Laboratory Performance Study for passive sampling of nonpolar chemicals in water

Kees Booij *,†, Foppe Smedes[‡$], Steven Crum[‖]

* corresponding author, present address

PaSOC, Greate Pierwei 25, 8821 LV Kimswerd, The Netherlands

T +31 517 234 174

E keesbooij@pasoc.eu

† NIOZ Royal Netherlands Institute for Sea Research, Texel, The Netherlands

[‡] Deltares, Utrecht, The Netherlands

[$] Masaryk University, Faculty of Science, Brno, Czech Republic

[‖] QUASIMEME, Alterra Wageningen University Research, Wageningen, The Netherlands

*Address correspondence to keesbooij@pasoc.eu

Key words: organic contaminants, passive sampler, analytical chemistry, quality assurance, interlaboratory study, proficiency testing

Running head: Laboratory performance study for silicone passive samplers

ABSTRACT

Two laboratory performance studies with 21 and 11 participants were carried out for passive sampling of nonpolar chemicals in water, using silicone samplers that were deployed for 7 and 13 weeks at 2 river sites in the Netherlands. Target analytes were polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, hexachlorobutadiene, hexachlorobenzene, and a number of performance reference compounds (PRCs). Calculation of aqueous concentrations based on prescribed input values and a prescribed uptake model was also included. Between laboratory coefficients of variation (*CV*) in the analysis of target compounds were approximately 20% at concentrations of 100 ng g^{-1} and approximately 100% at concentrations of 0.01 ng g^{-1}, which was similar to previous results for the analysis of biota samples. The analysis of PRCs yielded water sampling rates with a between laboratory *CV* of 18 to 30%. The sampling rate model showed a near perfect match with the consensus values of retained PRCs. The implications of the present study for future interlaboratory exercises are discussed.

INTRODUCTION

Despite efforts to reduce nonpolar chemicals emissions to the aquatic environment, these compounds remain a source of concern, and chemical monitoring of their concentration levels is prescribed by national and international legislation and treaties, such as the USA Clean Water Act, the European Water Framework directive, and the Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic. Concentration levels can be assessed by the collection and analysis of batch water samples, fish, shellfish, sediments, and suspended matter. Several authors have stressed the importance of passive sampling methods because of their toxicological relevance, data comparability among sampling sites, low detection limits, and lack of confounding matrix effects [1–6]. Quality control of passive sampling methods has been identified as an area where major improvements

are needed, including the analysis of certified reference materials, participation in interlaboratory comparison studies, and the use of standardized methods [1,2].

The results of 3 interlaboratory comparisons for passive sampling of nonpolar compounds revealed relatively high between-laboratory variations [1]. For example, robust coefficients of variation in reported aqueous concentrations of PAHs was 90% (22 laboratories, 5 sampler types) [7]. In a further evaluation of the NORMAN interlaboratory study on passive sampling of contaminants of emerging concern, it was concluded that the chemical analysis of the sampler, and the conversion of absorbed amounts to aqueous concentrations were the main source of between-laboratory variation (70-660%) for polybrominated diphenyl ethers (5 to 14 laboratories) and that the effect of sampler type was minor [8]. The estimation of aqueous concentrations from amounts that are accumulated in nonpolar samplers includes the measurement of retained fractions of performance reference compounds (PRCs), the selection of a sampling rate model, and the estimation of site-specific sampling rates. Each of these steps can contribute to the between-laboratory variation.

The purpose of the present study was to gain further insight in the sources of between-laboratory variation of passive sampling of nonpolar compounds. To this end, 2 development exercises were carried out as part of the proficiency testing scheme organised by QUASIMEME (www.quasimeme.org). Participants were asked to report the concentrations of nonpolar compounds and the fractions of retained PRCs in field exposed silicone passive samplers. In addition, participants were asked to calculate aqueous concentrations based on provided data for 5 target analytes and 10 PRCs, to evaluate the contribution of the calculation step in between-laboratory variation of passive sampler data.

MATERIALS AND METHODS

Sampler preparation, exposure, and data reporting

Silicone sheets (Altesil translucent, 5.5 × 9.5 cm, 3 g, 0.5 mm thickness) were pre-extracted with ethyl acetate (100 h) to remove silicone oligomers, and were spiked with PRCs, following the methods described elsewhere [9]. In year 1 (October 2014 to January 2015), biphenyl-D10 and PCB congeners 1, 2, 3, 10, 14, 21, 30, 50, 55, 78, 104, 145, 204, were used as PRCs. In year 2 (November 2015 to February 2016), biphenyl-D10 and PCB 30 were omitted, because these compounds were in use as internal standards by some of the laboratories. Sheets were distributed by 3 in a jar, which was closed with a lid lined with a stainless steel disk. Half of the samplers were set aside to serve as a control. Samplers were deployed in the Western Scheldt (91 d) for year 1, and in the River Rhine (49 d) for year 2, using open exposure cages that allowed unrestricted access of the flow [9]. After exposure the samplers were lightly overgrown with perifyton, which was removed by scrubbing with a scourer in a stainless steel dish under local water. No major differences in fouling were observed among samplers. Three randomly selected exposed sheets and 3 control sheets were sent to 24 (year 1), and 15 participants, of which 21 (year 1) and 11 (year 2) reported results. A sample homogeneity test (year 1) yielded *CV*s of approximately 16% (concentrations between 0.01 and 1 ng g^{-1}) and 6% for higher concentrations.

Participants were asked to report concentrations of PCBs (congeners 28, 52, 101, 118, 138, 153, 180), PAHs (acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene), PBDEs (congeners 28, 47, 99, 100, 153, 154), hexachlorobenzene (HCB), and hexachlorobutadiene (HCBD), as well as the fractions of retained PRCs in the exposed samplers, but were not obliged to report all of these analytes. During data reporting for year 1, several participants commented that results for benzo[*b*]fluoranthene actually referred to the sum of the *b* and *j* congeners, or to sum of the *b* + *k* congeners. The determinands for year 2 were

87 therefore amended with benzo[*j*]fluoranthene and the sum of *b*+*j*, *b*+*k*, and *b*+*j*+*k* congeners. For the
88 same reason, the sum of chrysene and triphenylene was added as a determinand, and benzo[*a*]pyrene
89 was included in year 2.

90 *Passive sampler modelling*

91 Modelling of uptake kinetics was based on methods described elsewhere [9], and briefly was as
92 follows. Sampling rates (R_s) were modelled as

93

94 $$R_s = \frac{\beta_M}{M^{0.47}} \quad (1)$$

95 where M is the molecular weight of the analyte and β_M is an exposure specific parameter that accounts
96 for the effect of flow on the uptake rate. Equation 1 is a mechanistic sampling rate model for WBL
97 controlled sampling kinetics. The factor $M^{0.47}$ accounts for the effect of molecular size on R_s, and
98 originates from the facts that R_s is proportional with the aqueous diffusion coefficient (D_w) to the power
99 2/3 [10,11], and that D_w is proportional to molecular weight to the power -0.71 [12]. The site specific
100 parameter β_M is determined from the dissipation rates of PRCs. Fractions of retained PRCs (f) are related
101 to β_M by

102 $$f = \exp\left(-\frac{R_s\ t}{m\ K_{pw}}\right) = \exp\left(-\frac{\beta_M\ t}{m\ K_{pw} M^{0.47}}\right) \quad (2)$$

103 where m is the sampler mass, t is time, and K_{pw} is the sampler-water partition coefficient. Fitting f as a
104 function of $K_{pw}M^{0.47}$ using nonlinear least squares [13] yields a best estimate of β_M, which in turn is used
105 to calculate aqueous concentrations (C_w) from the accumulated amounts (N) using

106 $$C_w = \frac{N}{m\ K_{pw}\left[1 - \exp\left(-\frac{\beta_M\ t}{m\ K_{pw} M^{0.47}}\right)\right]} \quad (3)$$

107

Data Assessment

Concentration data were reported by 21 participants in year 1, and by 11 participants in year 2. Two laboratories in year 2 received an additional set of samples, because of delayed customs clearance of the first shipment. These participants reported results for both sample shipments.

All data were analysed by QUASIMEME based on ISO 13528 [14], the Advanced Draft of the IUPAC International Harmonised Protocol for Proficiency Testing [15], with the amendment that Cofino statistics was used to obtain robust means (consensus values) and between-laboratory coefficients of variation [16–18]. Cofino statistics is routinely used by QUASIMEME because it is better capable of dealing with extreme values and with cases where there is an effect of methodology on the measurement, e.g., in the case of digestion of sediments for trace metal analysis.

Model means, between-laboratory coefficients of variation (*CV*s), and number of reported results are listed in the supplemental data (S1). Reporting units for non-PRCs were ng per sampler for year 1. Following suggestions from the participants, it was decided to change the reporting units of these analytes to ng g^{-1} for year 2. For the purpose of the discussion, the results for year 1 were converted to ng g^{-1} units, adopting an average sampler mass of 9.3 g.

Calculation exercise

The purpose of the calculation exercise was to address the effect of data processing on between-laboratory variability of passive sampler based aqueous concentrations. To this end, historical data of silicone passive sampler exposures by the Dutch Ministry of Infrastructure and the Environment were provided to the participants (amounts of target analytes and PRCs in an exposed and control sampler, sampler mass, exposure time, and sampler-water partition coefficients), i.e., all participants were provided with exactly the same input data. Participants were asked to calculate aqueous concentrations

based on Equation 3 (hexachlorobenzene, PCB 28, PCB 153, phenanthrene, pyrene, benzo[*ghi*]perylene for year 1, and hexachlorobutadiene, PCB-101, PCB-180, anthracene, and benzo[*a*]pyrene for year 2).

RESULTS AND DISCUSSION

Target analytes

Between-laboratory *CV*s for PCBs, PAHs and PBDEs in the samplers were in the range 3 to 97%, and were inversely related to the concentration level (Figure 1). *CV*s were similar to the values of 13-182% obtained for the 2014 QUASIMEME exercises BT2, BT4, BT9 for organochlorine compounds and PBDEs in fish, and PAHs in shellfish (Supplemental data, S2) . This result suggests that laboratories do not experience more difficulties with the analysis of passive samplers than with the analysis of biota, but more definite conclusions can of course only be drawn when results over multiple years become available in the future. Some rather high *CV*s were found in year 2 for PCB28 (80%) and in year 1 for HCBD (89%), acenaphthylene (86%), anthracene (97%) and chrysene (73%). However, also in the biota studies mentioned at the beginning of this sub section, some high *CV*s were observed for a number of compounds: acenaphthene (123%), acenaphthylene (154%), benzo[*ghi*]perylene (152%), indeno[1,2,3-*cd*]pyrene (141%), BDE153 (182%) (Figure 1 and Supplemental data, S2). In addition, some rather low *CV*s were also found in year 2 for phenanthrene (3%), BDE 47 (8%) and BDE 154 (11%). When viewed on a log scale, none of the high or low *CV*s stand out as exceptional (Supplemental data, S2), suggesting that log transformation of concentration data may provide a better basis for the data analysis of interlaboratory studies [8]. Observed *CV*s are similar to the values that are expected based on the Horwitz equation [19,20]

$$CV = 2C^{-0.5\log 2} \quad (4)$$

where *C* is the compound's mass fraction (g g^{-1}) in the analysed matrix, and the *CV* is given as a percentage. The *CV*s for year 2 were somewhat smaller than for year 1 (root mean squared values 33% versus 44% in year 1), with less extreme values and a weaker concentration dependence (Figure 1).

The analytical methods used by the laboratories were rather diverse. Polar, nonpolar, and mixed extraction solvents were used for the extraction (e.g., cyclohexane, hexane/acetone, methanol). Some laboratories used no clean-up method at all; others applied extensive clean-up methods: silica, alumina, gel permeation chromatography, and sulfuric acid (the latter in the case of PCB and PBDE analysis only). A wide variety of analytical columns was used in gas chromatographic analysis. No relationship could be found between analytical methods used and the percentage of Z-scores between -2 and 2.

PRCs and sampling rates

The *CV* of retained PRC fractions for year 1 remained relatively constant at a level of approximately 20% down to $f \approx 0.10$, and steeply increased to values between 46 and 103% at $f < 0.10$ (Figure 2). The *CV*s of retained PRC fractions for year 2 were generally lower than for year 1, which may be the result of the greater experience of the participating laboratories with the analysis of the PRCs. The *CV*s for PCB21 were relatively high considering the retained fractions of 0.19 (year 1) and 0.56 (year 2). This may be an indication of interfering compounds on the analytical columns used by some participants.

Consensus values of the retained PRCs fractions are well described by the model (Equation 2), with a residual error of 0.03 (year 1) to 0.04 (year 2) (Figure 3). This suggests that the consensus values are close to the true values, and that Equation 2 and the adopted partition coefficients are adequate. The resulting R_s for pyrene (M=202) was 61.1 L d^{-1} with a standard error of 2.7 L d^{-1} (~ 4 %) for year 1, and 42.4 ± 3.0 L d^{-1} (~7%) for year 2. Sampling rates based on the PRC retention data reported by the individual laboratories in year 1 (Supplemental data, S3) included several extreme values that were up to 3 times higher or 14 times lower than the consensus value (Figure 4, left panel). In year 2 one extreme value was observed. Large uncertainty estimates are associated with deviating R_s estimates (Figure 4),

suggesting that the standard error of an individual R_s estimate gives a good indication of its possible deviation from the consensus R_s value. The scatter of retained PRC fractions around the model fit is also indicative of the quality of individual R_s estimates (Figure 5). Sampling rates based on PRC retention data that showed no visual sign of insufficient quality (filled symbols in Figure 4) had a *CV* of 30% (year 1) and 18% (year 2).

Calculation exercise

The results of the calculation exercise in year 1 (n = 18) were promising. Ten participants strictly followed the protocol. One participant followed the protocol but omitted the data for PCB2 and PCB3, and normalised PRC retention data on the retained fraction of PCB204. Three participants used K_{pw} data that differed slightly from the values suggested in the protocol. Taking these differences into account, 14 participants (78%) calculated aqueous concentrations that were correct within 2.5%. Four participants submitted results that deviated up to a factor of 750 from the target values. In year 2, acceptable calculations were submitted by 6 out of 10 laboratories. Results for the other 4 laboratories deviated up to a factor of 2 from the target values. These results show that the assessment of calculation methods needs to be included in this type of studies.

OUTLOOK

Results of the present study suggest that the chemical analysis of target analytes in silicone passive samplers matrix yields between-laboratory *CV*s that are similar to those observed for the analysis of biota samples. A more in-depth evaluation that covers multiple studies in which the same laboratories participate would be needed to further address this suggestion.

The between-laboratory *CV*s show a profound increase with decreasing concentration level. This implies that standards of achievable accuracy should take this concentration dependency into account. Although this phenomenon is well documented for interlaboratory studies, its consequences are not

always appreciated. For example, the EU QA/QC directive postulates that an accuracy of 50% (2 times the *CV*) at the level of the environmental quality standards (EQSs) would be achievable, irrespective of the actual value of the EQS [21]. The concentration dependency of the *CV*s also suggests that the accuracy of sampling rate estimations can be increased by the use of higher PRC concentrations.

Participation in interlaboratory studies is a valuable action for laboratories to compare their passive sampling results with those of others, particularly because certified reference materials for passive samplers are not (yet) available. Six out of 8 laboratories that participated in both years had a higher percentage of acceptable *Z*-scores in year 2, suggesting that continued participation in such studies results in improvement of data quality. It is therefore regrettable that some laboratories with a lower percentage of acceptable *Z*-scores in year 1 did not participate in year 2.

It is reassuring that the consensus values of PRC retention data were well described by the sampler-water exchange model, and that the nonlinear least squares procedure for estimating sampling rates for the individual laboratories yielded 95% confidence intervals that fully or nearly embraced the consensus value. Considering the fact that several laboratories had little previous experience with the analysis of PRCs, it can be expected that appreciable improvement of data quality can be achieved.

The occurrence of errors in the modelling and calculation of aqueous concentrations by some laboratories stresses the importance of including this step in future exercises. This also shows that the calculation of aqueous concentrations is not a trivial issue, and that training of passive sampling practioners in the application of calculation methods may be appropriate.

ACKNOWLEDGMENTS

We thank the laboratories that participated in this exercise for submitting their data, for their feedback on the design of the laboratory performance study, and for their responses to queries.

225 *Supplemental data* - Summary data for year 1 and year 2 (consensus values, *CV*s, and number of
226 observations (S1), Coefficients of variation (*CV*) for the analysis of passive samplers and biota (S2),
227 Fractions of retained PRCs as reported by the individual participants (S3).
228 *Data availability* - The raw data are provided in the Supplemental Data.

REFERENCES

1. Booij K, Robinson CD, Burgess RM, Mayer P, Roberts CA, Ahrens L, Allan IJ, Brant J, Jones L, Kraus UR, Larsen MM, Lepom P, Petersen J, Pröfrock D, Roose P, Schäfer S, Smedes F, Tixier C, Vorkamp K, Whitehouse P. 2016. Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. *Environ. Sci. Technol.* 50:3–17.
2. ICES. 2013. *Report of the Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD).* ICES, Copenhagen:1–54. Available from http://www.ices.dk/sites/pub/Publication%20Reports/Expert%20Group%20Report/SSGHIE/2013/WKPSPD13.pdf.
3. Lohmann R, Booij K, Smedes F, Vrana B. 2012. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ. Sci. Pollut. Res.* 19:1885–1895.
4. Lydy MJ, Landrum PF, Oen AMP, Allinson M, Smedes F, Harwood AD, Li H., Maruya KA, Liu JF. 2014. Passive sampling methods for contaminated sediments: state of the science for organic contaminants. *Integr. Environ. Assess. Manag.* 10:167–178.
5. Mayer P, Parkerton TF, Adams RG, Cargill JG, Gan J, Gouin T, Gschwend PM, Hawthorne SB, Helm P, Witt G, You J, Escher BI. 2014. Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* 10:197–209.
6. Reichenberg F, Mayer P. 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environ. Toxicol. Chem.* 25:1239–1245.
7. Miege C, Mazzella N, Schiavone S, Dabrin A, Berho C, Ghestem JP, Gonzalez C, Gonzalez JL, Lalere B, Lardy-Fontan S, Lepot B, Munaron D, Tixier C, Togola A, Coquery M. 2012. An in situ intercomparison

exercise on passive samplers for monitoring metals, polycyclic aromatic hydrocarbons and pesticides in surface waters. *TRAC-Trends Anal. Chem.* 36:128–143.

8. Vrana B, Smedes F, Prokeš R, Loos R, Mazzella N, Miege C, Budzinski H, Vermeirssen E, Ocelka T, Gravell A, Kaserzon S. 2016. An interlaboratory study on passive sampling of emerging water pollutants. *TrAC Trends Anal. Chem.* 76:153–165.
9. Smedes F, Booij K. 2012. *Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers.* International Council for the Exploration of the Sea, Copenhagen:1–20. Available from http://www.ices.dk/sites/pub/Publication%20Reports/Techniques%20in%20Marine%20Environmental%20Sciences%20(TIMES)/times52/120621%20TIMES%2052%20Final.pdf.
10. Booij K, Hofmans HE, Fischer CV, van Weerlee EM. 2003. Temperature-dependent uptake rates of non-polar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environ. Sci. Technol.* 37:361–366.
11. Rusina TP, Smedes F, Koblizkova M, Klanova J. 2010. Calibration of silicone rubber passive samplers: experimental and modeled relations between sampling rate and compound properties. *Environ. Sci. Technol.* 44:362–367.
12. Schwarzenbach RP, Gschwend PM, Imboden DM. 2003. *Environmental organic chemistry.* 2nd Edition, John Wiley & Sons, Inc., Hoboken, New Jersey.
13. Booij K, Smedes F. 2010. An improved method for estimating in situ sampling rates of nonpolar passive samplers. *Environ. Sci. Technol.* 44:6789–6794.
14. International Organization for Standardization. 2015. *Statistical methods for use in proficiency testing by interlaboratory comparison*. ISO 13528:2015. International Organization for Standardization, Geneva. [cited 8 June 2016]. Available from http://www.iso.org/iso/catalogue_detail.htm?csnumber=56125.

15. Thompson M, Ellison SLR, Wood R. 2006. The International Harmonized Protocol for the proficiency testing of analytical chemistry laboratories (IUPAC Technical Report). *Pure Appl. Chem.* 78.
16. Cofino WP, van Stokkum IHM, van Steenwijk J, Wells DE. 2005. A new model for the inference of population characteristics from experimental data using uncertainties: Part II. Application to censored datasets. *Anal. Chim. Acta*. 533:31–39.
17. Cofino WP, van Stokkum IHM, Wells DE, Ariese F, Wegener JWM, Peerboom RAL. 2000. A new model for the inference of population characteristics from experimental data using uncertainties. Application to interlaboratory studies. *Chemom. Intell. Lab. Syst.* 53:37–55.
18. Wells DE, Cofino WP, Scurfield JA. 2004. *The application of the Cofino model to evaluate laboratory performance study data using the bandwidth estimator*. Fisheries Research Services, Marine Laboratory, Aberdeen, UK:p71. [cited 8 June 2016]. Available from http://www.gov.scot/uploads/documents/0404.pdf.
19. Horwitz W. 1982. Evaluation of analytical methods used for regulation of foods and drugs. *Anal. Chem.* 54:67A–76A.
20. Horwitz W, Kamps LR, Boyer KW. 1980. Quality assurance in the analysis of foods and trace constituents. 63:1344–1354.
21. European Union. 2009. Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. *Off. J. Eur. Union*. L210:36–38.

Figures

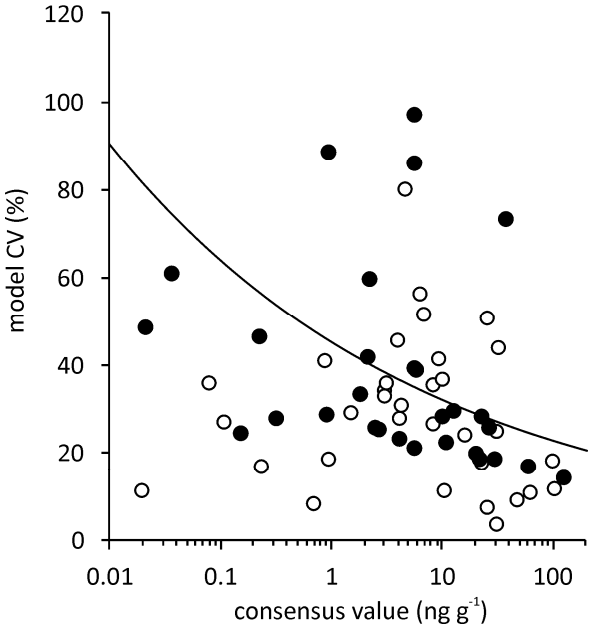

Figure 1. Between-laboratory coefficients of variation (*CV*s) as a function of analyte concentration in silicone passive samplers in year 1 (filled circles) and year 2 (open circles). The Horwitz equation is shown as a drawn line for reference.

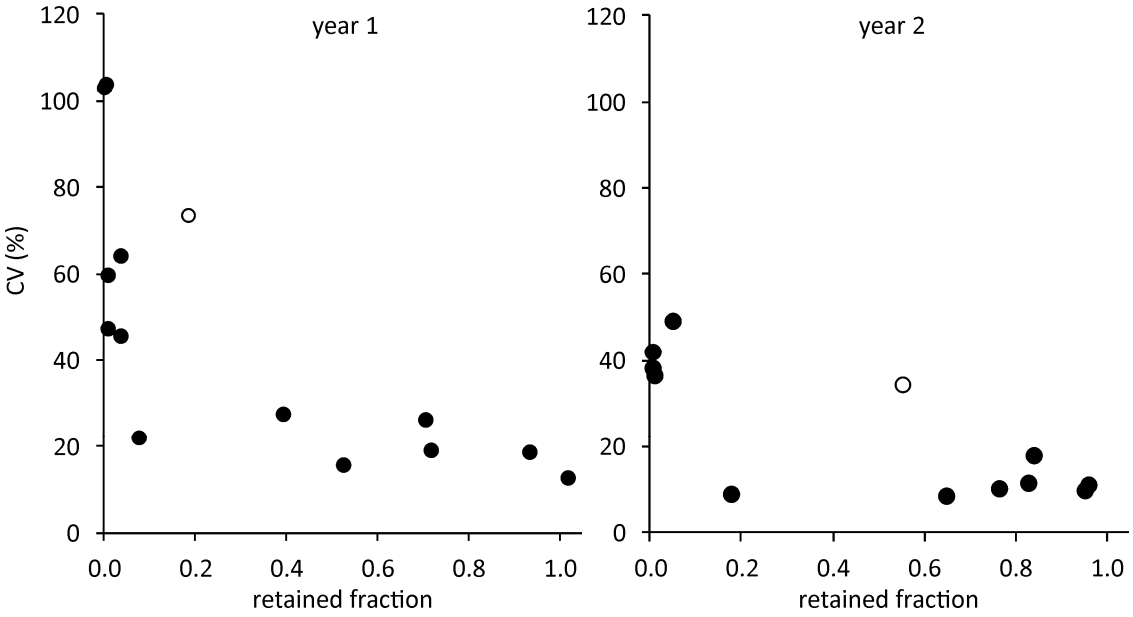

Figure 2. Between-laboratory coefficients of variation (*CV*s) of the fractions of retained performance reference compounds in silicone passive samplers for year 1 (left) and year 2 (right). The relatively high *CV*s for PCB21 are shown as open symbols.

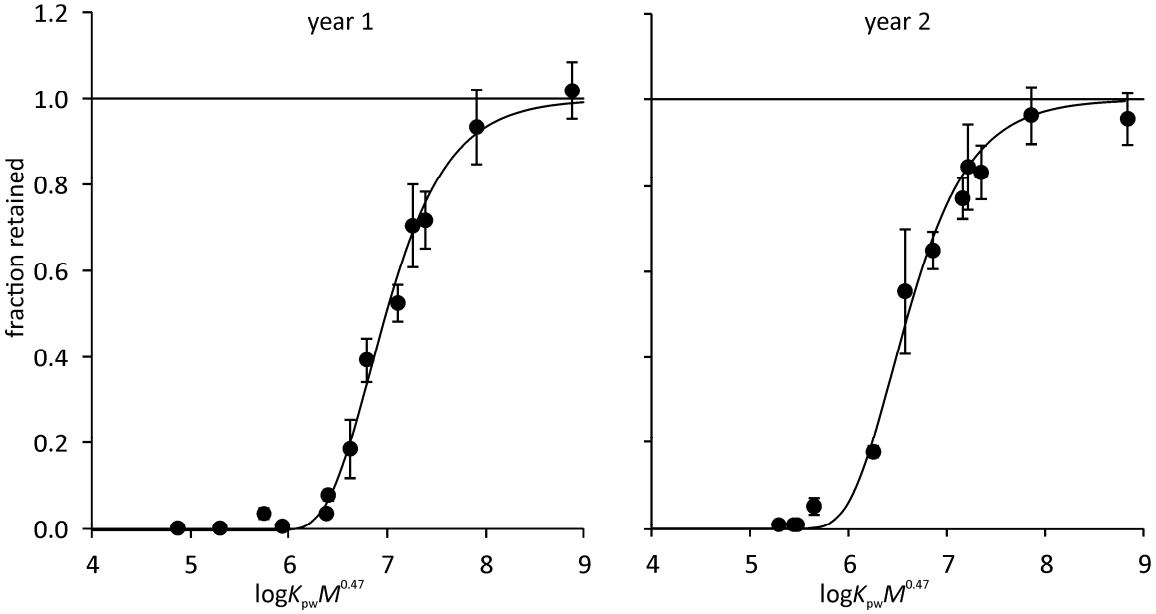

Figure 3. Model fit of consensus values of retained fractions of performance reference compounds for year 1 (left) and year 2(right). Error bars span the 95% confidence range of the mean.

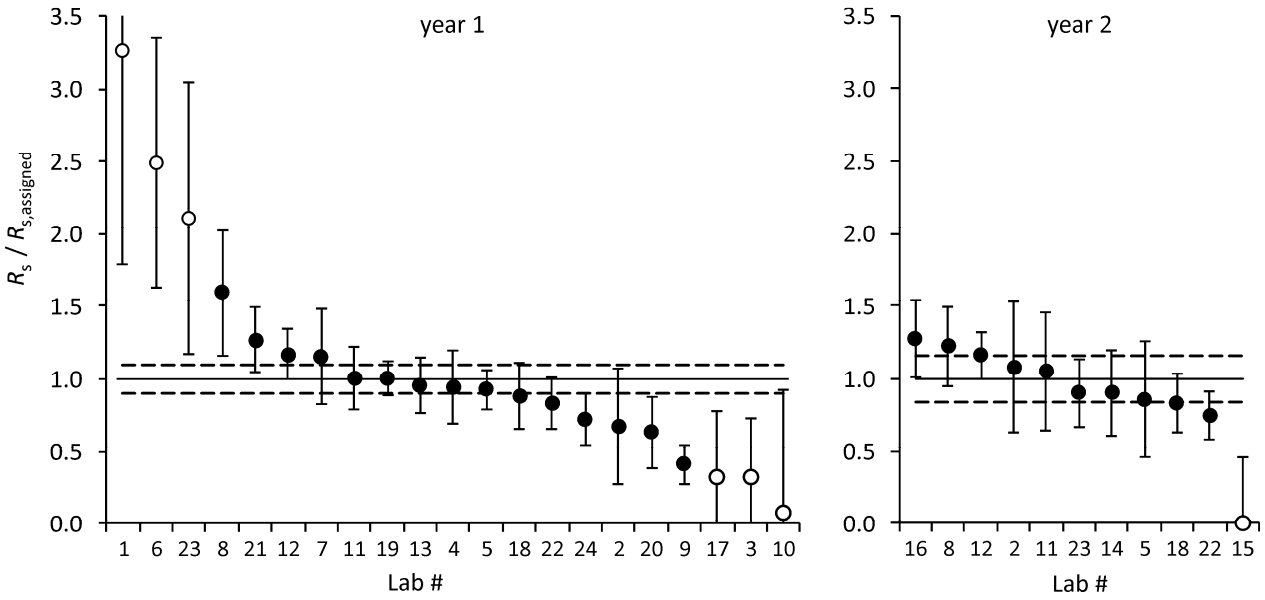

Figure 4. Sampling rates (R_s), based on performance reference compound retention data of individual laboratories for year 1 (left) and year 2 (right). Data for both years was normalised on consensus values of R_s to allow easy comparison between years. Error bars span the 95% confidence ranges. Open symbols represent extreme values (based on visual inspection of the model fits, Figure 5). Dashed lines span the 95% confidence range of the consensus value of R_s .

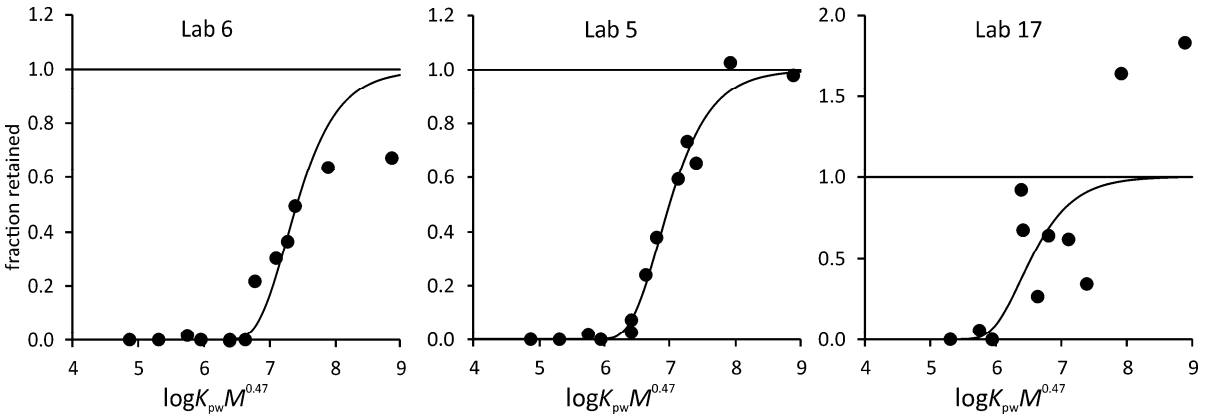

Figure 5. Model fits of performance reference compound retention data from year 1 that yielded R_s estimates that were very high (left), very low (right), or close to the consensus value (middle).

Laboratory Performance Study for passive sampling of nonpolar chemicals in water
Supplemental data

Kees Booij, NIOZ Royal Netherlands Institute for Sea Research
Foppe Smedes, Deltares and Masaryk University, Faculty of Science
Steven Crum, QUASIMEME, Alterra Wageningen University Research

S1. Summary data for year 1 and year 2

		year1			year 2		
Determinand	Units	Mean	*CV* (%)	*n*	Mean	*CV* (%)	*n*
non-PRCs							
hexachlorobutadiene	ng/g	0.95	88.7	11	25.8	7.0	6
hexachlorobenzene	ng/g	1.86	33.3	17	7.09	51.5	11
PCB 28	ng/g	5.58	39.1	20	4.81	79.9	13
PCB 52	ng/g	21.85	18.6	21	9.44	41.3	13
PCB 101	ng/g	22.55	28.1	21	8.57	26.2	13
PCB 118	ng/g	5.77	39.0	19	3.06	33.8	12
PCB 138	ng/g	12.74	29.3	21	4.47	30.5	13
PCB 153	ng/g	20.30	19.6	20	4.08	45.3	12
PCB 180	ng/g	4.11	23.2	21	0.91	40.8	12
Acenaphthene	ng/g	2.15	41.9	17	16.3	23.8	13
Acenaphthylene	ng/g	5.53	85.9	18	3.16	35.6	12
Fluorene	ng/g	2.21	59.6	18	8.41	35.2	13
Phenanthrene	ng/g	5.52	20.9	17	23.3	17.2	13
Anthracene	ng/g	5.73	97.0	19	6.45	56.2	13
Fluoranthene	ng/g	58.96	16.8	20	101	18.0	13
Pyrene	ng/g	124.09	14.0	20	107	11.3	13
Benzo[a]anthracene	ng/g	26.63	25.7	20	48.7	8.8	12
Chrysene	ng/g	37.01	73.1	19	31.9	3.2	7
Chrysene + triphenylene	ng/g				64.2	10.5	6
Benzo[b]fluoranthene	ng/g	29.71	18.5	16	25.7	50.5	7
Benzo[k]fluoranthene	ng/g	10.84	22.3	15	10.5	36.6	7
Benzo[b]+[j]fluoranthene	ng/g				31.8	24.5	4
Benzo[b]+[j]+[k]fluoranthene	ng/g				32.6	43.9	8
Benzo[a]pyrene	ng/g				10.6	10.9	12
Benzo[ghi]perylene	ng/g	9.88	28.2	19	4.27	27.5	13
Indeno[1,2,3-cd]pyrene	ng/g	2.71	25.3	19	3.06	32.6	13
Dibenzo[a,h]anthracene	ng/g	2.52	25.6	17	1.52	29.0	13
BDE 28	ng/g	0.22	46.5	14	0.082	35.6	10
BDE 47	ng/g	0.91	28.5	16	0.699	8.0	11
BDE 99	ng/g	0.31	27.8	15	0.236	16.4	11
BDE 100	ng/g	0.15	24.4	15	0.107	26.6	11
BDE 153	ng/g	0.02	48.7	14	0.953	18.4	11
BDE 154	ng/g	0.04	61.1	12	0.017	11.0	8
PRCs							
Biphenyl-D10	fraction	0.003	103	4			
PCB 1	fraction	0.005	104	10	0.011	36.1	10
PCB 2	fraction	0.008	59.7	10	0.010	38.1	10
PCB 3	fraction	0.008	47.3	10	0.010	41.7	11
PCB 10	fraction	0.036	64.1	15	0.052	49.0	11
PCB 14	fraction	0.036	45.8	18	0.179	8.8	12
PCB 21	fraction	0.188	73.4	19	0.556	33.9	11
PCB 30	fraction	0.079	21.9	16			
PCB 50	fraction	0.393	27.5	21	0.651	8.4	11
PCB 55	fraction	0.525	15.7	18	0.768	10.1	13
PCB 78	fraction	0.706	26.3	18	0.845	17.5	13
PCB 104	fraction	0.719	19.1	21	0.832	11.3	12
PCB 145	fraction	0.935	18.5	19	0.965	10.8	12
PCB 204	fraction	1.021	12.6	19	0.957	9.4	12

S2. Coefficients of variation (*CV*) for the analysis of passive samplers (present study) and biota.

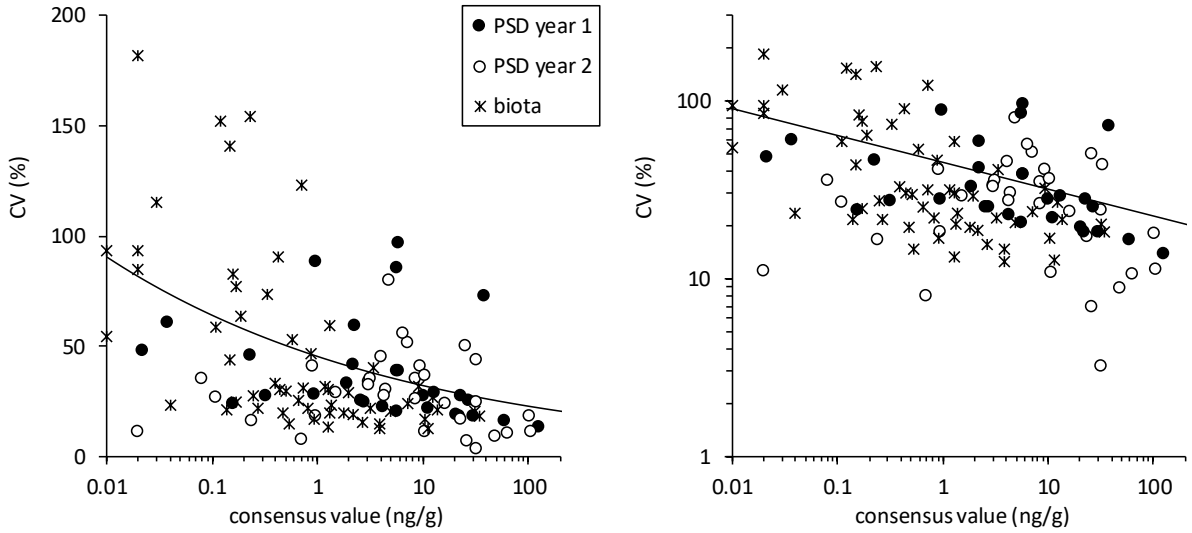

Figure S2-1. Between-laboratory coefficients of variation (*CV*s) as a function of concentration for the analysis of silicone passive samplers (closed circles: year 1, open circles: year 2) and biota (asterisks: 2014 QUASIMEME laboratory performance study for chlorinated organics in fish, polycyclic aromatic hydrocarbons in mussels, and polybrominated diphenyl ethers in fish). The Horwitz equation is shown as a drawn line for reference. Left panel: linear y-axis, right panel: logarithmic y-axis.

S3. Fractions of retained PRCs

Year 1

Lab #	1	2	3	4	5	6	7	8	9	10	11	17	18	19	20	21	22	23	24	12	13
Biphenyl-D10	0.006				0.001	0.000	0.000		0.034					0.003		0.000	0.000	0.000	0.000	0.000	0.000
PCB 1	0.023				0.002	0.000	0.000	0.037	0.017		0.007	0.000	0.009	0.003	0.000	0.004	0.000	0.000	0.000	0.003	0.002
PCB 2	0.033				0.006	0.000	0.000	0.028	0.171		0.014	0.000		0.008		0.006	0.010	0.000	0.000	0.007	0.005
PCB 3	0.019				0.006	0.000	0.000	0.025	0.109		0.009	0.000	0.014	0.009		0.007	0.000	0.000	0.000	0.007	0.006
PCB 10	0.019	0.025	0.720		0.025	0.025	0.000	0.071	0.058	0.207	0.055	0.066		0.040	0.000	0.025	0.000	0.032	0.000	0.005	0.039
PCB 14	0.044	0.367	0.390	0.020	0.034	0.000	0.000	0.066	0.291	0.367	0.034	0.932	0.052	0.040		0.030	0.030	0.027	0.045	0.031	0.029
PCB 21	0.094	0.154	0.610	0.150	0.246	0.000	0.000	0.075	0.564	0.645	0.240	0.276	0.098	0.250	0.490	0.164	0.150	0.059	0.332	0.101	0.236
PCB 30	0.046	0.394	0.080		0.077	0.000	0.000		0.444	0.367	0.074	0.688	0.101	0.080		0.074	0.080	0.330	0.173	0.081	0.084
PCB 50	0.200	0.567	0.530	0.470	0.382	0.224	0.390	0.295	0.380	1.740	0.380	0.648	0.452	0.370	0.400	0.287	0.490	0.180	0.410	0.399	0.397
PCB 55		0.479	1.680	0.540	0.595	0.309	0.498	0.432		4.140	0.520	0.634	0.569	0.510		0.442	0.600	0.540	0.658	0.487	0.492
PCB 78		0.814	0.940	0.650	0.740	0.371	0.832	0.560	0.905	2.327	0.660		0.805	0.640		0.505	0.870	0.350	0.819	0.602	0.605
PCB 104	0.430	0.521	0.760	0.850	0.656	0.501	0.599	0.551	0.771	2.796	0.740	0.352	0.827	0.740	0.730	0.823	0.770	0.420	0.802	0.705	0.863
PCB 145	0.600	0.832	1.080		1.032	0.645	0.949	0.691	1.063		0.890	1.652	1.046	0.970	0.910	0.843	1.080	0.680	1.133	0.836	1.061
PCB 204	1.100		1.100	0.980	0.980	0.679	1.113		1.104	6.276	0.780	1.840	1.136	1.010	1.030	0.994	0.960	0.810	1.200	0.983	0.955

Year 2

Lab #	2	5	8	11	18	22	23	12	14	15	16
PCB1		0.011	0.018	0.009	0.034	0.019	0.008	0.012	0.012		0.010
PCB2		0.015	0.025	0.013	0.041	0.005	0.008	0.011	0.011		0.010
PCB3		0.012	0.023	0.008	0.039	0.012	0.007	0.013	0.012	1.458	0.010
PCB10	0.195	0.063	0.077	0.056	0.058	0.041	0.069	0.019	0.019		0.010
PCB14	0.104	0.183	0.195	0.167	0.270	0.280	0.175	0.186	0.176	1.505	0.180
PCB21	0.409	0.684		0.634	0.443	0.538	0.665	0.404	0.588	2.234	
PCB50	0.793	0.638	0.666	0.599	0.707	0.701	0.630	0.627	0.872	4.859	
PCB55	0.852	0.735	0.720	0.718	0.908	0.933	0.810	0.770	0.707	1.004	0.770
PCB78	0.875	0.914	0.777	0.810	1.004	0.986	0.840	0.828	0.713	2.087	0.740
PCB104	0.761	0.774	0.825	0.764	0.946	1.019	0.820	0.892	0.833	4.772	0.840
PCB145		1.265	0.904	0.793	1.033	0.986	0.925	0.997	0.910	0.855	1.020
PCB204	0.967	1.063		0.826	0.976	1.056	0.935	0.892	0.964	0.763	1.020