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Interim Report of the Marine Chemistry Working Group (MCWG)

7–10 March 2016

Galway, Ireland

ICES International Council for the Exploration of the Sea

CIEM Conseil International pour l'Exploration de la Mer

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Conseil International pour l'Exploration de la Mer

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Executive summary

The Marine Chemistry Working Group (MCWG) met for the first meeting of its three-year term on 7–10 March 2016 at the Marine Institute of Galway, Ireland. The meeting was attended by 19 participants from 9 countries.

MCWG has eight Terms of Reference, with all but one due for completion in 2018. These terms of reference require the Group to (a) respond to requests for advice; (b) review developments in MSFD and WFD, in particular regarding emerging and priority substances (incl. EQS values, conversion factors (c) report on new developments in QUASIMEME and other proficiency testing schemes relevant to MCWG; (d) report and present new information on marine litter and its role as potential source of contaminants, incl. desorption in digestive tract of organisms concerned; (e) summarise and synthesise relevant info from other expert groups; (f) report from data, research and developments in Ocean Acidification; (g) report on QUASIMEME assessment of chlorophyll data, in particular regarding comparability of data and potential implications for existing measurement guidance, and to collect information in preparation of a TIMES manuscript; (h) report on intercalibration exercises on passive sampling with a view to adjustment of background assessment concentrations; obtain information regarding the use of C_{free} as a proxy of the effects of non-polar compounds, with a view to determining EACs, and review information on mixture toxicity derived from passive sampling/dosing .

Under ToR a): an adequate answer was formulated in response to a request from the ICES Data Centre concerning Content Governance on results from Passive Sampling (PS).

Under ToR b): EQS on Biota and PS and the Revised Draft under EC Decision Annex 3.

Under ToR c): the alternatives for QUASIMEME not offering Intercomparison Exercises (IE) for the analysis of dioxins and PCB in fish, the need for a new Workshop on Organotin analysis and the review of method codes were discussed.

Under ToR d): the Norwegian Plastox Project was presented.

Under ToR f): the outcome of the Quasimeme Workshop on Ocean Acidification was discussed.

Under ToR g): the drafting of a TIMES publication on the work carried out by QUASIMEME on the influence of methodology on analytical results for chlorophyll measurements was sorted out.

Finally, under ToR h): the efforts of the different participating countries in the incorporation of PS on WFD and MSFD monitoring was discussed and summarised.

Valuable inputs were made by staff of the host institute and researcher of the National University of Ireland on ToRs b) and f).

1 Administrative details

Working Group name

Marine Chemistry Working Group (MCWG)

Year of Appointment

2016

Reporting year within current cycle (1, 2 or 3)

1

Chair(s)

Koen Parmentier, Belgium

Meeting venue

Galway, Ireland

Meeting dates

7–10 March 2016

2 Terms of Reference a) – z)

ToR	Description	Background	Science Plan topics addressed	Duration	Expected Deliverables
a	Respond to requests for advice from Regional Seas Conventions (e.g. OSPAR, HELCOM, ICES Data Center, EU) as required.	Science or Advisory Requirements.	1, 13, 20, 21, 25, 31	3 years	Advice, revision, as appropriate
b	Review developments in MSFD and WFD, in particular regarding new (emerging) and priority (hazardous) substances and associated EQS values, conversion factors and other issues regarding monitoring for Descriptor 5, 7, 8, 9 & 10.	Follow-up on this matter is key in order to constructively guide the development process for environmental quality criteria.	1, 13, 19, 20, 21, 22, 25, 27, 28, 31	3 years	Advice, Environmental Quality Standards or Environmental Assessment Criteria, conversion factors, scientific review on emerging contaminants and risks involved

c	Report new developments in QUASIMEME (Quality Assurance in Marine Environmental Monitoring in Europe), and provide information on other proficiency testing schemes with relevance to MCWG.	Avaiability of high quality proficiency testing is vital to produce reliable results.	20, 21, 27, 31	3 years	Provide guidance for proficiency testing
d	Marine litter and its role as a potential source of contaminants: i) Report on new information regarding marine litter as a potential source of contaminants, with particular focus on field studies reporting elevated contaminant levels associated with plastics. ii) Present available information on contaminant desorption from plastic in the digestive system after uptake.	Effects of marine litter are poorly understood, and all additional information will increase our understanding of all processes involved.	1, 13, 19, 20, 21, 25, 27	3 years	Review paper in collaboration with the WG on Marine Litter.
e	Summarise and synthesise relevant information from other expert groups on the interface to MCWG:, incl. WGMS, WGBEC, WGEEL, WGSE, WGOH, WGPME	MCWG has always been very active in trying to interconnect different WGs, although tesponse has often been very limited. The collaboration with WGMS is exemplary.	13, 19, 20, 21, 22, 25, 27	3 years	Joint meetings, corporate advice, TIMES paper
f	Ocean acidification: Report from data, research and developments in Ocean Acidification and address recommendations to MCWG	Ocean adification, understanding how important it is, and being able to quantify its impact is crucial for a variety of scientific disciplines, and for ocean health.	1, 4, 13, 19, 20, 21, 25, 27, 28, 31	3 years	Data overview, TIMES publication

g	Report on QUASIMEME assessment of chlorophyll data, in particular regarding comparability of data and potential implications for existing measurement guidance, and to collect information in preparation of TIMES.	The aim is to solve problems for data comparability that exist for decades concerning chlorophyll measurements.	13, 25, 31	Year 1 & 2	Publication in TIMES: manuscript on chlorophyll determination methods
h	Report on intercalibration exercises on passive sampling and review data with a view to adjustment of background assessment concentrations; obtain information regarding the use of Cfree as a proxy of the effects of non-polar compounds, with a view to determining EACs, and review information on mixture toxicity derived from passive sampling/dosing.	PS seem inevitable in order to assess GES, as several EQS cannot be checked by standard methods. The possibility of Passive Dosing seems key in assessing mixture toxicity.	13, 19, 20, 21, 22, 25, 27, 28, 31	3 years	Improved quality control on delivered data

3 Summary of Work plan

Year 1	Respond to requests under ToR a Progress work towards completion of the remaining ToRs
Year 2	Respond to requests under ToR a Progress work towards completion of the remaining ToRs
Year 3	Respond to requests under ToR a Report on the remaining ToRs

4 List of Outcomes and Achievements of the WG in this delivery period

ToR A. MCWG asked the Data Centre to be ready to receive data different from the usual data format: Data on Passive Samplers, Ocean Acidification parameters, and new data types in general, like those from continuous measurements.

ToR B. MCWG was informed on new information concerning:

- Biota EQS
- The relation between Passive Samplers and EQS
- The revised draft on the EC Decision Annex 3

ToR C. New developments in Quasimeme or other proficiency testing schemes:

- Quasimeme does not offer intercomparison exercises for dioxins or PCBs in fish, but the Norwegian Institute of Public Health does.
- Quasimeme intends to organise an analytical Workshop on Organotin by the end of 2016 or in the first half year of 2017.
- Quasimeme is offering volunteers to take a look at the method codes for different exercises and see if these can be linked to observed performances, as was done for chlorophyll analysis, the aim is to have one or more publications as a result, or to present them on the Congress for the 25th anniversary of Quasimeme (date to be assigned)

ToR D. MCWG was informed on following work:

- The Norwegian Plastox Project (JPI Oceans) was presented, consisting of a smaller part focussing on sediment and a larger part focussing on the seawater.
- The Microconference (in May, Lanzarote): info to be requested to Miguel Caetano

ToR E. WGMS and WGBEC were contacted via e-mail for an update on "any other relevant info". An update on the outcome of WGEEL was provided by Michiel Kotterman.

ToR F. A report on the outcome of the Quasimeme Workshop on Ocean Acidification was presented, followed by a discussion on the outcome. This was considered valuable, and MCWG insist that Quasimeme takes further action to find out whether it is technically feasible to provide the OA community with test samples with a certain range of pH, pCO_2, TA and DIC values.

ToR G. There was valuable information, both from Pamela Walsham (Marine Scotland) and Steven Crum (Quasimeme) to look for a TIMES publication. The purpose of the meeting was to clear out with Quasimeme whether the findings would form one or two publications, unfortunately that could not be decided upon, and be dealt with intersessionally or during the 2017 meeting at the latest.

ToR H. A lot of countries (Norway, Germany, Portugal, Ireland, Belgium) are taking up efforts to gather monitoring results from Passive Samplers, but most of them are not to be reported yet, but from 2017 onwards, more info will be available.

5 Progress report on ToRs and workplan

ToR A. A recommendation to the ICES Data Center is provided in Annex 2.

ToR B. MCWG discussed which progress has been made regarding descriptors 5 and 8. In general the group was of the opinion that the new text is an improvement and is strengthening the role of the regional conventions. However, some critical comments were made on:

- D5 criteria Chlorophyll-a: although the majority of values set in Decision 2013/480/EU in the water column of coastal waters are based on methods not determining chlorophyll-a specifically;
- D5C4, Toxic blooms itself are not an indicator for Eutrophication;
- The extension of the regulations of the WFD for that criteria for which EQS on hazardous substances are set in the relevant directive (2013/39/EC) also for waters beyond 12 nautical miles. This would imply that riverine and deep sea oceanic waters have to be assessed in the same manner; same principal is proposed also for D1, 3 and 5;
- The boundaries are arbitrary based on a formal basis and not on environmental conditions; (e.g. at the Portuguese coast, you will have areas with deep sea conditions within the 12 NM zone);
- the application rules, which introduce the "one-out-all-out" principle on the parameter level and does not define any procedure for data aggregation, although recommended by the JRC Report; same principal is proposed also for D1, 3 and 5;
- D8C2, examples of criteria for population health (such as species composition/abundance changes at locations of chronic pollution) relate to descriptors D1, D3 and are indicating indirect and long term effects; "classical" general and contaminant specific biological effects, as specified e.g. in OSPAR-CEMP, are not addressed, although the hint on sub-lethal effects is pointing on these criteria;
- D8C3, (Spatial and temporal extent of significant acute pollution events is minimised and, where possible, eliminated) with regard to ship accidents and illegal release is subject to regulations other than MSFD and WFD (IMO);
- The status of the marine environment will be assessed against EQS, trends are not mentioned, also recommended by the Expert group as essential part for assessment.

MCWG was aware of the fact that this time the group cannot change anything anymore, and that the deadline for comments and proposals via the national delegates has passed. From the perspective of scientists it is to question whether the way how the participation of marine scientists and particularly the acceptance of their advice may be improved for future revisions.

MCWG discussed on CTTEE 12-2016-03 Proposal for a Commission Decision on GES criteria-V2 Draft. As major drawback to the text, it was noted that WFD might become the standard for marine environmental monitoring, since the water matrix is still proposed as the default monitoring matrix, albeit that alternatives can be proposed if motivated, accepted and agreed upon. EQS-values are not always adapted to the marine environment. MCWG also discussed on a pilot exercise using OSPAR data for mercury risk assessment based on recommendation technical guidance document 32 on the implementation of EQS biota. It was concluded that the use of generic factors to extrapolate to Trophic Level 4 may lead to large errors in converting EQS values to other trophic levels. TMFs are ecosystem specific, as are the Trophic Levels, and species change TL during their life cycle. The main target is to protect all animals, TL4 is not an adequate endpoint, it might be too high in one ecosystem, and too low in another. The inflation of

the uncertainty as a consequence of the calculations with numbers that are highly uncertain will yield figures that cannot be interpreted on a sound basis.

MCWG identified following (groups of) compounds as of importance as substances of emerging concern:

- Antifoulants: Irgarol (cybutryn), Sea-Nine (4,5-dichloro-2-n-octyl-4-isothialozin-3-one, Diuron and pyrithione (both Zn and Cu);
- Phosphorylated Flame Retardants;
- Alternative Brominated Flame Retardants;
- Per- and poly-fluorinated compounds (not PFOS/PFOA);
- Benzothiazoles;
- SCCPs;
- Siloxanes;
- Radiopaque substances;
- Anticorrosion agents, especially those used in windmill parks;
- Dechlorane plus.

ToR C. Steven Crum from Quasimeme attended the meeting and gave an update on changes within the Office and new developments. A new QA Officer is Peter Hazemberg, test samples will be prepared by Fred Bransen and Ann-Marie Ryan leaves the secretariat and will soon be replaced.

As most relevant information:

- Goole harbor samples are completely removed from stock after complaints of by far too high levels of brominated flame retardants.
- Samples codes: the old system is back in place
- Subscription fee unchanged thanks to an increased number of subscriptions.
- Z-scores: no numbers but figures are used
- Reports are again made Lab-specific. Old reports available from archive.
- Liver samples are added to the scheme, whole fish samples are being prepared.

For the moment, there seems to be no need for a Workshop on microplastics, a Workshop on Organotin analysis will be organized in 2017 by Koen Parmentier, and there are plans for a Jubilee WS for the 25th anniversary of Quasimeme. As is done for chl-a, a query will be undertaken whether there is any link between used methods and the quality of the outcome of test rounds. MCWG has several volunteers willing to assist on that for particular exercises: Philippe Bersuder, Peter Lepom, Lucia Viñas, Koen Parmentier, Bavo De Witte, Lutz Ahrens. It is suggested that Quasimeme contacts also members of WGMS for their interest (Craig Robinson, Celine Tixier).

ToR D. MCWG was informed on following work:

- The Norwegian Plastox Project (JPI Oceans) was presented, consisting of a smaller part focussing on sediment and a larger part focussing on the seawater;

- The Microconference (in May, Lanzarote): info to be requested to Miguel Caetano.

Little progress was made on how the final objective for the project can be reached, but there is continuing attention for work produced in this domain. The outcome is achievable but maybe not within the timeframe foreseen.

ToR E. MCWG exchanged ToRs with WGMS and WGBEC, feedback of WGEEL was provided by Michiel Kotterman through e-mail, nor really immediately relevant information was to be noted, but the feedback of this group is monitored closely as it might prove interesting for the group.

ToR F. MCWG was updated with the outcomes of the recent Quasimeme QA/QC OA workshop by Pam Walsham who along with Caroline Kivimae organised the workshop on behalf of the study group on ocean acidification (SGOA) and MCWG.

The workshop took place in the beginning of February 2016 and was hosted by the National Oceanography Centre in Southampton, with Andrew Dickson attending as a key invited speaker. Quasimeme was represented by SAB member Koen Parmentier, the chair of MCWG. An outline of the workshop and its aims is presented in Annex 4. A total of 33 participants took part in the workshop with a range of backgrounds and expertise. It was evident that increasingly monitoring laboratories are becoming involved in OA monitoring and these labs may not necessarily have the relevant expertise. There is a general assumption that if labs can measure chlorophylls and nutrients then this expertise is transferrable to OA monitoring.

Workshop participants agreed that sampling protocols are at a sufficiently mature state. However, instrument specific SOPs are not readily available and it was evident training on instrument use and acceptable daily acceptance criteria were missing, MCWG 2016 agreed to begin this process. There is general concern about the use of mercuric chloride as a biocide with some countries banning its use. To date no alternative biocide, which does not affect alkalinity, has been identified. Investment is therefore required if this issue is to be addressed.

There is one lab in the US at SCRIPPS Institute which produces reference materials for the OA community. This reference material is often misused by the community, with its use typically as a primary standard for the analysis. To ensure QA it was advised that a secondary local reference material was used as a QC check and monitored on control charts. Guidance was sought, by participants, on local reference material preparation. A sub-group of MCWG 2016 began preparing this guidance document.

There is no routine proficiency testing scheme available for the carbonate chemistry parameters. There was, however an ad-hoc inter-calibration exercise organised by Andrew Dickson's laboratory in 2013, the results of which was reported during the workshop. Labs performed well at TA/DIC concentrations in the range of the SCRIPPS reference material however performance decreased when these were changed. MCWG 2016 recommends another inter-calibration exercise be undertaken covering a range of salinities/nutrient load.

Participants highlighted the urgent need for a routine proficiency testing scheme to be developed. SCRIPPS could offer up an exercise using a current reference material but possibly not on the regularity of Quasimeme. It was suggested that an organisation such

as Quasimeme would be more suited to run such a scheme with guidance from Andrew Dickson. Historically when a new exercise is introduced, by Quasimeme, it has involved a development round, MGWG 2016 identified this as key to preparing carbonate chemistry analysis for monitoring as part of the CEMP.

SGOA 2014 identified the need to include discussions on uncertainty of measurements in the workshop, these should include uncertainty in sampling, analysis and data calculations. The data quality levels assigned by GOA-ON (uncertainty of +/2 ug/kg for TA and DIC and 0.003 for pH) may only be achievable by SCRIPPS laboratory. However, ecosystem response may not require this level of accuracy and a factor of 10 times may be sufficient but will require understanding of local area and input from the biological community. MCWG 2016 recommends this is raised with WGBEC or an OA working group if formed.

MCWG 2016 considers that the available quality assurance tools are not yet in place to support a monitoring programme under CEMP. A guideline on the development of an exercise that could be issued by Quasimeme is presented in Annex 3.

ToR G. Following ICES Data Centre comments on the MCWG2015 resolution on chlorophyll data held within the ICES data centre, MCWG2016 had a general discussion about the JAMP Eutrophication monitoring guidelines: Chlorophyll a in water (OSPAR Agreement 2012-11) and the terminology used to identify the parameter codes associated with the determination of chlorophyll.

MCWG 2016 recognises that the terminology used, particularly for "total chlorophyll-a" may lead to misinterpretations since the methodology used also measures, to some extent, other pigments. MCWG 2016 recommends that OSPAR revisit these JAMP guidelines and review current nomenclature.

A recent study undertaken as part of the joint monitoring programme for the North Sea and the Celtic Sea[1] highlighted the differences between the techniques. To meet statutory requirements for drivers such as MSFD and WFD, contracting parties are increasingly relying on the use of automatic and remote devices such as buoys, ferry boxes and satellites for inclusion in data sets for their assessments. Estimation of near-surface chlorophyll by satellite is obtained through algorithms based on the ratio between different wavelengths of light (colours blue and green) leaving the water surface. Normalised fluorescence line height, which is a relative measure of water-leaving radiance associated with chlorophyll fluorescence, is also available. These different satellite methods are not necessarily measuring the same components. There is no single analytical technique recommended for the calibration of these devices. It is critical that a consistent analytical approach is taken to calibrate such devices to ensure comparability.

As a result MCWG consider the current parameter codes within the ICES data centre ambiguous. The ICES parameter codes should be revised to reflect the current analytical

[1] Hanneke Baretta-Bekker, Anne Sell, Francisco Marco-Rius, Julia Wischnewski, Pamela Walsham, Lynda Webster, Malin Mohlin, Karin Wesslander, Hans Ruiter, Francis Gohin, Lisette Enserink, 2015. The chlorophyll case study in the JMP NS/CS project. Document produced as part of the EU project: 'Towards joint Monitoring for the North Sea and Celtic Sea' (Ref: ENV/PP 2012/SEA).
72 pp. (include ref.)

methodologies for chlorophyll in water. Data should only be reported as chlorophyll a if an HPLC method is used which can separate chlorophyll a from the other chlorophylls and pigments. MCWG 2016 considers that additional method metadata are required with data submissions to both the DOME and OCEAN databases.

ToR H. A lot of countries (Norway, Germany, Portugal, Ireland, Belgium) are taking up efforts to gather monitoring results from Passive Samplers, but most of them are not to be reported yet, but from 2017 onwards, more info will be available. Kees Booij, the driving force behind the TIMES publication, was not present at the meeting, but promised to devote substantial effort in drafting a publication intersessionally. If he is not able to join the 2017 meeting, he will upload a draft version on the MCWG sharepoint site for revision by the group.

Any other business: It is tradition in MCWG that the host country gets the opportunity to highlight their research by presentations. Presentations relevant to the ToRs are presented by several other members. Abstracts are presented hereunder when made available, the presentations (sometimes censored for confidentially of data, are available on the SharePoint site, or upon request by the authors or MCWG Chair.

Triona McGrath- (MI) Inorganic carbon chemistry of Irish coastal waters and of the Rockall Trough, no abstract available.

Prof. Peter Croot (National University of Ireland Galway) - Application of the Radium quartet to chemical oceanography along the Irish West Coast, no abstract available.

Brendan McHugh - Hg, OSPAR EACs and biota EQS – dealt with under ToR B.

Jane Kilcoyne - The marine biotoxins azaspiracids – isolation and toxicology.

Since the identification of azaspiracids (AZAs) in 1998 well over 30 analogues have been reported. LC-MS/MS is the EU reference method for detection of AZA1, -2 and -3 with a regulatory limit of 160 μg/kg AZA1 equivalents in raw shellfish. *Azadinium spinosum* produces AZA1 and -2 while AZA3 and many other analogues are shellfish metabolites. The availability of as many AZA variants as possible, in sufficient quantity and purity, is imperative to highlight the relevance of the different analogues for public health protection. Here we describe the isolation of 13 AZA analogues (in addition to AZA1−3) from shellfish and phytoplankton. Samples were purified in quantities sufficient for full structural elucidation by LC-MS/MS and NMR and were then used for preparation of reference standards. The influence of cooking on AZA toxin profiles in naturally contaminated shellfish was investigated. Results confirmed previous studies showing heat induced decarboxylation of the shellfish metabolites AZA17, -21, -19 and 23 to AZA3, -4, -6 and -9 respectively. Using the reference standards, high levels of AZA3 and -6 were quantitated in some cooked shellfish samples. Toxicological assessment using a Jurkat T lymphocyte cell assay revealed that all analogues were cytotoxic in a time- and concentration-dependent manner. AZA6 was found to be 5 fold more toxic than AZA1. These results highlight the degree to which AZA equivalents are underestimated in routine monitoring programmes where raw shellfish are tested, and suggest that AZA6 should also be regulated.

6 Revisions to the work plan and justification

N/A

7 Next meetings

The next meeting will take place in Hamburg, Germany, on 6–10 March 2017.

Annex 1: List of participants

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Annex 2: Recommendations

RECOMMENDATION	ADRESSED TO
1. Handling new data types	ICES Data Centre

From the chair of the MCWG

Dear

The Data Centre has for a long time and successfully being focussing upon high quality discrete data, gathered in comprehensive datasets with full Quality Assurance parameters going along with it. It is the concern of the Marine Chemistry Working Group that a lot of valuable data cannot be uploaded to the ICES Data Centre. The marine environment and the research upon is rapidly changing, so there is need for a new kind of data to be stored.

There is increased reliance on continuous data produced from sensors or online autonomous systems, but SGOA has identified the need for enhanced metadata (e.g. QA and method data), and MCWG recommends that ICES considers either setting up a format for hosting these datasets, or establish strong linkages to other databases.

Data on microplastics are not appearing in a standard format either, as not all researchers go in the same amount of detail when analysing the particles, or simply disagree on standard definitions. Although the latter topics have to be solved first by specialists on this matter, MCWG recommends that the Data Centre is ready to receive these datasets.

The field of Passive Sampler monitoring is developing rapidly, and further consideration on how datasets are best handled is required.

Furthermore, data have to be delivered to different organisations and data centres, and there is a degree of overlap. It would be highly beneficial if data centres agree on a standard data exchange protocol to make this process more efficient. MCWG would prefer that the ICES Data Centre plays a leading role in this respect.

Should the assistance of MCWG in this respect be asked, we are ready to address it during our next meetings, although other expert groups (such as the OSPAR ICG on Marine Litter for microplastics) might be better placed.

Respectfully yours

Koen Parmentier

Chair MCWG

Annex 3: Guidance for the Preparation of a Local Reference Material for OA monitoring

Bottle Treatment

Pyrex or equivalent bottles with ground glass stoppers must be cleaned, rinsed with DI water and baked out at 550 ^{o}C for 4 hrs,

Collection

Strict sampling protocol as per Dickson must be observed –consider production line approach. Same person to do given task. Need to consider range of salinities/alkalinities dependant on TA/DIC range of specific area.

Optimum time of year of collection will be region specific and labs need to consider particulate load and dissolved organic components.

May need to filter- need advice Bockman paper – on sharepoint site

For high/low DIC bottle on board, for equilibrium DIC can bottle in the lab

Consider sending samples from LRM batch to Scripps for analysis.

Use

This is not to be used to replace the SCRIPPS RM which is the primary standard and should be run at the beginning and the end of each day. For open ocean at similar conc to Scripps RM run at least one LRM during the day. For lower salinity waters at least a 2 point check using LRMS should be run at start of day after primary standard.

Intercalibration exercise at different salinity range – 15-25-30 psu, different nuts, alkalinity.

Identify lab to make batch of material – Koen/Quasimeme

Bottles

Who would participate? GOA-ON

Time frame – 2018?

A small working group volunteers to offer assistance: Pamela Walsham, Triona McGrath, Carlos Borges, Caroline Kivimae, Koen Parmentier.

Annex 4: Workshop on Quality Assurance (QA) for inorganic carbon system measurements in context of ocean acidification monitoring

Scope: 25 participants, with technical competence in marine chemistry

Timing and venue: February 2016 National Oceanography Centre, Southampton (NOC), UK

Organisers: Caroline Kivimae, NOC & Pam Walsham, Marine Scotland Science

Scientific justification:

Several initiatives are now underway to develop and connect ocean acidification monitoring activities at national, regional and global levels. ICES Marine Chemistry Working Group (MCWG) highlighted that as Ocean Acidification monitoring is taken forward as part of the OSPAR JAMP and other International monitoring initiatives such as MSFD there is a clear need to facilitate meaningful data comparison, collations and assessments across regions, but limited QC tools to support this (Hydes *et al.*, 2013). A consistent approach to sampling, sample pre-treatment, analysis, calculation of derived variables and an understanding of methodological limitations is required. To meet these requirements there is awareness that samples for carbonate chemistry parameter measurements will, in the near future, be analysed by a wider range of monitoring agencies with varying levels of experience in this field.

The carbonate chemistry parameters have recently been added to the OSPAR pre-CEMP (Coordinated Environment Monitoring Programme). Determinants can move from the pre-CEMP to CEMP once guidelines, assessment criteria and Quality Assurance (QA) are in place. Contracting Parties should be preparing to monitor pre-CEMP determinands in a co-ordinated manner through the development of monitoring guidance, quality assurance procedures and/or assessment tools. There are globally accepted standard operating procedures for sampling and testing in place (Dickson *et al.*, 2007), but further development is required. Quality assurance can be provided by the analysis of certified reference material (CRMs) and/or external proficiency testing. External proficiency schemes are not available for any of the four carbonate chemistry measurements; however reference materials are available for some. Andrew Dickson's laboratory at Scripps Institute of Oceanography (SIO) provides the only recognised reference material for ocean carbonate parameters. In 2010 MIME agreed that the monitoring of carbonate chemistry parameters should be included as a mandatory component of the CEMP as soon as monitoring guidance, quality assurance procedures and assessment criteria have been adopted.

Andrew Dickson has raised concerns that too many laboratories may be using the Scripps reference materials as calibration standards for their TA/DIC analysis without having a separate way of ensuring that their measurement system is in control and has a known linearity of calibration. Thus, even when reference materials are used there are likely to be unidentified uncertainties that could show up on a well-designed proficiency study. Moreover, although there are globally accepted standard operating procedures for sampling and testing (Dickson *et al.*, 2007), variations in how these are applied in different laboratories can contribute to measurement errors. The proposed workshop would help address some of these issues.

During ICES MCWG 2013 discussions were held as to whether there was a requirement to organise a workshop. Participants at MCWG felt that a workshop covering practices for carbonate chemistry monitoring would be valuable. MGWG recommended that a workshop to address these issues should be organised under the QUASIMEME banner as they have experience organising such events in the OSPAR context and would be able to handle the finances. The National Oceanography Centre (NOC) UK were willing to host such a workshop because they have a number of years' experience in the field and are one of the few labs to have multiple instruments available for demonstration purposes. MCWG felt it would be essential to invite Andrew Dickson (USA) as a leading expert in the field; being one of the editors of the Guide to best practices for ocean CO2 measurements (Dickson *et al.*, 2007).

The OSPAR/ICES Study Group on Ocean Acidification (SGOA) participants identified key aims and objectives of the proposed workshop;

Proposed aims of the workshop:

1) Introduction to Quasimeme Quality assurance and Quality assessment.

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

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

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

5) Consider the limitations of reference materials across the OSPAR region i.e. salinity ranges, open oceans and coastal waters.

6) To obtain a consistent approach to the calculation of the data because there a number of software packages currently available to the OA community.

7) Address data quality objectives needed for various assessment purposes. The Global Ocean Acidification Observing Network (GOA-ON) identified the need for two different levels of data quality to ensure the availability of data and permit assessment of short-term variability as well as longer term trends.

Potential outcomes:

Workshop report and if deemed appropriate the preparation of a technical guide for carbonate chemistry sampling, sample pre-treatment, sample storage, analysis, use of reference materials and calculation for use within the OSPAR context.