Quasimeme Laboratory Performance Studies

Round 2016 - 2

3 October 2016 - 31 December 2016

Exercise Protocol

Passive Sampling Development Exercise (DE-13)

Version 2: 1 October 2016

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Introduction Round 2016 - 2

Thank you for participating in the 2016 QUASIMEME Laboratory Performance studies.

The test materials for the exercises in Round 2016-2 that you have ordered will be sent to you by courier in the week of 3 October 2016. Please check that the contents of your package are correct and that all test materials are intact. If any test materials have been damaged in transit or if the wrong samples have been sent, use the form in Annex 1 of this document to request replacement materials within two weeks after receipt of the test materials.

This protocol covers the Passive Sampling Development Exercise DE-13

Round	Analysis Group Code	Matrix	Analytes
2016 - 2	DE-13	Field exposed silicone sheet	Polycyclic Aromatic Hydrocarbons Halogenated Organics Selected Performance Reference Compounds
		Non-exposed silicone sheet	Polycyclic Aromatic Hydrocarbons Halogenated Organics Performance Reference Compounds (PRCs)
		Calculation exercise	Selected compounds and PRCs

All data must be sent by e-mail to Quasimeme using the data submission form, no later than 31 December 2016

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ROUND	2016 – 2
DE-13	Nonpolar organic contaminants in silicone passive samplers
Test materials	Exposed PS, Control PS, and DATASET 1

Objective

This study covers the determination of nonpolar organic contaminants in silicone passive samplers (PSDs).

Test Materials and storage

The samplers were prepared at Masaryk University, Czech Republic. Samplers were exposed by PaSOC, Netherlands. Silicone sheets (SSP-M823, 0.25 mm thickness) were pre-extracted in a soxhlet to remove silicone oligomers. Test materials were first extracted with ethyl acetate for over 5 days and subsequently vacuum dried and washed with methanol The sheets were spiked with Performance Reference Compounds (PRCs): Biphenyl-D10 and PCB congeners 1, 2, 3, 10, 14, 21, 50, 55, 78, 104, 145, 204. Sheets were distributed by 3 in a glass vial and closed with a lid lined with aluminium foil. Half of the samplers were set aside to serve as a control and the other half of the samplers were deployed for 42 days at a moderately contaminated river site. After exposure the sampler fouling was removed by scrubbing with a scourer in a stainless steel dish in local water. Sheets were transferred to amber glass jars (3 sheets per jar), which were stored at -18 °C.

Test materials should be stored frozen (-4 °C or lower).

Treat all test materials in the same manner as your routine samples.

Code	Description
DE13-2016 exposed	Exposed sampler. Yellow label.
DE13-2016 control	Non-exposed sampler for establishing the PRC amounts prior to exposure and preparation contamination of the target compounds. White label.
DATASET 1	Dataset to be used for calculating aqueous concentrations from amounts in passive samplers

Determinands and concentration ranges

Reporting requirements for Exposed PS and Control PS are listed in Table 1.

Please note the following:

- The amounts in the sheet are representative for a passive sampler deployment at a moderately contaminated site, i.e., typically between 0.1 -10, 1-100 and 0.1-2 ng g^{-1} for PCBs, PAHs and PBDEs respectively, but you may find somewhat higher or lower amounts for individual determinands. Individual sheets should not be subsampled.
- Results should be reported for as many of these determinands as possible.
- Reporting concentrations of chrysene, benzo[b]fluoranthene, and benzo[k]fluoranthene require your special attention. To prevent interpretation errors at our side, we ask you to report exactly what compound or mixture of compounds is reported. For example, if your chromatographic system allows to separate the b, j, and k congeners of benzofluoranthene, then please report the individual compounds as well as their sums. If you measure the b and j congeners together and the k congener separately, then report the the b+j and the k congeners, as well as the b+j+k congeners.
- PRCs are to be reported as a fraction relative to the non-exposed sampler, i.e., not absolute concentrations.
- We ask you to pay special attention to the reporting of sample mass for the following reason. We had to change manufacturer of the silicone sheets, because Altecweb discontinued Altesil translucent. The best available alternative was SSP-M823, 0.25 mm thickness, manufactured by Silicone Specialty Products, obtained from www.shielding-solutions.com. This material has a somewhat higher variability in thickness compared with Altesil. We want to assess whether or not sheet thickness has to be taken into account for the analysis of reported results. To this end, we ask you to double check the accuracy of sheet mass determinations (e.g., by re-weighing the sheets one day after the first mass determination). We also ask you to report length x width of the analysed sheets.
- If you encounter difficulties with identifying the PRCs in the chemical analysis, then please contact Foppe Smedes (smedes@recetox.muni.cz) or Kees Booij (keesbooij@pasoc.eu).
- Although biphenyl-D10 is not a target PRC for this exercise, it was spiked into the samplers. The reason for this was that we had to use an existing sampler batch to keep the cost of this exercise within limits. The expected amount of biphenyl-D10 in the exposed sheets is << 1 femtogram, which is unlikely to cause any difficulties, even for participants who use biphenyl-D10 as an internal standard for the PAH analysis. High amounts of biphenyl-D10 can be present in the control sheets, but since these are not analysed for PAHs, we do not expect difficulties with the control samplers either.
- Please check that the PRCs (see table below) do not interfere with the internal standards that you use.
- Some exposed sheets show red/brown stains near the mounting holes. These are iron oxyhydroxides. This is caused by sheet retention rods not having the required corrosion resistance. Some sheets show green spots <1 mm diameter. These are of unknown origin (likely biofouling). Neither of these stains are expected to have an effect on the uptake rates or extraction efficiencies.
- 4,4'-DDE and 4,4'-DDT are added to the list of determinands.

Table 1. Reporting requirements for Exposed PS and Control PS

Determinand	Reporting unit	to be reported for Exposed PS
Organochlorines		
Sample weight	g	yes
Sample length x width	mm^2	yes
Hexachlorobutadiene	ng/ g	yes
hexachlorobenzene	ng/ g	yes
4-4'-DDE	ng/ g	yes
4,4'-DDT	ng/ g	yes
PCB 28	ng/ g	yes
PCB 52	ng/ g	yes
PCB 101	ng/ g	yes
PCB 118	ng/ g	yes
PCB 138	ng/ g	yes
PCB 153	ng/ g	yes
PCB 180	ng/ g	yes
Polyaromatic hydrocarbons		
Sample weight	g	yes
Sample length x width	mm^2	yes
acenaphthene	ng/g	yes
acenaphthylene	ng/g	yes
fluorene	ng/g	yes
phenanthrene	ng/g	yes
anthracene	ng/g	yes
fluoranthene	ng/g	yes
pyrene	ng/g	yes
benzo[a]anthracene	ng/g	yes
chrysene	ng/g	yes
chrysene + triphenylene	ng/g	yes
benzo[b]fluoranthene	ng/g	yes
benzo[k]fluoranthene	ng/g	yes
benzo[b]fluoranthene + benzo[j]fluoranthene	ng/g	yes
benzo[b]fluoranthene + benzo[k]fluoranthene	ng/g	yes
benzo[b]fluoranthene + benzo[j]fluoranthene + benzo[k]fluoranthene	ng/g	yes
benzo[a]pyrene	ng/g	yes
benzo[ghi]perylene	ng/g	yes
indeno[1,2,3-cd]pyrene	ng/g	yes
dibenzo[a,h]anthracene	ng/g	yes
Brominated diphenylethers		
Sample weight	g	yes
Sample length x width	mm^2	yes
BDE 28	ng/g	yes
BDE 47	ng/g	yes
BDE 99	ng/g	yes
BDE 100	ng/g	yes
BDE 153	ng/g	yes
BDE 154	ng/g	yes

continued....

Table 1(continued). Reporting requirements for Exposed PS and Control PS

Determinand	Reporting unit	to be reported for Exposed PS
PRCs		
Sample weight of control sheet(s)	g	yes
Sample length x width of control sheet(s)	mm^2	yes
Sample weight of exposed sheet(s)	g	yes
Sample length x width of exposed sheet(s)	mm^2	yes
PCB 1	fraction relative to non-exposed sampler	yes
PCB 2	fraction relative to non-exposed sampler	yes
PCB 3	fraction relative to non-exposed sampler	yes
PCB 10	fraction relative to non-exposed sampler	yes
PCB 14	fraction relative to non-exposed sampler	yes
PCB 21	fraction relative to non-exposed sampler	yes
PCB 50	fraction relative to non-exposed sampler	yes
PCB 55	fraction relative to non-exposed sampler	yes
PCB 78	fraction relative to non-exposed sampler	yes
PCB 104	fraction relative to non-exposed sampler	yes
PCB 145	fraction relative to non-exposed sampler	yes
PCB 204	fraction relative to non-exposed sampler	yes

Analysis

non-PRCs in **Exposed PS** and **Control PS.** Use your normal validated methods and procedures to analyse the test materials. The methods described in section 4 from Smedes and Booij (2012) can be considered but are not mandatory.

PRCs in Exposed PS and Control PS. The same methods as above can be used. Participants may not have calibration standards available for all PRCs. Retention times on a DB-5MS column are provided below (Table 2). We expect that this will allow you to identify the PRCs in your chromatograms. Let us know if you encounter difficulties with this.

Weight of the samplers. After extraction the sheets are dried and the weight of the extracted sheets are reported. Please double check the sampler mass.

Length x width of the sampler. Please report sampler length x width after the extraction. Measure length and width preferably with an accuracy of 0.5 mm.

Table 2. Retention times of PRCs and some commonly analysed PCBs on a 30 metre DB-5MS column. Temperature program: 60 °C, hold 1 min, increase at 20 °C /min to 120 °C, increase at 6 °C /min to 250 °C, increase at 17.5 °C/min to 300 °C, hold 2 min. (source: Deltares/TNO, Utrecht, The Netherlands.)

Compound		Ret. Time (min)
PCB 1	(PRC)	11.82
PCB 2	(PRC)	13.04
PCB 3	(PRC)	13.18
PCB 10	(PRC)	13.90
PCB 14	(PRC)	15.75
PCB 50	(PRC)	18.18
PCB 28		18.24
PCB 21	(PRC)	18.55
PCB 52		19.34
PCB 104	(PRC)	19.86
PCB 55	(PRC)	21.62
PCB 101		22.09
PCB 78	(PRC)	22.61
PCB 145	(PRC)	22.90
PCB 118		24.00
PCB 153		24.68
PCB 138		25.51
PCB 204	(PRC)	27.10
PCB 180		27.19

Aqueous concentrations from DATASET 1.

Calculate aqueous concentrations as follows

- Use the calculation scheme described in section 6 from Smedes and Booij (2012)
- Use the amounts listed in Table 3 below
- Adopt a sampler mass of 18.7 g, an exposure time of 63 d, and an exposure temperature of 20 °C
- Neglect the effect of ionic strength on the partition coefficients.
- Adopt the sampler-water partition coefficients for Altesil silicone listed in Table 3

Table 3. DATASET 1. Logarithms of sampler water partition coefficients ($\log K_{sw}$), molecular weight (MW), and amounts in an exposed sampler, for calculating aqueous concentrations. $\log K_{sw}$ values are from Smedes et al. (2009) unless indicated otherwise.

Determinand	**MW (g mol^{-1})**	**logK_{sw} (L kg^{-1})**	**amounts in exposed sampler (ng)**
non-PRCs			
PCB 28	257.5	5.53	204
PCB-153	360.9	6.72	76
pyrene	202.3	4.68	2010
chrysene	228.3	5.25	770
benzo[ghi]perylene	276.3	6.02	178
PRCs			
	MW (g mol^{-1})	**logK_{sw} (L kg^{-1})**	**fraction retained**
Biphenyl-D10	164.3	3.63)[1]	0.005
PCB 1	188.7	4.22)[1]	0.007
PCB 2	188.7	4.41)[1]	0.020
PCB 3	188.7	4.36)[1]	0.020
PCB 10	223.1	4.55	0.162
PCB 14	223.1	5.14	0.206
PCB 21	257.5	5.43	0.432
PCB 30	257.5	5.24	0.363
PCB 50	292.0	5.70	0.703
PCB 55	292.0	6.00	0.767
PCB 78	292.0	6.05	0.811
PCB 104	326.4	6.17	0.874
PCB 145	360.9	6.65	0.980
PCB 204	429.8	7.59	1.020

)[1] Smedes and Beeltje (2010)

Table 4. Reporting requirements for DATASET 1

Determinand	**Reporting unit**	**to be reported for DATASET 1**
PCB 28	pg/L	yes
PCB-153	pg/L	yes
pyrene	pg/L	yes
chrysene	pg/L	yes
benzo[ghi]perylene	pg/L	yes

Reporting

Report determinands in Exposed PS and DATASET 1 using the workbook "DE13-2106 data reporting". Summarise information on analytical methods using Annex 2 of this protocol.

All submitted data is strictly anonymous. Links between laboratory codes and laboratory names are only known to the QUASIMEME project office, and will not be communicated to the outside world.

References

Smedes, F., and Booij, K. 2012. Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers. ICES Techniques in Marine Environmental Sciences No. 52. 20 pp. http://www.ices.dk/sites/pub/Publication Reports/Techniques in Marine Environmental Sciences (TIMES)/times52/120621 TIMES 52 Final.pdf

Smedes, F., Geertsma, R. W., van der Zande, T., and Booij, K. 2009. Polymer - water partition coefficients of hydrophobic compounds for passive sampling: application of cosolvent models for validation. Environmental Science and Technology, 43: 7047 – 7054.

Smedes, F., and Beeltje, H., 2010. Silicone Rubber-Water Partition Coefficients for Passive Sampling. Report 1201893-000. Deltares, Utrecht.

Reporting of Results and Analytical Methods

Units

The units of measurement are given in the data submission forms. Ensure that the concentration of each determinand is reported in the units given. This may differ from your normal units for reporting; it is essential that all data reported are comparable. It is not possible for you to alter the units for reporting in the data submission forms.

The precision of the reported results should reflect the level of uncertainty of the measurement in your laboratory

Reporting Left Censored Values

If the concentration of a determinand is below the detection limit of your method we ask you to report this concentration as a "smaller than" value.

Return of Data

Report all data to QUASIMEME by using the Excel file which was sent separately to your contact person. Return the results to the QUASIMEME Project Office in Wageningen no later than 31 December 2016. Data arriving after this deadline may not be entered into the database or appear in the report.

If you have further information on additional methods used or specific ways in which we can improve the data transfer, please inform the QUASIMEME Project Office. Your co-operation is appreciated and will help the assessors in the data analysis and in providing appropriate advice in case of any analytical difficulties.

Please observe the following guidelines, to reduce the need for additional checks, replies and enquires:

Data should only be submitted to the QUASIMEME Project Office when all quality checks have been made. If data are submitted beyond the deadline, they might not be included in the report. Data submitted after the issue of the report will not be included in the report, and these data will also not be included as part of the consensus value. Any certificate prepared with data submitted late will include the statement "Data submitted after report issued". No data will be re-entered into the database after the report is issued. No data will be changed in the database UNLESS there is evidence that QUASIMEME or data transfer has caused an error. In such cases QUASIMEME will undertake a quality query to investigate the problem and inform the participant of the outcome of the Query.

The assigned values will be calculated based on the assessment of all data returned, using the Cofino model. The report for each study, including each laboratory's individual assessment and z-scores, will be distributed to participants no later than 28 February 2017. Background information on the data assessment will be provided with the reports.

Collusion and Falsification of Results

QUASIMEME accepts that most participants operate with professional integrity and that data returned as part of the LP studies are correct and are submitted without interference or collusion. However, in some circumstances, data or information may be influenced by, for example, (i) repeated analyses and submitting mean data, or (ii) collaboration with colleagues undertaking the same study.

QUASIMEME checks for evidence of collusion and confirm to all participants that such activity is contrary to professional scientific conduct and will only nullify the benefits of the LP studies to accreditation bodies and analysts alike.

QUASIMEME reserves the right to withdraw participation of any institute who, in the opinion of the Scientific Assessment Board, has submitted data following collusion or falsification. This statement is made as a formal requirement for accreditation for Laboratory Performance Studies under ISO17043.

ANNEX 1 Notification of damaged test materials.

You do not need to notify QUASIMEME if the test materials arrived in good condition

Laboratory Code : .....

Damaged container number : .....

Loss of weight container number : .....

I request a new test material for :..... Because : .....

Date : .....

Signature :.....

Name of participant :.....

Name and address of institute : .....

.....

.....

Telephone number :.....

Fax number :.....

Return this form to :

QUASIMEME Project Office
Wageningen UR
P.O. Box 8005
NL-6700 EC Wageningen
The Netherlands

Fax No : +31(0)317 486 546
E-mail : QUASIMEME@wur.nl

ANNEX 2 Method information DE-13

Copy the text below to a new document, and send this together with the data reporting file to the QUASIMEME project office. Only main method identifiers are required. For example: extraction by ASE with hexane, cleanup with florisil, analysis GC/MS/MS with CI, 25 m Carbowax column, etcetera.

QUASIMEME laboratory code: .....

Organochlorines

Extraction method
Clean-up method
Instrumental analysis, Instrument
Instrumental analysis, Column type
Instrumental analysis, Detector type

Polyaromatic hydrocarbons

Extraction method
Clean-up method
Instrumental analysis, Instrument
Instrumental analysis, Column type
Instrumental analysis, Detector type

Bromodiphenylethers

Extraction method
Clean-up method
Instrumental analysis, Instrument
Instrumental analysis, Column type
Instrumental analysis, Detector type

Aqueous concentrations from DATASET1

No step-by-step calculation is required. We may ask you for further information if necessary.

Difficulties encountered during this exercise

We value your feedback on difficulties that your encountered and suggestions for possible improvements.