Passive Sampling Trial Survey of for hydrophobic contaminants Water and Sediment; Including laboaratory intercalibration.

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1 Introduction

Partly in response to the decision of OSPAR SIME to support a field trial of passive samplers, WGMS and MCWG agreed that the two WGs should work together on a water-sediment trial survey using passive samplers, particularly of silicone rubber. A trial survey would be organised and coordinated by a Coordinating Group consisting of Foppe Smedes, Céline Tixier and Ian Davies from WGMS and Patrick Roose, Ton van der Zande and Jacek Tronczynski of MCWG.

The core of the trial survey would consist of water samplers to be hung out on buoys. The uptake of passive samplers will provide estimates of the activity of the analytes in water, expressed as free dissolved concentration in the water phase.

In parallel sediment samples are collected at about the same locations and equilibrated with passive samplers in the laboratory (IVPS, In-Vitro Passive Sampling). Through the uptake of compounds by the sampler an estimate of the free dissolved pore water concentration is obtained.

By choosing various locations through the ICES area, a spatial distribution is obtained. By including sampling and analysis of water and sediment living organisms the survey will expand the validation of the method beyond the areas studied so far.

Analyses of water and sediment samplers by both the participating laboratories and a central reference laboratory also allows the trial to act as an analytical intercalibration.

Therefore, the objectives of the trial are to:

- extend the geographical range of the validation of the use of passive samplers in water.
- transfer knowledge of the methods more widely within the ICES community
- to gain experience in the use of passive samplers
- estimate the contribution of the analytical component to total variability
- to gain further information towards the validation of passive samplers in sediment

2 Environmental validation aspects

The passive sampling of the ***water*** phase is ideally done in parallel with deployed mussels to investigate the relation with passive sampling results on wider scale. A good relation over time and space was previously observed in field experiments in the Netherlands. Obviously it will not be possible to do that with the same species (*Mytilus edulis*) for the whole ICES area because of different climate conditions or salinities, but it would be preferable, to select sampling sites where it would be possible to either collect or deploy *Mytilus edulis*. Laboratories maintaining a mussel watch program should find it relatively straightforward to include mussels in the survey. Alternatively, native mussels could be collected although interpretation can be obscured by influences from sediments. For that reason, mussels collected from hard substrates (quay poles, stones of a Sea Wall) are preferred. Mussels collected from sediment need to be depurated. On a small scale, mussels for deployment could possibly be provided by RIKZ or FRS. The objective is to compare the results of the passive

sampling of the water mass with the results obtained by the mussel-analysis as validation for the passive sampling.

Passive sampling of ***sediments*** is essentially an estimation of concentrations of dissolved compounds in pore water. In order to have more validation on the sediment sampling, it was agreed to link the results with a worm (*Nereis*) exposure experiment, but this would be optional. It was pointed out that native worms could be used where available. The results of the passive sampling of sediments and of the water mass could indicate if the sediment serves as a source or a sink for the contaminants of concern. Further on, it would be a possibility to see spatial gradients in contamination not obscured by differences in bulk sediment composition.

In Figure 1 a schematic overview is given of the sampling for water and sediment and possible side activities. The A-line is the core of the survey and the intention is that at least one B activity, B1 or B2 is included. The C activities are optional. More optional side activities can be considered

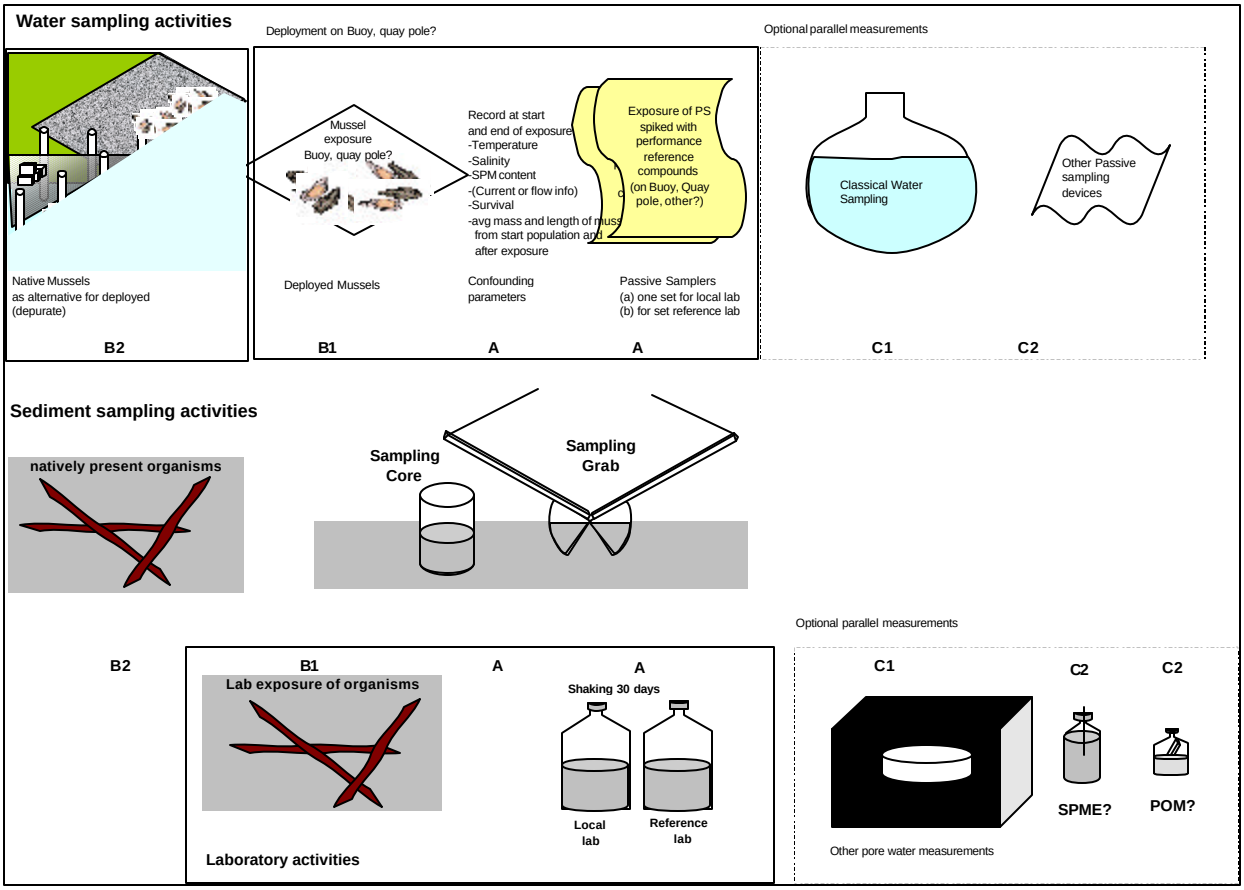

Figure 1

Overview of possible activities horizontally ordered. The A-activities are the core of the PSTS, The B activities are for validation purposes and the C activities are optional.

3 Participants

Ideally, participatating laboratories are experienced in sampling and analyses of various environmental samples, organisms as well as sediment. Alternatively cooperation can be sought from colleagues in other institutes to ensure that all aspects are covered at each sampling location.

Presently the laboratories of IEO (ES), FRS (UK), NIVA (N), NERI (DK), RIKZ (NL), IFREMER (F), MUMM (B), BSH (D), FIMR (FI), RIVO (NL), IOW (D) and the Marine Institute (IRL) have been identified as potential participants.

The survey-intercalibration is an open exercise and all results will be identifiable to participant and available to all participants through the exercise report. Any subsequent use of the intercomparison data in publications should be communicated to the coordinating group and appropriate reference used.

4 Criteria for station selection

At this stage it is not the intention to investigate the limits of possibilities of passive sampling and therefore the selection of stations is focused on obtaining useful results to validate the principle and obtain a realistic impression on between-laboratory analytical comparability. Intentionally 2 stations in a pollution gradient were seen as an optimum between organisational feasibility and obtaining relevant results. One station will nevertheless contribute to spatial coverage of the ICES area. On the other hand some laboratories may cover such a large area that three stations would be appropriate. (Three stations might be possible if the final number of participants is low or several choose to join with one station). In this non funded survey a total of 20 stations is maximally feasible. Therefore it is prerequisite that they are carefully selected. The text below attempts to give some criteria and guidance on selecting the appropriate stations especially in the case of multiple stations. This will likely not apply to all possible areas and should not be seen as strict directions.

Participants are invited to open a discussion with the coordinators to jointly make the most appropriate selection. The guidance below assumes two stations for a certain region.

4.1 Water

Basically each participant will obtain material for sampling at proposed stations. Optimally these stations should be selected to have a difference in pollution level of a factor 2 to 4, preferably supported by measured concentrations in organisms. This is to ensure that differences between sites are significantly greater than the likely analytical and experimental variance. Furthermore the principle of uptake by organisms can be confirmed; i.e. that a proportional higher concentration in the water phase is reflected by the concentration in the organism. Ideally these stations are in a salinity range where the same *Mytilus Edulis* can be deployed or occur. The difference in pollution level may also be obtained by locating one station in a reference area and the other in a contaminated part of an estuary.

If no data on native or deployed mussels are available, e.g. due to salinity restrictions, the two water sampling points could be selected only on the basis of a large difference in pollution level, based on concentrations in other matrices (e.g. organic carbon normalised concentrations in sediment) or some other types of information. For example a deployment upstream and down stream of a pollution source, or deployment in high and low SPM content waters. may be looked for.

4.2 Sediment

Stations for sediment sampling are preferably close to the stations selected for water sampling. A sedimentation area slightly upstream from the water sampling point would be suitable. As water samplers are usually placed on buoys that are used to mark the channel, the exact stations are generally inappropriate for sediment sampling. The bottom is often very much influenced by shipping and current, and could be very sandy. Sediments collected should contain at least 1% organic carbon and preferably consist of muddy material. Muddy sediments are required because the low capacity of sandy sediments for contaminants, and aspects of sample handling for sandy sediments make them unsuitable for an intercalibration.

4.3 Station selection

Practically the best way to select the stations is:

1. to identify the stations that are candidate for water sampling (suitable pollution range, buoys available, mussels can be deployed or alternatively mussels are naturally present)
2. the same for sediment (fine grained, exposure tests with worms done or possible, other properties known).
3. Then recognize the stations where they coincide or match in some other way.
4. Choose two stations that have about a factor 2-4 difference in concentration of contaminants in local organisms. If more stations apply those with highest flow conditions have preference.

5 Analytical organisation

Spiked rubber samplers and coated bottles will be distributed from a central laboratory. Bottles will be numbered, engraved, by a letter and a number. Silicone rubber sheet samplers are contained in labelled bottles. The samplers have numbers engraved on them to ensure control of which sheet sample is placed on top or bottom of the sampler. Samplers for water as well as sediment sampling are spiked with Performance Reference Compounds (PRCs). These will (partially) release during exposure. For water passive sampling the release will be used to estimate the sampling rate that may differ due to variable flow conditions. In sediment passive sampling the PRCs are a QA measure to indicate if depletion has occurred. The selected PRCs may coincide with internal standards used by laboratories (see also below).

For passive sampling of the **water phase,** each laboratory will receive a sampler (see PSTS homepage) for each station and silicon rubber sampler sheets spiked with PRCs. Sheets are packed in glass bottles lined with aluminium foil that are stored in freezer when not deployed (i.e. before and after sampling). For the measuring the water phase, 3 sets of spiked sheets will be delivered for each station. One will act as a reference for analysis of the initial concentrations of PRCs (this sample will also act as storage and transport blank). Two sets of sheets are deployed (together with mussels). After deployment, one set is sent back to the coordinating lab for analysis, and the other sample and reference is analysed by the participating lab together with the mussels, deployed or native. The sampler frame allows samplers to be mounted in three positions. The third position can be used to deploy mussels.

To investigate **sediments**, for each station a laboratory will receive 3 bottles spiked with Performance Reference compounds, one reference and two for shaking with the sediment. The reference (also transport and storage blank) and one bottle will be analysed in the local participating laboratory, and the other will be sent to the central laboratory as a duplicate for analysis.

Calibration. Laboratories may need to slightly adapt their analytical procedures as the PRC compounds may interfere with their normal recovery and/or internal standards. Presently, the PRC mix contains deuterated compounds of Naphthalene, Anthracene, Fluoranthene, Pyrene, Chrysene and Perylene, and for PCBs CB004, CB029, CB155 and CB204. Concentrations of these compounds do not need to be measured as absolute concentrations as the data interpretation only requires the ratio with to unexposed reference to be known. Therefore, the compounds do not need to be present in the calibration mix for the measurement. Once the retention time is known, the response factor of the parent compound can be used (or in the case of PCBs another closely eluting CB). The coordinating lab will supply with the samplers a non-quantitative solution that can be used to identify retention times and/or tune the masses in case of GCMS, and wavelengths in case of HPLC.

Additional Analyses. The sediment should be analysed for total concentrations of contaminants in the traditional way by the local participating laboratory. QA for this is provided through participation in QUASIMEME. This is also the case for supporting analyses of deployed/exposed, or locally collected biota.

6 Procedural arrangements

All materials will be delivered to participants by the coordinating laboratory. This includes sampling cages. The costs of sending Sampling cages to the participants and back to the coordinating lab will be paid by the participating labs. Laboratories that wish to keep the samplers can place an order at the producer in the Netherlands, for delivery at the coordinating lab. Similar arrangements should be made if the sampler is lost by theft, improper fixing or is seriously damaged. Participants are free to reproduce the samplers at a local producer.

Samplers will be deployed for 6 weeks period in de months October and November 2006.Temperature, salinity, a measure of turbidity, (by SECCHI, SPM content or both) should be determined at the day of deployment and recovery. The main batch of samplers would be recovered in November, and the appropriate samples sent to the coordinating lab. Sediment samples may be collected independently earlier, for example at the time the water samplers are deployed. Analysis of the samples and including reporting the data should be completed by 1st of February 2007, in order to allow time (!) for the Coordinating Group to prepare a report before the next meeting of MCWG/WGMS (5-9 March 2007, Hamburg)). A more detailed list of actions will be made later.

7 What to do at this stage

Contracting parties will reply to Foppe Smedes to confirm their ability to participate, the characteristics of the sites that they had available, accompanying deployments/measurements they can or will include, etc. The tables below should be used to simplify collation of the information (MSWORD versions can be downloaded from the ICES-PSTS home page). After this, an evaluation will be made by the coordination group of laboratories offering to join the water-sediment trial survey and confirmation of participation would be given in July 2006.

Participants are requested to express their intention to participate and fill the forms as soon as possible, but before June 15th 2006. If you can confirm participation with first application please do so. If more time is required to follow internal administrative procedures confirmation can be given up to 15th of July. The coordinating group will evaluate the participations with a view on targets and maximal amount of stations and give a further confirmation by 15th of July.

An drawing of the type of samplers used can be viewed at the IC ES-PSTS home page. This may help to estimate your possibilities to hang it.

Participating laboratory	……
Participant information	
Institute or organisation	
Contact person 1, email	
Contact person 2, email	
Contact address	
Address for delivery of materials	
Status of participation	Intentional/confirmed
Remarks	

Participating laboratory	……		
Analytical aspects			
Shaker available 2.5 cm amplitude/150 rpm?			
Is Soxhlet extraction equipment available?			
Concentration method			
Remarks			
Presently used PRCs that can coincide with IS you may apply: Deuterated compounds of Naphthalene, Anthracene, Fluoranthene, Pyrene, Chrysene and Perylene, and for PCBs CB004, CB029, CB155 and CB204			
Parameters	Method	Recovery standards or internal standards used	QUASIMEME participation? Sediment /biota
PCB			
PAH ??			

Participating laboratory	……	
Station information		
Name		
Coordinates		
General Description		
Known sources of contaminants		
Station type		
Temperature range		
Salinity Measure of turbidity (SECCHI and/or SPM)		
Flow regime		
Specific info for WATER sampling		
Possibility to hang passive samplers in water		
Relevant biota species present for sampling in water (indicate deployed or native)		
± CB52 and CB153 in specified species(µg/kg DW)		
± Flu and BaP in specified species (µg/kg DW)		
Remarks		
Specific info for SEDIMENT sampling		
Sediment type Sediment TOC range		
Relevant biota species present for sampling in sediment		
± CB52 and CB153 in specified species(µg/kg DW)		
± Flu and BaP in specified species (µg/kg DW)		
Analysis of deployed worms or native worms?		
Other parallel programs, SPM collection? Total analyses of water? Others		

8 Timetable for field trial and intercalibration

Activity	Completion date	Responsibilities
Draft protocol for the experiment	May	Coordinating Group
Get firm commitments from participants.	June	Coordinating Group and participants.
Notionally up to 10 labs and 2 locations per lab		
Determine degree of replication *	July	Coordinating Group
Confirm participants and locations	July	Coordinating Group
Draft Guidelines	End of July	Coordinating Group
Purchase samplers	June – Aug	Participants
Prepare and spike samplers	Aug –Sept	Foppe Smedes
Purchase of bottles	June – Aug	Participants
Prepare, spike and distribute bottles	Aug - September	Foppe Smedes
Build frames to support samplers	July – Sept	Participants
Purchase mussels or use local animals	October	Participants
Distribute samplers	Late Sept	Foppe Smedes
Deploy mussels and samplers and sediment	Early October. Greenland can not be later than August.	Participants
Record supporting data (CTD-data)	Simultaneous with the sampling	Participants
Recover mussels and samplers	November	Participants
Shake sediment	Oct – Nov	Participants
Send sediment samplers to central lab	November	Participants
Send water samplers to central lab	November	Participants
Analyses of samplers at central lab	Mid Feb.	Foppe Smedes
Complete analyses at local labs	Mid Feb	Participants
Send data to central lab	Mid Feb	Participants
Collate data	End of Feb	Foppe Smedes
Review data	At WGs next year	All

185 *Currently the programme only includes replication of analyses between participants and central lab only. If participant numbers are small, the degree of replication could be larger.