NORMAN

Network of reference laboratories and related organisations for monitoring and bio-monitoring of emerging environmental pollutants

Joint Programme of Activities

Workplan/actions for 2009

TOPIC: PASSIVE SAMPLING

Interlaboratory calibration study on passive sampling of emerging pollutants

Recommendations of the expert group meeting on passive sampling

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1 State of the art

Recently, the Advisory Committee on the Marine Environment of the International Council for Exploration of the Sea (ICES) recommended that the ICES member countries should continue working on passive sampling techniques as a monitoring tool, and recommended to the Oslo and Paris Commission (OSPAR) for the protection of the marine environment of the North-East Atlantic that the draft guidelines for integrated monitoring should be formulated in such a way that these techniques can be included[1]. Moreover, in addition to previous documents under the WFD Common Implementation Strategy, a new guidance document has recently been produced by a pan-European drafting group for the chemical monitoring of surface water under the WFD[2]. The document lists passive sampling techniques as useful tools that can help to improve the water quality assessment while benefiting from reduced monitoring costs. Recently, the British Standards Institute (BSI) published the first more general guidance document for the determination of priority pollutants in surface waters using passive sampling, the Publicly Available Specification PAS-61[3], which has formed the basis of a draft ISO norm[4]. However, in order for passive sampling to be accepted by regulators and other end users, activities that will demonstrate the reliability of the technology, such as **interlaboratory calibration studies** and **field validation trials** are necessary. Field validation can be focused on evidencing that equal concentrations are found compared to spot sampling or showing the relation of PS results with exposure levels to organisms. An overview of performed, or possible future activities in this field is given in Section 5 (References).

2 Recommendations of the expert group meeting

A NORMAN expert group meeting was held on 27th May 2009 in Prague. Participants discussed the feasibility of interlaboratory exercises within the NORMAN network. The discussion provided several recommendations to the potential organisers of such a study. For a NORMAN network activity the setup below was suggested.

2.1 Design of the study

The design is presented stepwise with a sampler comparison exercise that can be extended stepwise to cover individual aspects in the passive sampling process, such as analytical comparability and comparison with spot sampling.
The levels suggested in the study design are:

1. The main network activity would be to showi the **present variability in data** by comparing results from various passive samplers sent by participating laboratories to be exposed to water at a single (reference) site. For selection of target compounds see Section 2.2.1.

   This could be extended by one or more levels such as:
2. Participating laboratories analyse a standard solution in parallel with step 1
3. The central organising lab produces multiple passive samplers to be analysed by all participating labs

4. Alternatively, participating labs send samplers in duplicate and after exposure one sampler is analysed in a central laboratory
5. Data from the passive samplers above will be compared with contaminant concentrations in frequently collected bottle samples and/or continuous water sampling.

Ideally, after Step 1, all labs will derive the same aqueous phase concentrations from the sampler results, and those results will also equal those from the continuous water sampling. If not ideal, the results will serve as a good illustration of the variability over different samplers.
Steps 1, 2 and/or 3 will help to exclude sources of difference such as analytical bias by allowing the differences between samplers to be studied.
Step 4 would allow comparison of samplers excluding interlaboratory variation. But a single lab is unlikely to have full experience of analyses of all the different sampler types.
Interpretation of Step 5 would gain from all labs also analysing a grab water sample from the selected reference site.

2.2 Selections in setup

2.2.1 Selection of target compounds

The study can be performed within and across three sub-groups of passive samplers with the aim of providing a set of harmonised passive sampling methods for monitoring selected pollutants of emerging concern. The sub-groups are:

1. Passive samplers for **hydrophobic organic compounds**, e.g. polybrominated diphenylethers (PBDE), polyfluorinated organic surfactants (PFOS) etc.
2. Passive samplers for the **polar (hydrophilic) organic compounds** such as pharmaceuticals, polar pesticides or illicit drugs
3. Passive samplers for monitoring trace **metals and organometallic compounds.**

From these three sub-areas, area 2 (polar organic compounds) was identified by the expert group as the most interesting within the NORMAN JPA, since a majority of emerging pollutants are polar organic compounds.

The selection of the target group of compounds is the most important decision. The criteria for selecting the compounds are:

a) there should be sufficient evidence of environmental hazard of these compounds
b) compounds should be found in a freshwater environment and present/ identified/expected Europe-wide (or even global)

A suggested approach to selecting target compounds is that the organizers put together a longer list of “potential candidates” that will be circulated to potential participants to identify their interest in being included in the study. Relevance and technical feasibility will play a role in the selection.

2.2.2 Reference site

The trial will be performed at a single reference site. This will allow the participants to explore the concept of the use of standard test sites for the validation studies of passive samplers in the absence of suitable certified reference materials.

The site should be selected to

a) *cover a desired spectrum of emerging contaminants and exposure conditions* (hydrodynamics, water temperature, particulate matter content, salinity, pH etc.), e.g. a river, a marine harbour, a wastewater treatment plant, or a lagoon system used for tertiary wastewater treatment. Another possibility would be an artificial stream system. Such a system exists in the south of France close to Pau, owned by Total Petrochemicals.

b) *be close to an on-site laboratory facility* capable of on-line monitoring of target analytes and necessary supporting parameters in water to provide a reference value of TWA concentration of target analytes in water by frequent spot sampling during the sampler deployment. There are such sites in Eijsden, The Netherlands and on the River Rhine in Germany.

The laboratory operating the on-site facility should provide the participating laboratories with supporting parameters (temperature, pH, DOC and TOC content, conductivity, salinity, flow velocity, discharge, unusual events etc. during the sampler deployment).

The expert group showed a preference to conduct the study in surface water. Not only is this most relevant, but wastewater may be too complex a matrix, with a lot of concentration and flow fluctuations. Drinking water may contain such low levels of target compounds that there is a risk of failing to detect the compounds.

2.2.3 Central laboratory

There are different tasks that need to be performed in a central laboratory. Commitment of a laboratory or laboratories to perfom these tasks is crucial for the success of the study. Depending on the level (2.1) at which the study will be performed, the following tasks can be identified:

a) Control exposure conditions at the reference site and exposure of samplers sent by the participants under equal conditions, evidenced by exposing equal samplers at different positions
b) Provide a standard solution of analytes
c) Provide equally exposed passive samplers (2.1, Level 3) to participating laboratories, including homogeneity test
d) Participants will send duplicate samples for exposure under a) and the central laboratory will perform the analysis of one of the exposed samplers to compare passive samplers and reduce analytical variation
e) Collect and analyse frequent spot samples of water and/or samples from continuous water sampling during passive sampler exposure to provide the mean value of analyte concentrations in water during sampler deployment at the reference site.
f) Collect and report the data from the whole study, evaluate and report on the results.

Obviously, experienced laboratories should be involved in these tasks.

An agreement is needed on the selection of the sampler to be applied under point c) between the core organisers of the study and the laboratory that will provide the samplers.

2.2.4 Study results

a) Passive samplers. The study will consist of passive samplers hung out on buoys (or deployed in a similar way) to sample the water phase at a single reference site.
Participating laboratories are free and encouraged to deploy all types/designs of passive samplers at the reference site. For this step in the exercise participants will be requested to supply for each target compound the amount sampled by their sampler and the aqueous phase concentration they derived from the uptake.

b) Standard solution. This will show the variability of applied instrumental methods and is a simple first step to allow correction of data for analytical deviations.

c) Provided passive sampler. The replicate provided samplers and their analysis by both central and participating laboratory will allow an intercalibration of the analysis of passive samplers and an estimate to be made of the contribution of the analytical component to total variability.

d) Duplicate samplers exposed. One laboratory analysing duplicates of all samplers applied under a) will give a comparison of all samplers with strongly reduced analytical variability. Alternatively a significant portion of duplicates (including 3 samplers from each type) can be used for this purpose.

Ad e) Spot sampling in water. The arithmetic mean value of concentration of analytes measured in frequently taken spot samples of water during sampler deployment will provide the comparison with a conventional sampling approach. Uptake of passive samplers is proportional to the dissolved concentration in water and, provided the sampling rate is accurately known, a direct comparison with the spot sampling average is possible.

Depending on how many levels are included, the results obtained will allow a realistic evaluation of the passive sampling of the selected compounds and give participating laboratories information about whether a particular passive sampling method provides comparable results within the variability of the exercise.

2.3 Reported values

1. Amount of target compounds determined by the participant laboratory in their own passive samplers;
2. TWA value of concentration in water derived by the participant laboratory using their own passive samplers;
3. Amount determined in the provided standard;
4. Amount of target compounds in provided passive samplers.

3 Resources and budget:

The crucial role in the organisation of the study will be the availability of sufficient funding. Depending on the budget, different steps can be added (2.1). Participants should provide a statement of their willingness to support this activity financially.

4 Timescale:

Many potential participants expressed an interest in joining the activity in 2010 and some indicated that funding to participate in such activity may be available in 2010 but probably not beyond.

5 References

1. International Council for Exploration of the Sea (ICES): Passive sampling techniques for contaminants. Report of the Advisory Committee on the Marine Environment (ACME), section 2.3.5., ICES, Copenhagen, 2005 (cf.: http://www.ices.dk/advice/icesadvice.asp).
2. P. Lepom, G. Hanke, J. Wollgast, Ph. Quevauviller (eds.), Guidance on surface water chemical monitoring under the Water Framework Directive, (see http://circa.europa.eu/Public/irc/env/wfd/library...)
3. British Standards Institute, PAS 61:2006, Determination of priority pollutants in surface water using passive sampling, 24 pages, London 2006.
4. ISO/CD 5667-23 Water quality. Sampling. Part 23: Determination of significant pollutants in surface waters using passive sampling. – a draft.