpose d), the sampling strategy for nutrients should be in accordance with the sampling strategy for the eutrophication effect parameters, i.e. phytoplankton and benthos. (There should be some discussion/mention of the eutrophication effect parameters in the introduction)

5. Sampling equipment

5.1 Equipment

A variety of sampling bottles can be used for the collection of nutrient samples. These are deployed on either a CTD-rosette or are clamped to a hydrowire and lowered to the prescribed depth. Reliability of CTD and depth measurements should be ensured and documented.

Working in (shallow) estuaries and coastal areas sometimes requires special equipment and sampling, e.g. samples collected by pumping water through a flexible plastic hose deployed over the side of the ship. It is however essential to validate that the equipment used is demonstrated as adequate for the desired purpose.

It is important to use suitable bottles to collect and store samples, i.e. glass bottles may leach silicate and phosphate into samples. Polyethylene or polypropylene bottles may be used. The sample bottles and containers should always be rinsed with sample water before filling.

5.2 Contamination

Sampling activities always include the risk of contamination, which may have various sources depending on specific sampling situations. Care should be taken to ensure good laboratory practice during sampling procedure (e.g. avoidance of contamination from ship, cleaning of instrumentation and bottles, etc.). It is recom-

mended that laboratories performing measurements check contamination risks and document how they minimize and control potential contamination during sampling. Among the common nutrients ammonia is usually the most challenging to determine due to airborne contamination, both onboard ship and onshore. Contact with cigarette smoke has to be avoided (both in the air and on workers' fingers). At all times the exposure of samples to the atmosphere should be minimised.

6. Storage and pre-treatment of samples

6.1 Storage

Nutrient determinations should be carried out as soon as possible after sampling. Ammonia should be determined immediately after sampling, while nitrate, phosphate and silicate should be determined within a few hours after sampling with samples protected from light and stored in a refrigerator between sampling and analysis.

If immediate analysis is not possible samples must be preserved. Commonly used preservation methods are freezing the samples or adding a preservative, e.g. HgCl₂. If the sample contains amounts of particulate matter which may compromise the analysis, it should be filtered to remove the particles before freezing (see section 6.2). Samples for the determination of silicate, which have been frozen, should be defrosted for sufficient time for de-polymerisation to occur. This is particularly important for water with high silicate concentrations. (These last 2 sentences belong with the analysis discussion)

Since no preservation method for nutrients can, at present, be recommended for general use, each laboratory must validate, and document, its storage methods for each nutrient before they are used routinely. The validation should be done over the whole seasonal cycle to investigate varying conditions e.g. during high and low nutrient concentrations and during high and low primary productivity. The QUASH (Quality Assurance of Sampling and Sample Handling) project (1996–2000) carried out an intercomparison of sampling handling and preservation methods for nutrients in seawater for a number of laboratories. The outcome demonstrated the need for laboratories to validate and document their procedures and highlighted the particular challenges of preserving samples for subsequent ammonia analysis (QUASH, 2000).

6.2 Pre-treatment

Unnecessary manipulation of the samples should be avoided, however, filtration at constant pressure or centrifugation may become necessary in particle-rich waters (i.e. in coastal zones, estuaries, or during phytoplankton blooms). Filtration with glass fibre filters (e.g. Whatman GF/F) or hydrophilic cellulose acetate filters (e.g. Sartorius Minisart 0.45 µm pore size) should generally be adequate. Each laboratory should validate the filtration methodology on test samples, including the pressure at which filtration is carried out and for potential contamination from filters, before using them routinely. If unfiltered samples are analysed the need for a correction for turbidity should be assessed. (Are routine procedures available to do this assessment?)

7. Analytical procedures

The determination of nutrients is largely based on colorimetric methods (e.g. Grasshoff *et al.*, 1999). There are also fluorometric methods available, e.g. for the analysis of ammonia in seawater (Holmes *et al.*, 1999; Aminot *et al.*, 2001) and UV spectrophotometric methods for the direct determination of nitrate (Johnson & Coletti, 2002).

Most methods commonly used are manual methods or manual methods adjusted to automated analytical equipment (continuous flow analysis or flow injection analysis) (Kirkwood, 1996). In addition to the validation of the chemical method itself, the validation of the handling procedures and maintenance of the automatic equipment is important.

Manuals are available, which detail what to consider especially when working at sea with continuous flow analysis of nutrients (Aminot & Kerouel, 2007; Hydes *et al.*, 2010).

8. Analytical quality assurance

The quality assurance programme should ensure that the data are fit for the purpose for which they have been collected, i.e. that they satisfy detection limits and levels of accuracy compatible with the objectives of the monitoring programme. The quality assurance procedures must cover all steps of the nutrient determinations, including sampling, storage of samples, analytical procedures, maintenance and handling of the equipment, training of the personnel, as well as an audit trail. It is recommended that the laboratory is accredited to EN ISO/IEC 17025. The laboratory should also take part in intercalibration exercises and proficiency testing, as provided by e.g. QUA-SIMEME, to provide external verification of results.

Specific technical information on quality assurance is to be found in Kirkwood (1996) and Vijverber & Cofino (1987) and in the Nordtest report (Nordtest, 2006). In the laboratory performance tests described in these references a “Z score” (from -2 to +2) is considered a minimum requirement for a satisfactory analysis. The standard score (Z) is: $Z = (x-u)/\sigma$ where: x is the individual result to be converted to standardised score; μ is the mean of the population; σ is the standard deviation of the population.

Certified Reference Materials (CRMs) for nutrients in seawater are commercially available from:

- KANSO Technos in Japan (<http://www.kanso.co.jp/eng/production/index.html>), currently for nitrate plus nitrite, nitrite, phosphate and silicate.
- National Research Council of Canada (http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_files_e/MOOS-1_e.pdf) for nitrate plus nitrite, nitrite, phosphate and silicate.
- Eurofins, Denmark (<http://www.eurofins.dk/dk/milj0/reference-materialer/certified-reference-materials.aspx>) for ammonia, total nitrogen, total phosphorous, nitrate plus nitrite, nitrite, phosphate and silicate.

(Addresses for the suppliers should be given in an annex. Urls change so reference to a physical address may be useful in the future.)

Use of these materials should enable comparability of data to be achieved to within a few percent for silicate and approaching 1 % for nitrate and phosphate for samples with concentrations greater than 100 times the detection limit of the method.

Performance requirements for the methods applied in individual laboratories will depend on the concentrations they are required to measure in their samples. Laboratories should determine their limits of detection and also limits of quantification at which they can reliably quantify nutrient parameters and these should be appropriate for the specific monitoring requirement and target waters. For determining temporal trends of winter nutrients in European Atlantic shelf waters (to S-35 psu),

laboratories should aim at the following limits of quantification: Approximately 0.2 μM for TOxN ; 0.03 μM for nitrite; 0.06 μM for phosphate; 0.2 μM for silicate and 0.3 μM for ammonia.

9. The use of in situ nutrient analysers

9.1 Platform types

Autonomous nutrient analysers have been increasingly used for providing *in situ* semi-continuous measurements of nutrient concentrations. Where a static platform is used (such as on a mooring), high frequency measurements of nutrient concentrations at a single point may be obtained. When used with a ship's pumped seawater supply (such as Ferrybox), a map of nutrient concentrations over a wide area may be obtained. A Ferrybox system allows samples from a fixed depth to be obtained. A mooring may allow deployment of analysers at multiple depths. These techniques are especially useful in environments where there is a substantial temporal and spatial variability of nutrient concentrations. Such platforms should be considered to be part of a wider monitoring programme which includes ship based observations providing a wide spatial coverage as required within section 3. (Reference should also be made to newer/evolving technologies like AUVs and depth-cycling platforms like SeaHorse (Rolls Royce))

9.2 Instrument selection

Sensors for *in-situ* applications are based on wet chemistry colorimetric methods or a direct optical UV spectrophotometric measurement (nitrate only). Reviews by Moore *et al.* (2009) and Johnson *et al.* (2007) discuss different types of sensor. Potential problems faced with *in situ* sensors are biofouling, and power constraints. Biofouling may be more readily overcome on a Ferrybox system where cleaning of the measurement system may be programmed into the routine cycle. Controls implemented on some *in situ* optical sensors include wiped sensors, guarding with copper mesh and chlorination. Power constraints on a Ferrybox system will not usually be a problem but may be a consideration on a mooring. The extent of biofouling and power considerations will contribute to determining the length of time sensors can be left *in situ*. Coloured dissolved organic matter (CDOM) has a spectral component to its absorption curve and thus appreciable CDOM may interfere with nitrate measurement when using optical sensors, although in general this is unlikely to be an issue in many marine applications.

9.3 Quality assurance

Appropriate calibration and ongoing quality control must be implemented to ensure that data collected are fit for purpose. Routine laboratory testing and validation of results against discrete samples analysed in the laboratory must be undertaken to ensure that comparable results of known and acceptable quality are obtained.

10. Reporting requirements

Data collected as part of the Eutrophication Monitoring Programme should be reported to the ICES database using the latest ICES reporting formats (currently ERF 3.2 http://www.ices.dk/env/submitting_data.asp).

Table 1 in Annex 1 presents the ICES field codes recommended for reporting. These include comprehensive metadata regarding analytical method and quality control

data. It is recommended that Uncertainty of Measurement (UCM) is reported. Guidance on calculating UCM is available from OSPAR (2011) and Nordtest (2006).

In addition to the ICES field codes Table 1 of Annex 1 also identifies further information recommended for reporting by the GO-SHIP manual (Hydes *et al.*, 2010). A standard electronic form is being developed and will be made available via the GO-SHIP web portal to enable efficient and consistent reporting of metadata across the global marine nutrient measurement community.

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Annex Oxygen

Revised JAMP Eutrophication Monitoring Guideline: Oxygen

1. Introduction

Biological activity and hydrodynamic processes are the main causes of change in the oxygen concentration in seawater. Nutrient enrichment/eutrophication may give rise to decreased oxygen concentrations and saturation percentages, increased frequency of low oxygen concentrations and increased rate of oxygen consumption, mainly in deeper layers of stratified waters. Dissolved oxygen concentration is used as an indicator of ecosystem health. The use of dissolved oxygen concentration as an Ecological Quality Objective (EcoQO) has been established within an Ecological Quality Framework for an eco-system based approach to the management of the North Sea. It is also used within the Water Framework Directive and European Marine Strategy Framework Directive. These guidelines are intended to support the minimum monitoring requirements of the OSPAR Eutrophication Monitoring Programme and will also support monitoring in accordance with the above directives. The reader should refer to detailed guidance on sampling and measurement of dissolved oxygen in marine waters provided in Aminot, 1997.

2. Purposes

The measurement of oxygen concentrations in water is carried out for, *inter alia*, the following purposes:

- to establish the spatial distribution and frequency of low oxygen concentrations;
- to establish temporal trends in oxygen concentration over periods of several years;
- as a component of the Eutrophication Monitoring Programme.

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) of the marine areas concerned.

It is intended that the region-specific temporal trend monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 50%) over a selected period (e.g. 10 years). To clarify the situation and to help define objectives Contracting Parties should undertake statistical analyses of their existing data sets. This would help to determine the representativeness of the monitoring stations and thus the selection of suitable sampling stations and sampling frequencies. (Oxygen concentration is submitted to a daily cycle more or less pronounced depending on the intensity of photosynthesis and respiration (whose outcome changes with depth). Therefore, I am not sure that to fix a threshold value of oxygen concentration to detect a time change over a selected period is sense (see comment 2))

The spatial distribution monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in oxygen concentrations. This would include a definition of the extent of the monitoring area and some understanding of the randomness of the monitoring stations.

4. Sampling strategy

Oxygen deficits tend to occur in the deeper layers of stratified water, including semi-enclosed basins and in some specific environments such as light limited deep channels and dredged estuaries. Low oxygen concentrations can be found at times of increased oxygen consumption following maximum primary production and are concomitant with certain meteorological and hydrographic conditions (including temperature and wind speed). Oxygen concentrations may vary considerably from year to year as a result of many influences and therefore trends may be difficult to establish. However, it may be possible to establish trends in some semi-enclosed basins. (This last sentence contradicts the Quantitative Objectives. Anyway, I am in agreement with temporal trends in oxygen concentration could be useless in most of the marine areas. Probably, the best parameter to use is the time trend in frequency of oxygen deficit episodes and/or the time trend in extension of the affected area.)

Frequent measurement during and after the production season should take place in relation to phytoplankton bloom events, at stations suitable for this purpose, e.g. at stations characterised by vertical stratification or sited in semi-enclosed basins. Sampling should be conducted so that oxygen concentration gradients are resolved, especially those near to the seabed. In order to assess oxygen consumption rates, (is this a reference to BOD/COD measurements?) time-series measurements are required covering appropriate periods of time with high oxygen consumption. If hydrogen sulphide occurs, the concentration should be determined using the methylene blue method (Fonselius *et al.*, 1999). Concentrations of hydrogen sulphide should be given in $\mu\text{mol l}^{-1}$ rather than in negative oxygen equivalents.

For the interpretation of oxygen measurements it is essential to have corresponding measurements of temperature and salinity in order to calculate oxygen saturation which is needed for the assessments of effects on the biota (Many organisms respond to the DO concentration not the %saturation). For some areas additional information including nutrients, organic matter, chlorophyll, pigments, turbidity, hydrographic characteristics of the water column such as stratification at the sampling site may be necessary.

5. Sampling equipment

Many different water samplers may be used to collect discrete samples for oxygen determination. It is essential however, that the water sampler used completely isolates the sample from the surroundings so that no leakage or exchange occurs. In particular circumstances it may be necessary to use a special bottom water sampler. (Wording – I presume the intent is to say that standard water samplers may not work for the collection of near bottom samples)

Immediately after taking the water sample, an aliquot has to be transferred into a calibrated Winkler bottle. Care must be taken to minimize contact between the water sample and atmosphere, especially in samples with low oxygen concentrations. This includes the process of transferring the water from the sample bottle into the Winkler bottle as well as by introducing air into the sample bottle due to leakage. As this transfer of the sample is one of the steps in the whole determination procedure which is responsible for the greatest error, only well trained personnel should be allowed to take the samples.

Oxygen may also be determined using sensors. These sensors may be used attached to a CTD system, as part of an autonomous system on moored platforms or installed on ships for continuous measurements. The advantage of sensor measurements is the

provision of high resolution data in space or time, depending on the instrumentation used. Sensors can be particularly useful, compared with conventional discrete sampling techniques, for determining temporal and spatial variability and for capturing short term oxygen deficiency or supersaturation events. On a commercial basis Clark type and Optode type sensors are widely available (Moore *et al.*, 2009).

As all sensors have limitations in their performance, no type of sensor can be generally recommended. These limitations may include the sensitivity, the precision of measurement, low response time, instability of measured results, instability due to varying environmental conditions, poisoning in anoxic waters, etc. Therefore it is necessary to test different sensors and select the one most suitable for measurements in the area to be observed.

Apart from a proper selection of a sensor, the calibration and handling of any sensor has to be validated. Furthermore, regular control, using the Winkler method as reference, is essential. Intervals of calibration, control of measurements and maintenance depend on the type of sensor and the environmental conditions in which the sensor is used. These intervals have to be evaluated and controlled as one element in the validation process of the sensor. The validation process also includes a description of the handling of the sensor in order to obtain the specified precision of the sensor.

6. Storage and pre-treatment of samples

Oxygen in discrete samples must be fixed immediately after collection to bind the oxygen in the sample. The precautions mentioned above must be maintained. After fixation, samples have to be kept in a dark place at a constant temperature - if possible the same as the *in situ* temperature - for at least one hour. The fixed sample should be titrated within 24 hours of collection. In some cases longer storage of the fixed sample may be necessary. Although not recommended, longer storage is possible, provided that storage conditions and handling procedures are validated and clearly documented. Zhang *et al.* (2002) noted that storage under seawater is advisable in such circumstances. Sensors for oxygen determination are designed for *in situ* measurements and should not be used for analysis of discrete samples.

7. Analytical procedures

Standard procedures for the determination of oxygen in discrete water samples are based on the Winkler method. Modifications of this method, which have been verified in intercalibration exercises, are described elsewhere (e.g. Carpenter, 1965; Grasshoff *et al.*, 1999; Strickland and Parsons, 1968). Modifications mainly concern composition of the reagents, titration devices (manual titration, automatic systems) and the method used for detecting the end point of the titration step (e.g. visible colour change of indicator dyes, conductivity measurement, photometric detection). As verified by intercalibration exercises, reliable results can be obtained with all methods, if validated procedures are used by well trained personnel.

Oxygen sensors should only be used if their calibration, handling and maintenance is properly validated (see section 5), including procedures for regular checks of calibration and correct functioning of the sensor (stability, reproducibility, precision of results). The Winkler method should be used as reference method for this purpose. Care should also be taken to avoid unreliable results caused by ignoring the technical limitations of the sensor used for the measurements (see section 5) or by calibrating over an inappropriate range.

8. Analytical quality assurance

At present there is no Certified Reference Material available for oxygen in water. For the Winkler method it is therefore recommended to use internal laboratory procedures according to *Grasshoff et al.* (1999). In order to demonstrate reliable results, each laboratory must establish, validate and document a quality assurance system, which is adequate for the samples to be analysed. Specific technical information on quality assurance is to be found in Carpenter (1965b), Vijverber and Cofino (1987), Aminot (1997), and in the Nordtest report (2006). It is recommended that the laboratory has a quality system in place such as under EN ISO/IEC 17025. The effectiveness of the quality assurance system should be verified by participation in appropriate intercalibration exercises, where available, as often as possible.

9. Reporting requirements

Oxygen must be reported in together with in situ salinity, temperature and sample depth data. Data reporting should be in accordance with the requirements of the latest ICES reporting formats, together with QA information on methods used, detection limits, reference values and any other comments or information relevant to an assessment of the data (e.g. participation in intercalibration exercises).

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