



International **Passive **S**ampling **I**nterlaboratory **C**omparison (IPSIC 2010)**

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Introduction

Dear IPSIC participants,

Passive sampling methodology is widely used in environmental monitoring of aquatic pollutants worldwide. The application of appropriate quality control (QC) measures is essential in environmental monitoring projects that use passive samplers. These measures are important in sampler exposure as well as in the subsequent sampler processing and instrumental analysis. In general, quality control (QC) should be implemented throughout all procedures including preparation, handling (transportation, deployment and retrieval) and storage processes. With increasing demands for quality analyses, many laboratories have based their standards for passive sampling on ISO/IEC 17025. So far, only a limited number of interlaboratory proficiency tests, which are required for a full method validation, have been performed; e.g. the trial survey on passive sampling of water and sediment, under the initiative of ICES* MCWG[†] and WGMS[‡] (see www.passivesampling.net). More interlaboratory comparison studies are underway and are urgently needed.

Following discussions on possible activities within the International Passive Sampling Workshop and Symposium 2009, we have decided to organize an interlaboratory comparison for selected passive sampling devices, namely SPMDs for non-polar organics and DGTs for metals. This interlaboratory comparison study shall serve as an external QC scheme which can be used in the GLP or accreditation process of participating laboratories.

During the start up phase, we are relying on the experience in both intercalibration and passive sampling technology of the experts organizing this study. The scope of the start up of this study is narrow. However, in the near future we intend to include more passive sampling devices, e.g., POCIS and Chemcatcher, and additional test parameters as well. These would include toxicity tests and chemicals such as PCDD/Fs and PBDEs. Of course, any broadening of the study scope will have to go hand in hand with demands on the passive sampling collaborators.

The IPSIC intercalibration study has been accredited by CAI (Czech Accreditation Institute), under the accreditation system of CS Lab, Ltd. In the organization of IPSIC, CS Lab's expertise in the organization of proficiency testing for the analysis of samples from various environmental matrices has been combined with the Institute of Public Health Ostrava's knowledge with various pilot and monitoring applications of passive sampling technology.

Tomas Ocelka, on behalf of organizing committee and realization team

* International Council for the Exploration of the Sea

† Marine Chemistry Working Group

‡ Working Group on Marine Sediments

Organizing committee

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Objectives

The main goal of this study is an interlaboratory comparison of passive sampling devices which have been exposed to analytes present in surface water. This comparison shall contribute to quality improvements in passive sampler applications for water analysis. These contributions mainly include the following aspects:

1. overall insights into the variability of the major steps of exposure and analytical treatment of exposed samplers by various methods,
2. sharing experiences and an increase of professional awareness using passive samplers in selected aquatic environments,
3. performance of validation steps supporting the use of passive sampling devices under agreed (standard) conditions.

This study will help analytical laboratories, who are closely involved in the sampling and analysis process and are the main target groups of this study. Other important end-users are administration bodies evaluating the sampler performance within GLP or accreditation standards.

Study setup

Within the IPSIC study, analysis of selected parameters (concentrations of organic pollutants and metals) will be performed in field exposed passive sampling devices. Exposure of passive sampling devices will be performed in surface water (a river). Based on further demands in next rounds of IPSIC, other systems (e.g. drinking water in a large reservoir) can be selected.

1. Analyzed materials

The material subjected to analysis of selected parameters by participating laboratories will be two types of field-exposed passive sampling devices: SPMDs for the analysis of hydrophobic organic pollutants and DGTs for the analysis of metals.

2. Analytes

Non-polar organics (to be analyzed in field exposed SPMDs):

- Polychlorinated biphenyls (PCBs): PCB28+31, PCB52, PCB101, PCB118, PCB153, PCB138, PCB180
- Organochlorinated pesticides (OCPs): α -, β -, γ -, δ -HCH, HCB, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT
- Polycyclic aromatic hydrocarbons (PAHs): Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(ghi)perylene, Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene
- Polybrominated diphenyl ethers (PBDEs): PBDE28, PBDE47, PBDE99, PBDE100, PBDE153, PBDE154, PBDE183
- A suite of performance reference compounds (PRCs) – see below.

Metals (to be analyzed in field exposed DGTs)

- Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn

3. Standard solutions

Study participants will be provided with a set of test standards.

Standard 1 (SPMDs relevant):

Type of sample: A standard solution of non-polar organics
PAHs 1-500 µg/l, OCPs, and PCBs 1-500 ng/l in nonane
Sample origin: Wellington Laboratories, Canada, or equivalent
Weight: ca 600 µl
Package material: Closed amber glass ampoule within a metal container with
absorbent material

Standard 2 (DGTs relevant):

Type of sample: A standard solution of metals: Al, Cd, Co, Cr, Cu, Fe, Mn,
Ni, Pb, Zn 1-100 µg/l in 2M HNO₃
Sample origin: Analytica, Ltd., or equivalent
Weight: ca 3 ml
Package material: Closed amber glass ampoule within a metal container with
absorbent material

4. PRCs blank (SPMDs relevant)

Purpose: Calculation of analyte concentrations in water from field exposed SPMDs.

The following PRC compounds will be used:

PAHs: deuterated PAHs: D₁₀-Acenaphthene D₁₀-Fluorene, D₁₀-Phenanthrene, D₁₂-
Chrysene

OCPs, PCBs isotopically (¹³C) labeled: PCB3, PCB8, PCB37, PCB54

It is advisable to analyze all recommended parameters. Ambient concentrations will be reported using PRCs by application of a prescribed protocol (delivered with exposed PS). No alternative results are accepted.

For evaluation of ambient concentration of metals (from DGTs) the temperature of exposure will be provided.

5. Dialysates (SPMDs and DGTs relevant)

Purpose: for uncertainty evaluation of used analytical method.

SPMDs

Type of sample: Two SPMD dialysates, extracted in the reference laboratory
by described procedures with the final solution in nonane.
Weight: cca 1 ml
Package material: Closed amber glass ampoule within a metal container with
absorbent material

DGTs

Type of sample: Two DGT extracts, prepared in the reference laboratory
upon described procedure. The solution will be in 2M HNO₃.
Weight: cca 3 ml
Package material: Closed amber glass ampoule within a metal container with
absorbent material

Time schedule (in 2010)

Preliminary request form (RF): 28th May 2010
Evaluation of RF, preparation: 15-30th May 2010
Deployment (range)[§]: 1st June - 31st July 2010
Sample distribution: August - September 2010
Results submission by participants: September - October 2010
Preliminary reporting (validation): December 2010
Final reporting: January 2011

[§] Based on weather conditions and predicted flow water

Sample exposure/distribution

All logistics are planned so that exposed samplers will be distributed immediately after their retrieval from the field site. Samplers will be exposed by the organizer's sampling group. Each sample trial will consist of:

1. 2× field exposed SPMDs with PRCs (for each of the two sampling sites)
2. 2× dialysates from field exposed SPMDs (for SPMDs and DGTs and each sampling site)
3. 2× control SPMDs (for PRCs evaluation)
4. a solution of PRCs for the purpose of instrumental analytical method setup (not for PRC quantitation)
5. 2× DGTs (for each of the two sampling sites)

Sample exposure will be performed according to a sampling plan.

Among exposed SPMDs and DGTs for trial, extra SPMDs and DGTs will be exposed, extracted and delivered to the participants as dialysates/extracts and used as reference materials, to be available after result submission and evaluation.

Exposure and distribution of samples will be performed by IPH Ostrava, as the official collaborating partner of CS Lab Ltd.

Data collection

Results from all participants will be collected in a standardized form, based on an MS Excel spreadsheet template. The name of the file will have the following notation: "IPSIC RR, CODE.xls", where RR is abbreviated year of the round, CODE is number code assigned to the participant laboratory after registration. No other format will be accepted. Simultaneous mailing to the addresses IPSIC@animaracio.com and Tomas.Ocelka@zuova.cz is required.

Following collection of results, they will be subjected to a first round of evaluation. If there are any doubts or any inadequate parameters, relevant participants will be notified for completion.

Summaries of results shall be provided as customary for any participating laboratory.

Methods

Guidance documents will be provided for methods that can be used by participating laboratories in sample extraction, cleanup and instrumental analysis. The IPSIC addresses laboratories that have experience with the use of SPMD and DGT. Nevertheless, participation of laboratories that want to test the method and check their performance is also encouraged.

For the instrumental analysis in laboratories where analysis of passive samplers has been established, consider the samples as routine and use your own sample extraction, dialysis, clean up, spiking and analysis protocols. For organic contaminants, participants are encouraged to avoid co-elution of the individual target compounds during analyte separation by using appropriate columns.

For reporting of used methods, additional sample sheets will be available, allowing selection and appropriate description of procedural steps for unification. All methods are to be delivered together with reported measured values. Methods based on GLP principles and/or with accordance to EC ISO/IEC 17025 standard are recommended.

The CS Lab, Ltd. is an accredited for organization of Interlaboratory Studies by the Czech Accreditation Institute. The accreditation is based on the ILAC G-13:2000 guideline.

Evaluation/reporting

Participants will be provided with data report forms. Log transformed data will be subjected to (i) exploratory, (ii) statistical and (iii) gnostic analysis. For final analysis, outliers will be omitted. The following statistical parameters will be used: minimum, maximum, mean, median, standard deviations (mean and median), and the coefficient of variation.

For each of the runs, robust mathematic methods will be used to outlier's tests, after that repeatability and reproducibility will be calculated.

Performance evaluation will be performed on following parameters, as proposed by ISO Guide 43-1:

1)

Percentage difference, D%:
$$D\% = \frac{X_i - X_{REF}}{X_{REF}},$$

where:

X_i individual value measured (per participant),

X_{REF} referenced value (taken from all laboratories). For data sets with outlier results, *median* value will be used; otherwise the *average*, based on exploratory data analysis.

Results for $|D\%| \leq 2\sigma/X_{REF} \cdot 100$ are considered as satisfactory, $|D\%| > 2\sigma/X_{REF} \cdot 100$ as unsatisfactory.

2)

z-score, Z:
$$Z = \frac{X_i - X_{REF}}{\sigma},$$

where:

σ standard deviation from the data set.

Results for $|Z| \leq 2$ are to be considered as satisfactory, $2 < |Z| \leq 3$ as questionable, and $|Z| > 3$ as unsatisfactory.

Results will be reported after each round of trial, issue is described in the schedule above. Each participant will receive confirmation of participation upon his individual code, with annual report. Codes are strictly confidential and are subjected to the changes each round.

References

1. ISO/IEC Guide 43-2:1997, Proficiency testing by interlaboratory comparisons - Part 2: Selection and use of proficiency testing schemes by laboratory accreditation bodies
2. ASTM E1301-95 Standard Guide for Proficiency Testing by Interlaboratory Comparisons
3. ISO 3534-1:1993, Statistics - Vocabulary and symbols - Part 1: Probability and general statistical terms
4. ISO 5725-1:1994, Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions
5. ISO 5725-2:1994, Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method
6. ISO 5725-4:1994, Accuracy (trueness and precision) of measurement methods and results – Part 4: Basic methods for the determination of the trueness of a standard measurement method
7. Eurachem document 2000 (Second edition): Quantifying Uncertainty in Analytical Measurement
8. ISO/TS 21748:2004 Guide to the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation.
9. EN14136:2004 Use of external quality assessment schemes in the assessment of the performance of in vitro diagnostic examination procedures.
10. ISO 13528:2005 Statistical methods for use in proficiency testing by interlaboratory comparisons.

Appendixes

1. Preliminary request form
2. Format of collected results