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Interim Report of the Working Group on Marine Sediments in Relation to Pollution (WGMS)

14–18 March 2016

Oostende, Belgium

ICES
International Council for the Exploration of the Sea
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Executive summary

The Working Group on Marine Sediments in Relation to Pollution (WGMS) met on 14–18 March 2016 in Oostende, Belgium. The meeting was co-chaired by C. Tixier (FR) and C. Robinson (UK) and attended by 8 other members from 6 countries, by two local members of the ICES Marine Chemistry Working Group and additionally received contributions from three staff of the host institute.

WGMS has six Terms of Reference due for completion in 2017. These require the Group to (1) respond to requests for advice; (2) work to progress the use of passive sampling in sediment contaminant monitoring; (3) report on the applicability of modelling to explain the distribution of sediment-associated contaminants in relation to potential sources; (4) to advise on deep sea sediment monitoring protocols; (5) investigate/review the potential for release of contaminants from marine renewable energy activities; (6) review emerging issues (e.g. microplastics, deep sea mining) as potential risks for environmental contamination by hazardous substances.

In 2016, good progress was made on all ToRs except ToR 5, for which the most interested member could not attend the meeting. Valuable inputs were made by staff of the host institute to ToR 3 (modelling), whilst special focus was put on the potential impacts of deep-sea mining (ToR 6b), with fruitful discussion involving experts from the host institute, the ICES Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT) and from WGMS members involved with deep sea mining projects. Work to progress the ToRs further was agreed and will be finalised at the next meeting in Ancona, Italy (6–10 March 2017).

1 Administrative details

Working Group name

Working Group on Marine Sediments in Relation to Pollution (WGMS)

Year of Appointment within current cycle

2015

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

2

Chair(s)

Céline Tixier, France

Craig Robinson, UK

Meeting venue

Oostende, Belgium

Meeting dates

14–18 March 2016

2 Terms of Reference a) – z)

1	**Respond to requests for advice from Regional Seas Conventions** (e.g. OSPAR, EU) as required.
2	**Passive sampling (PS) in sediment** 2a - Review of existing methods dealing with PS in sediment 2b – Complete Guidelines for monitoring with PS in sediments for hydrophobic organic contaminants / produce guidelines for PS of metals 2c - Improve the understanding of the relation between data obtained by passive sampling in sediment and environmental quality (biota data, toxicity data, EACs) 2d- Review on on-going or future projects with PS
3	**Explore the suitability / possibility of modelling to explain spatial distribution patterns of contaminants in sediment and inform on sources and hence possible MSFD measures**
4	**Deep sea sediment monitoring** To provide advice on sediment monitoring in the wider oceans as required for MSFD
5	**Impact of renewable energy devices (e.g. wind mill,…)** To explore the potential risk impact in terms of release of contaminants (corrosion, anti-corrosion agents…)
6	**Emerging issues:** To assess the relevance and the potential risk impact of these issues and follow up outcomes of other expert groups working in areas of interest to WGMS

- Microplastics in sediment - Deep sea mining - "new" priority substances to be considered under the MSFD - Emerging contaminants (flame retardants, pharmaceuticals, etc.)

3 Summary of Work plan

Year 1	Respond to requests under ToR 1 Complete review of techniques for passive sampling of marine sediments (ToR 2a; delayed, to be completed in year 3) Progress work towards completion of the remaining ToRs
Year 2	Respond to requests under ToR 1 Progress work towards completion of the remaining ToRs
Year 3	Respond to requests under ToR 1 Report on ToRs 2-6

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

ToR 1

- No specific requests for advice received;
- ICES Data Centre requested feedback on the new data portal, which WGMS provided by email during the meeting;
- Feedback was received from the 2016 MCWG meeting from local WGMS guests who were present at that meeting the previous week;
- Discussion was held on the latest (v2) draft of *CTTEE 12-2016-03 Proposal for a Commission Decision on GES criteria.*

ToR 2

- The meeting progressed with work on two review documents on sediment passive sampling techniques: one for hydrophobic contaminants and one for metals. The intention is to produce a Cooperative Research Report from the group at the 2017 meeting;
- Further progress was also made on a draft TIMES document for passive sampling of sediments. This will be finalised at the 2017 meeting and complement the existing document on passive sampling of water;
- Members updated each other on current passive-sampling projects and on the metals passive sampling conference held in September 2015.

ToR 3

- Further progress was made (with important contributions from staff of the host institute) on reviewing possible methods for modelling sediment contaminant distribution patterns and source identification.

ToR 4

- Existing monitoring guidelines reviewed and minor additional changes considered to be required to make fit for use in deep sea;
- Recommendation for minor correction of an error in the Section 5.3 of the JAMP Guidelines for Monitoring contaminants in Sediments (mercury analysis).

ToR 5

- In the absence of key group members, little progress was made on this ToR

ToR 6

- Microplastics: The group has an interest in the role of microplastics as contaminant vectors. It was noted that microplastics have recently been reported to be present in deep sea sediments and reports were received of two collaborative projects involving Portuguese members of WGMS. Two recent reviews on microplastics in the marine environment were brought to the meeting and will be considered next year for deeper review. The Group will continue to monitor developments in this area of research;
- Deep sea mining: Presentations were received from the host institute, the ICES Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT) and from WGMS members on their involvement with deep sea mining projects. These exchanges made useful contributions to the WGMS report for this ToR;
- Available information was collated regarding Member States' plans for marine monitoring of the Priority Substances newly listed under Directive 2013/39/EU.

5 Progress report on ToRs and workplan

ToR 1

Respond to requests for advice from Regional Seas Conventions (e.g. OSPAR, EU) as required.	3 years	Requested advice

There were no specific RSC requests for WGMS advice this year. The group responded via email to a request from the ICES datacentre for feedback on the new data portal, Dome views (http://dome.ices.dk/views/). WGMS much appreciated the new, user-friendly, portal and were encouraging of its widespread publicity. Some suggestions were made, particularly with regard to whom data users should acknowledge when making use of data held by ICES. A request was made that data providers be given feedback on the number of requests ICES receive for the data they have submitted.

Several members of WGMS are also members of OSPAR and EU Working Groups and the following updates were provided to inform WGMS of activities within those.

EU / JRC MSFD Expert Network on Contaminants

WGMS were informed of the latest developments regarding the proposed revision (CTTEE 12-2016-03 Proposal for a Commission Decision on GES criteria-V2 Draft) to the Commission Decision on criteria and methodological standards on good environmental status of marine waters (2010/477/EU). With respect to marine contaminants (Descriptor 8), the main thrust of this was to place further emphasis on the classifications undertaken by the WFD and that these must be undertaken to 12 nm. Mostly, WFD classification makes use of monitoring and classification by comparison to EQSs for water, which WGMS do not consider to be the most appropriate matrix for marine monitoring of contaminants. The views of WGMS were echoed by the members of MCWG who were present at our meeting and who had had similar discussions at their meeting the previous week. WGMS members were urged to influence their colleagues who were being consulted on the document and to seek recognition within the revised text for the roles, experience and expertise that the Regional Sea Conventions have to offer with respect to marine monitoring of contaminants.

OSPAR Working Groups on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME)

It was noted that OSPAR MIME drafted Assessment Sheets for the Common Indicators to be used in the forthcoming OSPAR Intermediate Assessment; in sediment these include PAHs, PCBs, Cd, Hg, Pb and PBDEs. The data assessment for these will be undertaken in summer 2016, to allow the sheets to be updated at the 2016 MIME meeting. All parties were encouraged to ensure that the ICES database holds the most up-to-date information and that any data queries from MIME are quickly addressed.

Feedback of the MCWG meeting – March 2016 – Galway

By being in Oostende, two members of the Marine Chemistry Working Group (including the Chair) were able to attend much of our meeting, and provided the following feedback of relevance to WGMS from their meeting of the previous week.

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 adopted 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.

Limited new information was reported with respect to marine litter and passive sampling. Regarding emerging contaminants, a list will be included in the MCWG 2016 report with relevant emerging compounds. For proficiency testing, Quasimeme asked to perform a data assessment on proficiency test data, linking data quality to method information. Since this involves also sediment analyses, WGMS members are encouraged to perform data analysis for specific groups of analytes.

The two MCWG Belgian members present at this meeting (Bavo De Witt and Koen Parmentier) gave a joint presentation on the *M/V Flinterstar* incident (Annex 3). Two cargo vessels, collided off the Belgian coast and led to the release of oil near the Dutch and Belgian coasts. The environmental impact monitoring program was presented and information on existing protocols/guidelines for similar cases in other countries was sought.

ToR 2: Passive sampling

ToR 2a

2a - Review of existing methods dealing with PS in sediment	Follow-up on the work of ICES WKPSPD	Year 3	Recommendation based on current status

A review of existing passive sampling methods (PSDs) to measure metals and organotins in sediments has been undertaken. This will be updated and finalised at the 2017 meeting. Limitations and advantages of the methods for passive sampling for metals in sediments are highlighted in the draft review. The PS approach can provide excellent information on the bioavailability and potential toxicity of metals in sediments. However, the development of usage guidelines, appropriate assessment criteria and proficiency testing schemes are also required before the approach can be used for monitoring and assessments such as are required by the Regional Seas Conventions or European Directives (i.e. WFD and MSFD).

In 2015, WGMS were presented with a Dutch document (Smedes, 2014) on passive sampling of hydrophobic organic contaminants in sediments that was offered for use by the group in developing its review on passive sampling of hydrophobic organic contaminants, once the work had been more widely published in the scientific literature. The author recently indicated that he no longer intends to publish the work, and that the group can make use of his work. WGMS will therefore continue to work on its review of passive sampling techniques for HOCs, and aim to have completed a review document at the 2017 meeting. The intention is that a resolution will be proposed from that meeting for these reviews to be published as an ICES Cooperative Research Report.

Reference

Smedes, F. 2014. *Monitoring Environmental Quality of Marine Sediment. A Quest for the Best.* Deltares report 1209377-004-ZKS-0001; Deltares, Utrecht, The Netherlands. 57pp

ToR 2b

2b - Complete Guidelines for monitoring with PS in sediments for hydrophobic organic contaminants / produce guidelines for PS of metals	Guidelines required for technique to be acceptable for monitoring purposes.	3 years	Working with MCWG experts, produce TIMES paper(s) on the use of PS in sediments

Following the near-completion of the review on passive sampling of metals in sediment undertaken as part of ToR 2a, experts at the 2016 meeting made good progress with the development of a guideline document that might be suitable for use as a Technical Annex to the OSPAR JAMP. This document will be completed at the 2017 WGMS meeting for subsequent consideration by OSPAR MIME.

A guideline paper on passive sampling of hydrophobic organic contaminants (HOCs) in sediments, to complement the existing TIMES paper on passive sampling of HOCs in water (ICES TIMES no. 52), was worked-on at WGMS 2016, and will continue to be developed intersessionally for completion at the 2017 meeting. This document is based on a previous draft of a guideline document on passive sampling of sediments using silicone rubber prepared in 2007 by WGMS. The intention is to propose a resolution for the publication of this as an ICES TIMES paper following the 2017 meeting.

ToR 2c

2c - Improve the understanding of the relation between data obtained by passive sampling in sediment and environmental quality (biota data, toxicity data, EACs)	Assessment criteria suitable to assess GES in sediments are lacking / require improvement. WGMS will work with WGBEC to attempt to close this knowledge gap.	3 years	Dataset and advice to OSPAR on progress as passive sampling, which ICES WKPSPD have recommended the approach go on the pre-CEMP.

In order to progress towards generating a dataset suitable for use in deriving assessment criteria, a database of papers had been established on the web-based citation manager www.mendeley.com. Papers suitable for use in establishing Environmental Assessment Criteria have been being added to this. In 2017 WGMS will mine this database and obtain data suitable for developing EACs; if possible, these will be reviewed by MCWG and WGBEC before being presented to OSPAR MIME.

WGMS were informed about the forthcoming Second International Conference on *Deriving Environmental Quality Standards for the Protection of Aquatic Ecosystems* (EQSPAE-2016, 18–20 June 2016, Hong Kong). This conference will focus on recent developments in the science and methodology for deriving standards and site-specific benchmarks, as well as advancements in their related policy and application for water and sediment quality management in different parts of the world. As such WGMS will review the outcome of the conference regarding approaches to sediment quality assessment, including passive sampling.

ToR 2d

2d - Review on-going or future projects with Passive sampling	Each year	Report to ICES

Reports on new passive sampling projects were received from Belgium and France, both of which had a focus on developing the methodology to make passive sampling suitable for monitoring of fresh and saline water (e.g. the "new" Priority Substances), and on investigating links between ecotoxicity and concentrations measured by passive sampling in order to derive new or improved Environmental Quality Standards.

The Belgian NewSTHEPS (Koen Parmentier, MUMM, Belgium, Annex 3) project concentrates on the marine environment, including metals, polar and hydrophobic organic contaminants. It will involve targeted and non-targeted (screening) monitoring, including emerging compounds such as pharmaceuticals. It also includes toxicity testing through passive dosing and hydrographic and sediment transfer modelling, linked with studies of stable isotopes, to attempt to investigate the sources of contaminated particulate matter.

The French programme (Céline Tixier, Ifremer, France) on passive sampling, coordinated by Aquaref (the French consortium of research institutes on aquatic media), is due to begin in 2017. This project, aims at assessing the suitability of integrative passive sampling for the monitoring of organic and metallic contaminants in waters. This project will combine at the same time and on the same sites regulatory monitoring based on grab water sampling, passive sampling and alternative methods such as bioassays, effect directed analysis, non-target analysis… It also includes an evaluation of the statistical requirements of monitoring programmes and training of the persons in charge of the monitoring.

Information was provided (Elvio Amato, University of Antwerp, Belgium; Annex 3) on an Australian project linking passive sampling of sediments with metals toxicity. This demonstrated that the Diffusive Gradients in Thin films (DGT) metals passive sampler is a suitable tool for measuring bioavailable metal concentrations, irrespective of sediment physico-chemical characteristics, and that sediment toxicity was strongly correlated to DGT-determined fluxes of metals at the sediment water interface interface (Amato *et al.*, 2014, 2015, 2016). Using DGT's has the potential to significantly improve sediment risk assessments based on existing sediment quality guideline values.

A report of the metals passive sampling conference hosted by Spain in autumn 2015 (http://www.azti.es/dgtconference/) was also received (Maria Belzunce-Segarra, AZTI, Spain; Annex 3). Eighty five experts from 18 different countries all around the word met in San Sebastian from 28 September – 1 October where they presented the latest advances in DGT techniques, discussed their advantages as new tools for risk assessment and highlighted their limitations and uncertainties as well as the need for further studies to promote the use of these techniques for regulatory purposes.

It was noted that the venue for the forthcoming 8th International Passive Sampling Workshop and Symposium (IPSW 2016) has been changed from Baku, Azerbaijan, to Prague, Czech Republic and will be held on 7–10 September 2016. WGMS will review the output of this at the 2017 meeting.

Federico Spagnoli (ISMAR, Italy; Annex 3) gave a short presentation on the use of benthic chambers as a tool to assess contaminants' availability at the sediment-water interface.

References

Amato, E. D., Simpson, S. L., Jarolimek, C. V., and Jolley, D. F. 2014. Diffusive gradients in thin films technique provide robust prediction of metal bioavailability and toxicity in estuarine sediments. Environ. Sci. Technol., 48, 4485–4494.

Amato, E. D., Simpson, S. L., Belzunce-Segarra, M. J., Jarolimek, C. V., and Jolley, D. F. 2015. Metal fluxes from porewaters and labile sediment phases for predicting metal exposure and bioaccumulation in benthic invertebrates. Environ. Sci. Technol., 49, 14204–14212.

Amato, E. D., Simpson, S. L., Remaili, T. M., Spadaro, D. A., Jarolimek, C. V., and Jolley, D. F. 2016. Assessing the Effects of Bioturbation on Metal Bioavailability in Contaminated Sediments by Diffusive Gradients in Thin Films (DGT). Environ. Sci. Technol., 50, 3055-3064.

ToR 3: Modelling

Explore the suitability / possibility of modelling to explain spatial distribution patterns of contaminants in sediment and inform on sources and hence possible MSFD measures	3 years	Report to OSPAR via ACOM

At present, according to the WGMS 2016 meeting participant knowledge, the suitability and possibility to explain spatial distribution patterns of contaminants in sediment are quite robust, while the determination of the sources deduced by modelling is quite difficult. The participants at WGMS 2015 meeting gave some inputs. Federico Spagnoli described how conservative tracers such as aluminium and rare earth elements could be used in multivariate statistical modelling (Davis, 1986) to explain the distribution of contaminants in the Adriatic Sea resulting from inputs from the River Po (Spagnoli *et al.*, 2014). This statistical approach allows the determination of contamination sources but requires a lot of real sample data and a good knowledge of the marine processes acting in the area to produce good results. Taking a different approach, Mário Mil-Homens showed how the use of stable lead isotopes and ratios of Pb/Al concentrations inform on the extent of anthropogenic Pb input from the River Tagus to the deeper areas of the Portuguese Atlantic Margin (Mil-Homens *et al.*, 2013). The multivariate statistical and chemical approaches described above present some limitations because they are subject to a certain degree of interpretation based on the scientific knowledge of the environmental settings (e.g. hydrodynamics, known sources, sedimentary processes, etc.). Birgit Schubert and Nicole Brennholt reported on the use of hydrodynamic and morphodynamic modelling to produce sediment transport models of the German Bight and German North Sea estuaries (BAW 2013; Heyer and Schott, 2013), including the Elbe (Seiffert *et al.*, 2014; Fricke, 2012). Back-modelling to source has provided support to a theory that pathogenic bacteria observed in the German Bight in 2010 originated from an outbreak in the Ems estuary. These studies suggest that modelling may be able to inform on sources of marine contaminants, and thus inform on measures under the MSFD and WFD.

At the WGMS 2016 meeting Katrijn Baetens (RINBS, OD-Nature, Belgium) presented a new ecological shelf seas model; it integrated an existing open source hydrodynamic module (COHERENS), a sediment transport module (Lagrangian particle model), a pollutant physico-chemical behaviour module and a biological (plankton) module. She considered that it might be possible for this to be developed and applied to identify the source of the sediment contamination by back-modelling analysis. Katrijn noted that in some circumstances backtracking of atmospheric tracers had been achieved to a point source using Eulerian models (Hourdin and Talagrand, 2006), but the situation was more complex in the marine environment, particularly if attempting to back-track non-conservative contaminants with multiple point sources or diffuse inputs. WGMS 2016 meeting considered that back-tracking in those circumstances was not yet possible. The main reason for this is the significant differences in the nature of sources and transport in marine and riverine environments. Marine interactions are more complex than rivers in terms of direction and source because they can have multiple sources, mixing of water masses and multiple transport directions at one place.

In any case, high quantity and quality of multi-parameter (chemical, hydrographical, morphological and sedimentological) datasets are needed for setting initial boundary conditions, forcing conditions and for validating every model to reach satisfactory results.

WGMS will keep this ToR open and update it with any further information that members are able to bring to the final meeting in 2017.

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Spagnoli, F. *et al.* 2014. Sedimentological, biogeochemical and mineralogical facies of Northern and Central Western Adriatic Sea. Journal of Marine Systems, 139, 183–203.

Walling, D.E. 2005. Tracing suspended sediment sources in catchments and river systems. Science of the Total Environment, 344, 159-184.

ToR 4: Deep Sea Monitoring

To provide advice on sediment monitoring in the wider oceans as required for MSFD	Monitoring of the deep sea is required for the MSFD. Technically this is more difficult than for shallow seas and advice should be developed	3 years	Advice to OSPAR via ACOM on deep sea sediment monitoring

Sampling procedures/techniques in the deep sea are similar to those developed for shallow marine sediments that are well described in the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments, originally developed by OSPAR Working Groups on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) and currently under review by the OSPAR Hazardous Substances and Eutrophication Committee (HASEC). However, major differences exist between the deep sea and shallower marine environments. These differences are related to the relatively low sediment accumulation rates, absence of direct pollution sources (excepting in the cases of aggregates, mining and oil / gas extractions) and the dominance of diffusive contamination sources (e.g., atmosphere, oceanographic transport) in the deep sea areas. Other differences are the technical conditions of sampling recovery in the deep sea that are critical and have specific requirements (e.g., pressure resistant equipment, larger vessels, corers, winches and cables), and also the time necessary for collecting each sample in deep waters. Therefore, the financial costs associated with each sample collection increases significantly in deep seas, even where these are relatively near-shore. For minimizing the costs to setup the sampling strategy a good knowledge of bottom morphology and sedimentological processes that occur in the survey area is needed. Additionally, it will be recommended to use a risk-based monitoring strategy based on the identification of the targets (issues) to be studied before, during and after the operation. Based on this, it will be possible to choose each station as representative of the widest area. In this way, the description of the sea-bottom can be carried out with the minimum number of samples. In order to optimize the sampling strategy in deep sea environments it is then recommended to:

- Compile bibliographic information available for the area concerning: bottom sediment features, hydrodynamic knowledge, other available geochemical/sedimentological data;
- Characterize the morphology and sedimentology of the sea-bottom through the use of geophysical surveys (e.g., side-scan sonar, multi-beam and seismic).

Furthermore, the sampling frequency and sampling depth need to be decided on the basis of knowledge of sedimentation rates, mixing rates and the aims of the monitoring program. Given the cost of obtaining deep sea samples, considerations should be given to archiving and storage of samples for future use (e.g. analyses of emerging contaminants, determination of baselines…).

The existing OSPAR guidelines on monitoring contaminants in sediments were considered by WGMS members present at the 2016 meeting to be adequate for deep sea monitoring. In addition to the points mentioned in the ICES 2015 Interim Report of the WGMS, the WGMS members present at the meeting added other topics to assure both a good control on the sampled area and also the collection of the interface water-sediment. Due to the small accumulation rates of the deep sea area, this interface (e.g., first 0.5 cm) is integrating the signal of last decades. Thus, the WGMS members present at the meeting recommend the:

- use of a digital system (video or camera) coupled to the sampling device (BOX or MULTI-CORER) to recover the image of the sea-bottom where the sediment samples are collecting;
- preferential use of multi-corer system in order to assure the collection of enough undisturbed surface samples and also a better preservation of the sediment-water interface respect to the box-corer. The subsampled uppermost surface layer (representing the most recent sediments) should be as thin as possible. It is also important to assure the verticality of the liner during the handling and the sub-sampling of the core and that the core is extruded by a piston from the bottom. Furthermore, because of the high costs of the deep sea sampling, the multi-corer is preferable because it allows getting enough material that can be preserved and used for complementary and future studies. Moreover, the use of a multi-corer allows determination of the contaminant heterogeneity of the surface sediment through the sub-sampling of several cores.

In addition, an error pertaining to sediment preparation and storage was identified in the existing JAMP Guidelines for Monitoring contaminants in Sediments. Section 5.3 of the guidelines, describing drying, states that samples for mercury analysis should not be freeze dried, but can be oven dried at < 105° C. This is incorrect, samples for Hg can be freeze dried and should not be oven dried above 60° C (Loring and Rantala, 1992).

Recommendation: WGMS recommends that for the existing JAMP Guidelines for Monitoring Contaminants in Sediments to be used for deep sea monitoring (as may be needed for the MSFD) they require modifications to include details of geophysical surveys, multi-corer sampling, digital imaging, and that an error in Section 5.3 should be corrected.

Reference

Loring, H.D. and Rantala, R. (1992) Manual for the Geochemical Analyses of Marine Sediments and Suspended Particulate Matter. *Earth-Science Review*, **32,** 235-283.

ToR 5: Impacts of marine renewable energy devices

To explore the potential risk impact in terms of release of contaminants (corrosion, anti-corrosion agents…)	Many hundreds of renewable energy devices are being placed in the marine environment. Resultant changes in hydrodynamics may release sediment-bound contaminants, there may be inputs of contaminants from their installation, operation and decommissioning.	3 years	Report to ICES (with recommendations, as appropriate)

A report on a Portuguese project undertaking baseline measurements of metal contaminants in an area to be used for wave generation was received (abstract in Annex 3). Unfortunately, the expert with most interest in this ToR was not able to attend this meeting and no further progress was made. Group members are requested to bring to the next meeting information from expert colleagues that may be suitable for use in this ToR.

ToR 6: Emerging Issues

To assess the relevance and the potential risk impact of emerging issues Follow up of outcomes of other expert groups		3 years	Report to ICES
6a) Microplastics in sediment	Microplastics are of emerging concern and may be a vector for contaminant transfer to sediments, or from sediments to biota		Develop link-ups to relevent expert groups on marine litter
6b) Deep sea mining	Mineral mining is a likely future source of anthropogenic disturbance to the deep sea and could result in the release of contaminants into otherwise relatively pristine environments		Link-up with WGEXT who have a ToR to report to produce a summary paper concerning deep sea mining (What is being mined, where this is occurring, techniques being developed etc).
6c) Other emerging issues			

ToR 6a: Microplastics

Two recent reviews on microplastics in the marine environment were brought to the 2016 WGMS meeting:

van Cauwenberghe *et al.* (2015) on "Microplastics in sediments: A review of techniques, occurrence and effects"

a book on "Marine Anthropogenic Litter" (2015; Eds. Bergmann M., Gutow L., Klages M.; available under open access) divided in five sections: A historical synopsis of marine litter research, abiotic aspects of litter pollution, biological and ecological implications of marine litter and microplastics.

However, due to the time dedicated to ToR2 and ToR 6b, WGMS could not consider these for deeper review. IPMA (Portugal) is one of the research institutions involved in two research projects focused on the topic of microplastics (MP):

- BASEMAN (JPI_Ocean) is an interdisciplinary and international collaborative research project that aims to overcome the problem of the establishment of standard operation protocols for microplastics sampling, extraction, purification and identification.

- PLASTICGLOBAL project (European Structural Funds) aims at assessing the MP-mediated chemicals transfer in marine food webs and its effects on the biota under climate change scenarios.

Three other research projects investigating the impact of plastic particles on the marine environment have been recently selected for funding from ten member countries of the JPI Oceans:

- EPHEMARE - Ecotoxicological effects of microplastics in marine ecosystems;
- PLASTOX - Direct and indirect ecotoxicological impacts of microplastics on marine organisms;
- WEATHER-MIC - How microplastic weathering changes its transport, fate and toxicity in the marine environment.

WGMS will keep informed and report on work/project dealing with the occurrence of microplastics in sediments and their impact on aquatic systems, particularly as regards their potential as vectors for contaminants. The outcomes of the OSPAR and EU working groups on marine litter, and international fora such as (MICRO 2016, Lanzarote, Spain, 25–27 May 2016) shall be reviewed along with the progress made on microplastics achieved by MCWG and WGBEC.

ToR 6b: Deep sea mining

Invited to the WGMS session on deep sea mining was Brigitte Lauwaert (OD-Nature, Belgium) of the ICES Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT). We exchanged information between WGMS/WGEXT on progress and scope of each other's ToR, and received a presentation on a major Deep Sea Mining project (JPI-Oceans) from Lieven Naudits (OD-Nature). The WGEXT ToR concentrates on physical impacts of deep sea mining (DSM), whereas our interest is contaminants. WGEXT have their annual meeting in April 2016 when Brigitte will update them of our work on contaminant-related aspects of DSM and suggest that WGMS contribute to a joint position paper that covers both aspects.

The scarcity of mineral resources on land deposits, together with the continuous and growing demand for metals and rare earth elements, motivates a future exploitation of these resources in deep sea areas. Certain target areas, such as hydrothermal vent fields, cobalt-rich crusts and poly-metallic deposits are good examples of possible exploitation sites. Mining activities threaten to disturb wide areas of deep-sea environments that until now have been maintained untouched by human activities and where resilience is very low. The exploitation of these resources can affect extensive areas of the deep seafloor (including areas far away from the exploitation sites) and the overlying water column (e.g. by releasing primary and secondary plumes of material). The environmental costs of the exploitation of the deep sea environment and the ecosystem services can be extremely high so that an urgent identification and assessment of the potential impacts of these activities is needed. Before commencing resource exploitation it is necessary to proceed to a correct evaluation of the potential mineral resources and also to develop environmental characterization of these sensitive environments. The European Commission and other countries funded research projects, such as MIDAS (http://eu-midas.net/), BLUEMINING (www.bluemining.eu), JPI-Oceans (www.jpi-oceans.eu), TREASURE (Towards Responsible ExtrAction of SUbmarine mineral Resources, a Dutch funded project) and more recently BLUE NODULES ((http://www.blue-nodules.eu/). All these projects aim to study environmental impacts of mineral extraction from deep sea environments, biogeochemical processes, and also to raise the technological and environmental challenges of the mineral exploitation in extreme conditions such as that existing in deep-sea environments.

On request of the French Ministry of Ecology and of the Scientific Council on Natural Heritage and Biodiversity (CSPNB), the environmental risks of deep sea mining were investigated in an Expertise report (Dyment *et al.*, 2014.). This report, elaborated by French expert researchers, presents the available knowledge on marine mineral resources, their exploration, and possible exploitation techniques to provide a consistent approach of their impacts. The report also identifies a set of knowledge gaps and how these can be addressed, stressing the importance of acquiring fundamental scientific knowledge that requires great investment in human (researchers) and technical resources as well as long-term financing.

Inside the ICES, the expert group with interest in deep sea mining is the the ICES/NAFO Joint Working Group on Deep-water Ecology (WGDEC). WGDEC met in February 2015 identified the different types of deep sea mining as outlined above and identified a number of potential impacts, including removal of substrate / loss of habitat, introduction of energy (noise, light), introduction of non-native species, smothering by sediment plumes, nutrient (Fe) enrichment altering plankton communities, and toxicity from introduced contaminants released incidentally (e.g. oil spills, sewage, flocculants) or as by-products of mining activities (e.g. release of toxic metals & radionuclides). The location of all exploration areas is available at the International Seabed Authority (ISA; www.isa.org.jm).

Another ICES Working Group on Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT) has a ToR to study the implications of deep sea mining (legislative/environmental/geological). In their 2014 report, WGEXT summarized the main types of potential mining interests and indicated that commercial development of these resources is not likely in the near to medium term. WGEXT also identified that the ocean floor outside of National waters are regulated by the International Seabed Authority (ISA; www.isa.org.jm) which has regulations for prospecting and exploration, whilst its code for exploitation of deep sea mineral resources is under development. About that, the ISA, on the 2015 draft regulation, recommends the implementation and approval of a reliable environmental plan of work for exploration before starting the exploitation. This plan includes, among others, the Impact Statement (EIS), the Environmental Management Plan (EMP) and Social Impact Assessment (SIA). According to ISA, all these documents should be made in accordance with Good Mining Practices and verified by independent environmental consulting firms.

The main requirements of EIS among others are the:

1) existence of an Environmental Impact Assessment (EIA) where are established the baseline of environmental conditions;

2) assessment of project related significant effects and impacts (including cumulative impacts).

The EMP main requirements are:

1) the description of the methodologies to be employed on sampling and archiving, the location of monitoring stations, the measurable criteria and threshold indicators;

2) reflecting the parameters for and functionality of Preservation Reference Zones (PRZs) and Impact Reference Zones (IRZs);

3) defining the measures / plans for monitoring, management, conservation, remediation, restoration / rehabilitation and control including those to avoid, minimize, mitigate, rehabilitate and offset, where appropriate, impacts on biological diversity within the impacted area and plans to prevent, minimize, mitigate impacts to water column;

4) to be supported by an approved environmental management system, subject to inspection regime and frequent independent audit.

Despite the remoteness of the majority of exploitation activities locations, no immediate communities or individuals potentially significantly affected by operations, the SIA consider important contributions of other users (public or private organizations) of the marine environment.

As regarded above, the participants at the WGMS 20016 meeting highlighted that each exploitation project should carry out all activities following the good mining industry practices correctly adapted to the marine environment to reduce and control the pollution as well as other hazards, in particular the protection and the conservation of the marine fauna and flora should be assured.

Lieven Naudts (RBINS-OD Nature, Belgium) was invited by WGMS to present the preliminary results of the JPI-Oceans project "*Ecological aspects of deep-sea mining*" (Coord: M. Haeckel, GEOMAR, Helmholtz Centre for Ocean Research, Kiel, Germany; https://jpio-miningimpact.geomar.de/home). The main goal of this four year multi-parametric project is to assess the impact of potential commercial mining activities on deep-sea ecosystems in two areas of the Pacific (the DISCOL Experimental Area, SE Pacific, and the Clarion-Clipperton Zone, NE Pacific). This project involved six work packages responsible for generating great amount of data that are still in processing:

- WP1 Hydroacoustic and visual habitat mapping
- WP2 Benthic diversity and recolonization potential
- WP3 Biogeochemistry and ecosystem functioning of nodule fields
- WP4 Sediment plume dilution and dispersion
- WP5 Communication with stakeholders, policy makers, offshore mining industry
- WP6 Data and sample management

Preliminary results were presented for the various WPs. The 37-years-old mining track is still visible and the nematode community inhabiting this track presents lower density and diversity than the reference site. WP3 focuses on biogeochemical and geochemical conditions and processes in sediments including solute and contaminant fluxes. Modified oxygen fluxes were observed where disturbance removed the surface sediment layer. Trophic interactions, energy flows and bioaccumulation of metals in the benthic food web are also considered in this WP. Ecotoxicological experiments were carried out *in situ* to assess the bioaccumulation of Cu^{2+} by megafauna exposed to an artificial sediment plume as well as various biochemical responses. Concerning WP4, this WP aims at collecting all information on sediment plume dilution and dispersion required for the implementation of adapted deep-sea 3D coupled ocean circulation sediment transport models. For this, artificial plumes were created. Plumes could be successfully observed by both acoustic and optical methods; however further work is required for quantifying the process.

During the discussion other questions were raised regarding the deep-sea mining activity that are:

1) what is happening for the concessions located in the national waters? Some doubts could be related to the development of correct EIA and to who should evaluate them;

2) If the national legislation actually covers the environmental requirements for attributing the exploration licenses and who as well as how is controlling the application of this requirement;

3) If the mandatory deliverables (e.g. EIA, EIS) are also accounting the requirements of a cost-benefit analysis (CBA), i.e the estimation between the net benefits of the mining activities against its net impacts. Furthermore, it is necessary to evaluate the baseline situation allowing the estimation of benefits and impacts.

4) If it is correct to compare terrestrial mining with marine mining because marine and terrestrial environments are distinct ecosystems. In fact, the potential impacts on land are well known contrary to the deep-sea environment.

5) The evaluation of EIS and EMP must be assured by international board composed by researchers / managers under the auspices of ISA or other independent and non-profit international authorities with recognized knowledge in these topics.

Following on from what was written before, some indication can be given associated with the disturbances in the deep sea caused by mining activities. The main factors affecting the surface sediments and the pathways of contaminants during deep sea mining can be attributed to resuspension of sediment particulate matter (SPM) during the operation of the mining vehicles on the seafloor as well as the SPM which are released during loading of the slurry into the riser, these together cause the primary plume close to the seafloor. A secondary plume is caused after separation of the nodules and dewatering of the slurry on board the mining vessel, when large amounts of sediments are pumped back into the sea through long vertical pipes. This SPM plume is located higher up in the water column and can spread out long distances in any direction depending on the prevailing current conditions.

The sediment surface in the nodule fields is in many cases oxic from the surface down to few centimetres only (Stummeyer and Marchig, 2001) below which it is suboxic. Nodule mining will dig into the suboxic layer which will release such sediment that will be immediately oxidized in the water column, partly releasing elements into the water phase. The sediments of the nodule fields are known to contain high concentrations of heavy metals (Stummeyer and Marchig, 2001) which will thus be released and transported by currents into large areas around the mining area, where they will accumulate. Another question is the physical blanketing of the seafloor by the SPM from the plumes. The results of the Midas project (finishing in the end of 2016) together with the results obtained for other projects, such as JPI-Oceans and TREASURE, will contribute to improve the knowledge of this remote and sensitive deep-sea environment towards to ensure their Good Environmental Status. They could also provide the background, to optimize the strategy for correctly implementing the EIA/EIS/EMP/SIA and also the planning of activities in the deep-sea marine environment. Based on the main findings and conclusions of these (and other) projects, it will be possible to complement the recommendations/warnings of this ToR to the stakeholders, policymakers (ISA, national governments, EC), industrial companies and scientists.

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ToR 6c) other emerging issues (e.g. "new" priority substances, pharmaceuticals, novel flame retardants, etc.)

The WFD list of Priority Substances was recently expanded with the publication of the revised Environmental Quality Standards Directive (2013/39/EU). These substances have to be assessed under the new round of River Basin Management Plans and the Marine Strategy Framework Directive is relying on the WFD to provide much of its information on contaminants under Descriptor 8 (because the WFD requires Good Chemical Status in territorial waters, i.e. to 12 nm offshore). However, marine monitoring of the "new" substances appears to be very limited in most States for which information were available at the meeting (Table 1). Belgian members present considered that it was likely Belgium would monitor all substances ("if we have to do it, then we will do it"), but could provide no information regarding sampling matrix, distance, or frequency. Germany, Portugal, Spain, France and the UK have included some of the additional substances, particularly those (such as DDT) that were previously required under the Shellfish Waters Directive (2006/113/EC) or Dangerous Substances Directive (2006/11/EC); both Directives were repealed in 2013. For the UK, most "new" substances are being monitored in a very limited number of locations and the programme will be reviewed based upon the occurrence and concentrations determined in 2016. No other information was available from the remaining member states. It is notable that there will be considerable variation of spatial and temporal coverage between Member States, and that no country will monitor for aclonifen, bifenox and cybutryne in marine environments.

Table 1. Marine monitoring plans for the Priority Substances newly listed under 2013/39/EU. Information was only available for France, Germany, Portugal, Spain, UK; if the country is not listed then it is not monitoring that substance. * E = estuarine; C = coastal (<1 nm); T = territorial (1–12 nm); O = offshore (>12 nm)

	New Substance	Member State	Matrix	Sampling distance*	Sampling frequency	
6a	Carbon tetrachloride	UK	Water	E	Not provided	1 site
		FR	Mussels, Sediment	E, C	Once / 6 years	
9a	Cyclodiene pesticides: Aldrin, Dieldrin, Endrin, Isodrin	UK	Water Mussels Sediment *(Dieldrin only)*	E, C E, C O	Monthly Annually Annually	
		DE	Water	O	Annual	
		SP	Water Sediment *(not endrin)*	E, C, T E, C, T	Monthly or annually Annually	
		FR	Mussels, Sediment	E, C	Once / 6 years	
9b	DDT (total); *p,p'*-DDT	UK	Water Mussels Sediment	E, C E, C O	Monthly Annually Annually	
		DE	Sediment *(p,p'-DDT)* Water	O	Annually	
		PT	Sediment, Water, Fish muscle and mussels	E, C, T, O	Not provided	
		SP	Water Sediment	E, C, T E, C, T	Monthly or annually Annual	
		FR	Mussels, Sediment	E, C	Once / 6 years	
29a	Tetrachloroethylene	UK	Water	E	Not provided	1 site
		FR	Mussels, Sediment	E, C	Once / 6 years	
29b	Trichloroethylene	UK	Water	E	Not provided	1 site
		FR	Mussels, Sediment	E, C	Once / 6 years	
34	Dicofol	UK	Water Mussels	E, C E, C	Monthly Annually	Review after 2016

35	Perfluorooctane sulfonic acid and its derivatives (PFOS)	UK DE FR	Water Mussels Sediment and biota (fish liver) Water Mussels Fish Sediment	E, C E, C O O E,C T,O E,C,T	Monthly Annually Annually Annually Twice / 6 years Twice / 6 years Once / 6 years	Review after 2016
36	Quinoxyfen	UK	Water Mussels	E, C E, C	Monthly Annually	Review after 2016
37	Dioxins and dioxin-like compounds	UK PT FR	Mussels (Fish for D9) Sediment Sediment and fish muscle *(PCB105, PCB118)* Mussels Fish	E, C T, O O E, C, T, O E,C T,O	Annually 2014 only 2015 only Not provided Annually	Review after 2016 Link to D9
38	Aclonifen					
39	Bifenox					
40	Cybutryne					
41	Cypermethrin	UK	Water	E	Not provided	1 site
42	Dichlorvos	UK DE	Water Water	E O	Not provided Annually	1 site
43	Hexabromocyclododecane (HBCDD)	UK FR	Water Mussels Sediment and biota (fish liver) Mussels Sediment	E, C E, C O E, C T, O	Monthly Annually Annually Twice / 6 years Twice / 6 years	Review after 2016
44	Heptachlor and heptachlor epoxide	UK	Water Mussels Sediment	E, C E, C O	Monthly Annually Annually	
45	Terbutryn	UK DE	Water Water	E O	Not provided Annually	1 site

Some members reported on their country's past/current work undertaken on "emerging contaminants" (e.g. pharmaceuticals, novel flame retardants, new antifoulants, rare earth elements, etc.), these included:

- The IMPACTA project from Spain aims to characterize the distribution of regulated and emerging contaminants (pharmaceuticals, perfluorinated compounds, organophosphorus pesticides, triazines, dioxin-like compounds, personal care products, nonylphenols and alkylated PAHs) and microplastics in marine sediments, in two Spanish areas (Atlantic and Mediterranean) and to evaluate the biological effects that they can cause (sublethal embryotoxicity tests, endocrine disruption and biomarkers). Sensitive and selective analytical methods are being developed and validated and they will be implemented in marine monitoring programs. Thus, relevant pollutants present in coastal and offshore areas are identified.
- A study from Moreno-González *et al.* (2015) showed that 20 pharmaceuticals in seawater and 14 in sediments were found at concentrations from low ng L^{-1} up to 168 ng L^{-1} (azithromycin) in seawater and from low ng g^{-1} up to 50.3 ng g^{-1} (xylazine) in sediments. Therefore their bioaccumulation was also determined in some representative organisms (Moreno-González *et al.*, 2016). On the other hand the occurrence, distribution and bioaccumulation of five endocrine disrupting compounds (4-*tert*-octylphenol, 4-*n*-octylphenol, 4-*n*-nonylphenol, nonylphenol and bisphenol A) in water, sediment and biota (*Corbicula fluminea*) collected along the Minho River estuary (NW Iberian Peninsula) were examined (Salgueiro-González *et al.*, 2015). The presence of linear isomers (4-*n*-octylphenol and 4-*n*-nonylphenol) was scarcely observed whereas branched isomers (4-*tert*-octylphenol and nonylphenol) were measured in almost all samples.
- The UK (Cefas) studied the occurrence of flame retardants (FRs) in the UK marine environment where over 20 halogenated flame retardants plus 16 PBDEs have been analysed in marine mammals and sediments. Preliminary results show that some FRs such as DBHCTD (HCDBCO), PBEB, PBT, 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and DDC-CO (DPs) are present in UK samples, currently at much lower concentrations than PBDEs. Over half of the non-BDE halogenated flame retardants analysed for were not detected in any samples
- The UK (Cefas) collaborated with the Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of Coastal Research in Germany to look at the fingerprint analysis of brominated flame retardants and Dechloranes in North Sea sediments: 53 brominated and chlorinated flame retardants were investigated in sediment samples from the German rivers Elbe and Weser, the German Bight, Jadebusen, East Frisian Coast as well as the UK East coast. The aim of the presented study was to investigate the prevalence of different halogenated flame retardant groups as contaminants in North Sea sediments, identify determining factors for the distribution and levels as well as to identify area specific fingerprints that could help identify sources. A fast and effective ASE extraction method with an on-line clean-up was developed as well as a GC-EI-MSMS and LC-ESI-MSMS method to analyse PBDEs, MeOBDEs, alternate BFRs, Dechloranes as well as TBBPA and HBCDD. A finger-

printing method was adopted to identify representative area-specific patterns based on detection frequency as well as concentrations of individual compounds. Concentrations in general were low, with<1 ng g^{-1} dw for most compounds. Exceptions were the comparably high concentrations of BDE-209 with up to 7 ng g^{-1} dw in selected samples and TBBPA in UK samples with 2.7±1.5 ng g^{-1} dw. Apart from BDE-209 and TBBPA, alternate BFRs and Dechloranes were predominant in all analysed samples, displaying the increasing relevance of these compounds as environmental contaminants.

- Since 2009, France has been carrying out a monitoring project (Veille-POP, Watch for new POPs in marine shellfish) on emerging contaminants using shellfish (mussels and oysters) as bioindicators of contamination. The samples were obtained from specimens collected within the French Monitoring Network (Réseau national d'Observation de la Contamination CHimique - ROCCH) operated by Ifremer. The studied contaminants included dioxins/furans (Munschy *et al.* 2008), brominated flame retardants (PBDEs, HBCDDs, BTBPE, DBDPE, HBB, BB-153) and perfluorinated compounds (PFCs) (Munschy *et al.*, 2013 and 2015). All studied contaminants exhibited low concentration ranges (< 1 ng/g wet weight- ww). Overall, non-PBDE BFRs revealed concentrations between 3 and 59 times lower than those of PBDEs. Although penta-BDE technical mixture has been withdrawn from the European market since 2003, BDE-47 (the predominant congener in the samples) was found at similar concentrations as those of α-HBCDD (predominant isomer), a still-used BFR employed in higher quantities than PBDEs in the past. Among PFCs, PFOS was the most detected compound and was predominant in samples from the English Channel and the Atlantic. In samples from the Mediterranean coast, the observed pattern was different, with the predominance of long-chain PFCAs (perfluorocarboxylic acids), suggesting the presence of alternative sources on the Mediterranean coast. Recently, this list of contaminants was extended to four synthetic muscs (galaxolide, tonalide, musk xylene and musk ketone). The two polycyclic musks (galaxolide and tonalide) were the predominant synthetic musks identified in all samples at levels reaching 9.4 and 1.4 ng g^{-1} ww (median value: 0.6 and 0.1 ng g^{-1} ww) respectively in the Seine Bay (English Channel). The contamination levels observed for the two nitro musks (musk xylene and musk ketone) were significantly lower (median value: 0.006 and 0.008 ng g^{-1} ww).

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6 Revisions to the work plan and justification

No revisions are proposed this year.

7 Next meeting

WGMS will next meet (year 3 of 3) in Ancona, Italy, 6–10 March 2017.

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Annex 2: Recommendations

RECOMMENDATION	ADDRESSED TO
1. That the existing JAMP Guidelines for Monitoring Contaminants in Sediments be modified as indicated in the WGMS 2016 report in order to allow their use in deep sea monitoring (as may be needed for the MSFD).	OSPAR Working Group on Monitoring & on Trends and Effects of Substances in the Marine Environment (MIME);
2. That an error relating to sediment preparation for Hg analysis in Section 5.3 of the JAMP Guidelines for Monitoring Contaminants in Sediments should be corrected, as indicated in the WGMS 2016 report.	OSPAR Working Group on Monitoring & on Trends and Effects of Substances in the Marine Environment (MIME);

Annex 3: Presentation abstracts

Several WGMS members gave presentations related to the different topics discussed within the meeting, abstracts from these are included here:

ToR 1

Bavo De Witt (ILVO, Belgium) – M/V Flinterstar incident (06/10/2015)

On 6 October 2015, two cargo vessels, *Al Oraiq* and *Flinterstar*, collided before the Belgian coast. As a result, the *Flinterstar* stranded near Zeebrugge, the Al Oraiq continued to its destination, Zeebrugge harbor. The environmental impact monitoring was presented at WGMS, including advice regarding fisheries activities, measurements of PAHs in marine biota and measurements of PAHs and methylated PAHs in marine sediments. No adverse environmental impact was found during the environmental monitoring campaigns. It was stated that Belgian research institutes (OD Nature and ILVO) revealed a quick response although no Belgian environmental monitoring guidelines were available for these kind of incidents. Information on similar cases in other countries was asked.

Oil patches stranded on beaches (in Belgium and the Netherlands) and samples of oil on the sea surface in the wide neighbourhood of the wreck were statistically compared with oil from the different tanks (diesel and heavy fuel oil; HFO) of the cargo vessel *Flinterstar.* The hydrocarbon fingerprinting technique used was the method proposed by OSINet (Oil Spill Identification Network), and analysis was performed by the laboratory of OD Nature and Rijkswaterstaat (The Netherlands). The results were presented to the WGMS group by Koen Parmentier. All samples could be linked to the different HFO tanks of the *Flinterstar*.

ToR 2d

Elvio Amato (University of Antwerp, Belgium) – Assessing the performance of the diffusive gradients in thin films (DGT) technique for predicting metal bioavailability in sediments

Many sediment quality assessment frameworks incorporate contaminant bioavailability as a critical factor regulating toxicity in aquatic ecosystems. However, current approaches do not always adequately predict metal bioavailability to organisms living in the sediment. The deployment of the diffusive gradients in thin films (DGT) probes in sediments allows labile metals present in pore waters and weakly-bound to the particulate phase to be assessed in a time-integrated manner *in situ*. The DGT technique was shown to be a suitable tool for measuring bioavailable metals in sediments irrespective of site-specific parameters (i.e. particles size, acid-extractable metals, organic carbon, sulfides, bioturbation). The use of a wide range of naturally contaminated sediments for laboratory tests allowed the evaluation of the performance of DGT technique under more realistic environmental conditions (i.e. exposure to contaminant mixtures).

Relationships between DGT measurements and biological responses of four different benthic species (*Melita plumulosa, Victoriopisa australiensis, Tellina deltoidalis, Hyridella aus-*

tralis) exposed to contaminated sediments were investigated. Strong dose-response relationships were found between DGT-labile metal fluxes and toxicity to the amphipod *M. plumulosa* in laboratory-based bioassays. The combined flux of metals (Cd, Cu, Ni, Pb and Zn) measured at the sediment water interface (SWI) provided a robust measure of the bioavailable pool of metals present in the sediment and in the overlying water. The normalisation approach (based on the use of water quality guidelines trigger values) adopted in the attempt to account for different toxicity caused by different metals significantly improved the relationship between DGT and toxicity. DGT-labile metal fluxes measured at the SWI provided robust predictions of metal bioaccumulation in *T. deltoidalis* and *H. australis* under laboratory and field conditions. The mismatched between laboratory and field bioassays emphasised the importance of performing *in situ* tests for environmental risk assessments. The increased metal bioavailability of zinc caused by elevated degrees of infaunal activity was successfully predicted by DGT. This also emphasised the importance of considering multispecies testing for sediment risk assessments.

Through comparison with current methods used for risk assessment, DGT demonstrated to be a useful tool for monitoring bioavailable metals in sediments and to have the potential to improve current sediment quality guideline frameworks.

Koen Parmentier (MUMM, Belgium) – New Strategies for monitoring and risk assessment of Hazardous chemicals in the marine Environment with Passive Samplers (NewSTHEPS)

NewSTHEPS will develop innovative approaches and novel practical techniques that address the current fundamental scientific and methodological issues related to the implementation of Good Environmental Status (GES) for Descriptor 8 of the Marine Strategy Framework Directive in national and European waters.

In this research project, novel and integrated passive sampler (PS)-based approaches (modelling and measurements) will be developed for both chemical exposure (monitoring) and biological effect assessment (passive dosing). Through the use of a broader array of PS techniques (such as DGT, PDMS, and Speedisks, will be used), applicable in a wide polarity range, the project will focus on the quantitation of an extended set of priority and emerging organic micropollutants and metals (targeted approach). Next to that, untargeted analysis with high-resolution mass spectrometry will be performed to develop qualitative screening approaches able to detect trace levels of a virtually unlimited number of known (suspect) and possibly unknown contaminants. For a selection of compounds, both the total concentration and labile fraction (i.e. bioavailable) will be determined.

Additionally, to trace the Suspended Particulate Matter (SPM) towards its origin, carbon (12C/13C) and nitrogen (14N/15N) stable isotope ratios will be measured, since organic matter from marine and terrestrial origin has a different isotopic C and sometimes N signature. In some cases, the sources of the organic matter present in the marine environment might be identified. In addition, modelling techniques will be of great support.

This novel and integrated approach allows (1) a better measurement of contamination levels in the marine environment, and (2) to assess the eco-toxicity of multi-component mixtures including possible synergistic and cumulative effects and compound profiling or identification. The development and validation of an integrated model to assess the environmental status of the Belgian coastal zone by predicting accumulation, trophic transfer and effects of chemicals in this specific (local) ecosystem are central issues in this project.

Maria J. Belzunce-Segarra (AZTI-Foundation, Spain) – International DGT Conference, 28 Sept – 1 Oct 2015

The fifth edition of the DGT Conference took place in the Campus of the Basque Country University, in San Sebastian, from 28 September to 1 October 2015. On this occasion the title of the conference was *DGT Conference 2015: From DGT Research to Environmental Assessment*, and it had the aim of stimulating discussions and initiatives to move the technique forward for use in environmental monitoring programs under the framework of national and international legislations. Eighty five experts from 18 countries met in San Sebastian and presented the last advances in DGT techniques, discussed their advantages as new tools for risk assessment and highlighted their limitations and uncertainties as well as the need for further studies to promote the use of these techniques for regulatory purposes.

The DGT Conference program was based on six sessions covering all aspects of the DGT technique (technical issues, advantages, weaknesses, latest advances and novelties….) in different environments: aquatic systems, sediments, soils and plants. There was a new session on bioavailability to encourage contributions discussing the relation between the DGT data and their effect in the biota; a session on Environmental Assessment and Legislation to debate the use of this technique to meet quality objectives set by the environmental legislations; and the Addendum session to sum up discussions, conclusions and final remarks.

The Conference was organized by AZTI-Foundation with the support of Lancaster University, the DGTResearchCenter and the Basque Water Agency. The Scientific Committee was composed by experts from the most represented countries:

Hao Zhang, Lancaster University, UK (chairperson)

Maria J Belzunce-Segarra, AZTI, Spain (co-chairperson)

Javier Franco, AZTI, Spain

Jun Luo, Nanjing University, China

Jean-Louis González, Ifremer, France

Marco Schintu, University of Cagliari, Italy

Dianne Jolley, University of Wollongong, Australia

Peter Teasdale, Griffith University Gold Coast, Australia

Natalia Montero, Ikerbasque, Spain

Notes from the Addendum Session, drawing together the conference conclusions:

About relating bioavailability and effects with DGT data

There have been increasing publications since 2000 on DGT-fluxes in relation to solute uptake, growth and toxicity. However, further studies are needed particularly regarding whether/how DGT-measured fluxes correlate with biological effects: tissue accumulation, growth, reproduction, cellular biomarkers?

Studies often assess DGT performance by comparison with measurements from different environmental compartments, but there is a need to interpret these comparisons appropriately, e.g., DGT-measured concentrations are often considerably lower than expected given the pore water concentration; this is likely due to the presence of colloids in the pore waters.

Some good relationships have been established between DGT-labile measurements and biological effects in bioassays, but more studies relating laboratory and field measurements are needed. Furthermore, information on chronic exposures at environmentally relevant concentrations (labile solutes) is needed. There are often poor relationships between bioaccumulation and bioavailability because solutes can exert effects without accumulating in tissues. Other biological effects endpoints should also be studied: growth, reproduction and biomarkers.

Advances in the use of DGTs (this mainly relating to water sampling)

<u>New studies</u> are mainly focused on extending the use of DGTs to **more compounds**, using:

- New resins;
- Optimized extraction & analytical steps;
- Improved DGT designs:
    - Multiwell DGT → vertical chemical gradients in flowing pore waters

<u>Limitations & future challenges</u> include:

- High blank values in commercially available DGTs for Hg
- Importance of considering different factors when interpreting DGT data:
    - Open vs restricted diffusive membranes;
    - Thickness of the diffusive gel;
    - Lability degree of complexes;
    - Reproducibility;
    - Elution efficiency;
    - DBL.
- New DGTs need a comprehensive laboratory evaluation prior to field deployments

New applications for DGTs include:

- Improved measurement of methylmercury, arsenic & uranium;
- To investigate metal mobilization due to ocean acidification;
- Environmental monitoring to comply with regulation requirements;
- Trace metal studies in environments affected by crude oil;
- Source tracking in sewage systems;
- The measurement of pharmaceutical and personal care products.

Other issues of discussion during the plenary discussion were:

- there is a need to produce guidelines for sediment monitoring using passive samplers, including DGT;
- assessment criteria for passive sampling monitoring data are needed;
- improved understanding is required of the relationships between the data obtained by passive sampling in sediment and environmental quality data (biota data, toxicity data, EACs);
- to produce environmental quality standards for DGTs, monitoring data are needed.

Federico Spagnoli (ISMAR, Italy) – Benthic chambers

Marine sediment could be subject to serious ecological alterations due to human activities. In fact anthropogenic pollutants (heavy metals, organic pollutants, nutrient in excess) can enter in the sea bottom sediments of a basin by the settling out of polluted particles of terrigenous or water column autochthonous biological and chemical origin. Once these pollutants are in the sediment environment they are subject to biogeochemical reactions that release or subtract them in the pore waters. As consequence of these processes a gradient at the sediment-water interface of these pollutants forms. This gradient results in dissolved benthic fluxes of these pollutants. So the quantification or calculation of dissolved benthic fluxes could be an important indicator of the degree of pollution and of bioavailability of a pollutant of the sediment.

Dissolved benthic fluxes can be measured (in order of reliability), *in situ*, by the deployment of benthic chambers on the bottom sea, by the incubation in laboratory of cores collected in the bottom sea sediments, or calculated by pore water modelling.

So it is suggested using dissolved benthic fluxes measurements as useful means to evaluate the degree of pollution and pollutant bioavailability of bottom sea sediments.

The dissolved benthic flux values could then be employed for the evaluation of the degree of pollution of sediment and also for the evaluations of the sediment role in the water column chemistry and ecology.

The dissolved benthic flux measurement can be an important information, useful to the management of polluted sediments or sediment that have to be moved (harbour dredging, beach nourishment, etc.).

ToR 5

Ana Gama (Instituto Hidrografico, Portugal) – Geochemical Characterization of the Pilot Zone (S. Pedro Moel)

The Portuguese Pilot Zone is based on the Portuguese Law by Decree number 5 of 2008 and it has the purpose of production of electricity from wave energy, as well as other activities. The Pilot Zone is an area covering 320 km^2 near São Pedro de Moel, between Figueira da Foz and Nazaré.

In the context of a protocol between Hydrographic Institute and the company with the concession for generating electricity, a study was developed covering several areas. Sediment samples were collected and determinations of grain size, $CaCO_3$, Total Inorganic Carbon and several metals (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) undertaken. Textural analysis of the sediment indicates that the sediment is formed mainly of sand, particularly on the edges to the East and West of the area; the centre of the area has more gravel whilst in the extreme NW of the area, shallower than 85 m contains a greater fine fraction. Metals concentrations were compared with OSPAR Assessment Criteria (OSPAR, 2008). Average concentrations for the studied metals were lower than the EAC - maximum values that are expected not to cause toxicity - with the exception of As.

Several statistical analyses were carried out. In the Pearson Statistical Analysis it was possible to observe that Al, Mn, Cr, Zn and Hg have significant correlations with fraction $< 63\mu m$ and Fe, As and Pb have significant correlations with $CaCO_3$. In the Principal Component Analysis it was possible to distinguish two metal groups with different behaviours. Factor 1, which explains 46% of the data variance and associates the fraction $<$ $63\mu m$ with Cr, Zn, Hg, Mn and Al and Factor 2, which explains 36% of the data variance and associates $CaCO_3$ with Fe, Pb and As.

The spatial distribution of the fraction $< 63\mu m$ with Cr / Hg and the spatial distribution of the $CaCO_3$ with Fe / As were also studied. Cr / Hg and fines are in a relatively low levels, with a tendency to rise to the sandy deposit of the middle platform reflecting the general distribution of the fines; Fe / As and $CaCO_3$ are in a relatively low levels, with a tendency to higher concentrations in the extreme NW.