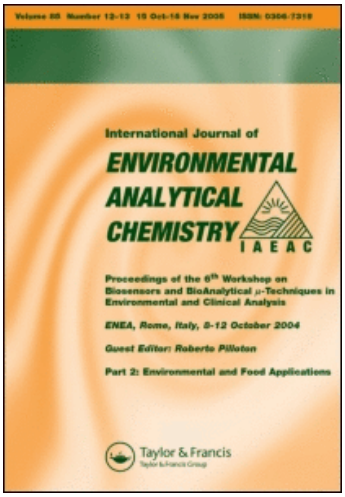

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An Evaluation of the Importance of the sampling Step to the Total Analytical Variance - a Four-System Field based sampling Intercomparison study for hydrophobic organic contaminats in the surface waters of the open Baltic Sea

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AN EVALUATION OF THE IMPORTANCE OF THE SAMPLING STEP TO THE TOTAL ANALYTICAL VARIANCE – A FOUR-SYSTEM FIELD-BASED SAMPLING INTERCOMPARISON STUDY FOR HYDROPHOBIC ORGANIC CONTAMINANTS IN THE SURFACE WATERS OF THE OPEN BALTIC SEA

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Correctly assessing the concentrations of hydrophobic organic contaminants in aquatic samples is faced with significant analytical challenges in terms of contamination, fractionation and sorptive losses to the sampling system. While little studied from an analytical perspective, the sampling step is likely to be the largest source of uncertainty in the total analytical chain. In this article, four different water-sampling systems for collection of particle-bound and dissolved polychlorinated biphenyls (PCBs) were evaluated in the surface water of the Baltic Sea. Individual concentrations of sixteen PCB congeners sampled with stainless steel tubing (system A) spanned between 0.04 and 3 fM (0.02 and 1 pg/L) in the particulate fraction and between 0.04 and 8 fM (0.01 and 2 pg/L) in the dissolved fraction. The sampling variance introduced to the data, expressed as relative standard deviation (RSD %) for single PCB congeners in system A varied between 14 and 77% (average 35%) in the dissolved fraction and between 8 and 20% (average 13%) in the particulate fraction. The implication of the constrained sampling and total variances is that variations in environmental data that are larger than about 50% RSD may be interpreted as reflecting natural processes as opposed to merely methodological variance.

Keywords: Polychlorinated biphenyls; Sampling techniques; Seawater; Analytical variance

INTRODUCTION

Hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) are persistent, subjected to long-range transport, bioaccumulating and cause toxic effects in various marine organisms, e.g. [1–5]. Hence, a large need exists to study the fate and transport processes and to monitor the level of these compounds in the aquatic environment. Correctly assessing the concentrations of HOCs in aquatic samples is however aggravated by their low abundance. Individual PCB congeners in seawater

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are usually present on a level of aM-fM [6–9]. Hence, due to the analytical challenges posed by the sampling step in terms of contamination fractionation and sorptive losses to the sampling system, this, the first step in the total analytical chain, is likely to be the largest source of uncertainty. Nevertheless, the sampling step is likely to be the least studied step of the total analytical chain.

Physico-chemical properties of a compound such as the octanol–water partition coefficient (K_{OW}) and the vapour pressure determine the fate of organic contaminants in the environment and their potential to interact with the sampling system material. Since the many PCB congeners span over a wide range of physico-chemical properties, the PCBs are very suitable as model substances for HOCs. Laboratory studies of seawater sampling are complicated by the large volumes (hundreds of litres) that need to be processed in order to realistically mimic a field situation. A few experiments have been performed in which large volume tanks have been used for parallel sampling using different *in situ* extraction methods (liquid–liquid (LLE), polyurethane foam (PUF), XAD-2, chromosorb-T) [10,11]. Both these studies indicated that the concentration data produced might depend on the choice of extraction method. Furthermore, it was shown that the sampled volume might have a major impact on the results [10]. However, the effects were large only for less hydrophobic compounds and for volumes above 400 L; little effect was seen for hydrophobic contaminants such as PCBs. Due to varying qualitative results, the authors suggested the use of LLE to reach 'best' results. Stemming from the large solvent volumes required in such methods, we suggest that LLE would likely cause a prohibitively large contamination if applied to HOC samples from unspiked natural seawaters (100s of litres). The PUF adsorption technique was clearly the method giving qualitative results closest to those of LLE [10]. The PUF adsorbent method is widely used to collect the 'free' HOC phase in air and water [2,6,12,13]. The traditional sampling equipment for HOC retrieval from seawater generally involves long plastic tubing with large surface areas onto which HOCs may potentially sorb. A recent study has shown the importance of sorption of PCB congeners in water solution even to glassware used in sampling [14]. Strategies to circumvent or minimise sorptive losses to tubing material include *in situ* pumps with *in situ* filtration [15] and the use of stainless steel tubing [7]. However, *in situ* pump systems are often prohibitively expensive and working with long stainless steel tubing on a ship is awkward.

We need to elucidate what variations in obtained seawater concentration data that may be interpreted as variations due to processes in the environment, as opposed to variability originating simply from the sampling and analytical handling. The urgent aims of this study were to test several common sampling configurations in order to (a) constrain the overall analytical variance of HOC concentration determinations in surface seawater, including the sampling step, (b) determine the contribution of the sampling variance to the overall analytical variance, and (c) investigate any possible fractionation of PCB congener patterns originating from the sampling step.

EXPERIMENTAL

Sampling Procedure

Sampling was performed June 15–16, 1999, at a frequently visited ocean time-series station in the open Baltic Proper (BY-31; Landsort Deep, 40 km offshore, 440 m depth). Four different sampling systems were used with varying configuration of

TABLE I Description of the intercompared sampling systems (HDPE: High Density Poly Ethylene; EPDM: Poly (Ethylene-co-Propylene); PVC: Poly Vinyl Chloride)

System	*Pump type*	*Pump head material*	*Tubing material*	*Volume in replicates* (L)
A	Deckboard, impeller	Stainless steel, neoprene	Stainless steel	500, 562, 635
B	*In situ*, serial centrifugal	HDPE	HDPE	190, 405, 435
C	*In situ*, serial centrifugal	HDPE	Silicone	374, 433
D	Deckboard, diaphragm	EPDM, santoprene	PVC	113, 126, 240

tubing and pumps prior to the sample extraction step (Table I). The intercompared configurations represented design and experience from previous sampling campaigns [6,7,13,16]. The *in situ* pump and/or the intake tubing were lowered in the water to a depth of 8 m for each system.

Types and dimensions of filters and adsorbents were unaltered between repetitions and sampling systems. It was attempted to keep flow rates and sampling volumes constant. The pumped water was split on deck into waste and a flow of approximately 2 L/min, which was pumped through a GF/F filter held in a 293 mm stainless steel filter holder, followed by a PUF adsorbent held in a cylindrical stainless steel holder. Several hundred litres of surface water were pumped for each sample and triplicates were taken for all samples. Filters and PUFs were changed in a laminar-flow clean bench in a laboratory on the ship. The filters (GF/F 293 mm, pore size 0.7 μm; Whatman International Ltd, Maidstone, England) were combusted (450°C, 4 h) prior to sampling and stored in aluminum pockets in plastic bags. The adsorbent holder contained two PUFs in series (diameter 37 mm, length 50 mm for each PUF), which were pre-cleaned (Soxhlet extracted 48 h toluene, 48 h acetone), dried under vacuum and stored in aluminum envelopes in plastic bags. The collected filter and adsorbent samples were placed in aluminum envelopes and were stored in double-sealed plastic bags in a freezer (−18°C) until further analysis.

Extraction and Quantification Steps

All glassware was combusted (450°C, 4 h), carefully cleaned and solvent rinsed prior to usage. The concentrations of 16 PCB congeners were determined in filters and adsorbents (PCB# 18, 28, 52, 70, 101, 110, 118, 105, 149, 153, 132, 138, 158, 180, 199, 194). Prior to extraction, seven ^{13}C-labelled PCB congeners (PCB# 28, 52, 101, 118, 105, 138 and 180) were added to each sample at levels of approximately 100 pg of each congener. The amount of standard added was adjusted to correspond to the levels of PCB expected to be present in the samples. Adsorbents and filters were Soxhlet extracted for 24 h with toluene as a solvent. All solvents were of glass-distilled quality (Burdick & Jackson, Fluka Chemie AG, Buchs, Switzerland). A Dean-Stark trap was attached to the Soxhlet extractor to remove water from the samples. The extracts were reduced in volume to approximately 1 mL using a rotary evaporator. Extracts from absorbent samples were eluted on an open silica gel column (deactivated with 10% water w/w) with toluene as mobile phase to remove remnants of polyurethane foam in the extracts. After volume reduction of PUF extracts, all extracts were eluted on a silica column with hexane as eluent. The eluate volumes were once again reduced prior to further cleanup and HPLC separation (Amino column, μBondapak NH_2, 7.8 × 300 mm; Waters Corporation, Milford, USA) of the PCB fraction from alkanes/monoaromatic hydrocarbons and polycyclic aromatic hydrocarbons [17]. The PCB

fraction was volume reduced and eluted with hexane on an open column containing three layers of modified silica (SiO_2/H_2SO_4 10 mm, SiO_2/KOH 10 mm and SiO_2/H_2O 10 mm) [18]. The eluates were finally volume reduced on a rotary evaporator and under a gentle stream of nitrogen gas. Samples were quantified on a Fisons 8060 gas chromatograph (GC) equipped with a PTE-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Supelco Inc, Bellefonte, USA) with a Fisons MD800 mass spectrometer (MS) operated in the electron impact mode. A ^{13}C-labelled recovery standard (PCB#153) dissolved in toluene was added to all samples before injection on the GCMS. Response factors for the analysed congeners were determined from a standard mixture. In parallel with field samples, field blanks and laboratory blanks were analysed to control any contamination originating from the described sampling and analytical steps. These blank values were subtracted from the data. The recoveries of the ^{13}C-labelled internal standards were 0.77 ± 0.16 (1 S.D.). The precision of the GCMS quantification step was calculated from six serial injections of a standard mixture and was constrained to a RSD of 7% (range 2–24%).

RESULTS AND DISCUSSION

Concentrations and Particle–Water Distributions

Quantified concentrations of single congeners sampled with system A spanned between 0.04 and 3 fM (0.02 and 1 pg/L) in the particulate fraction and 0.04–8 fM (0.01–2 pg/L) in the dissolved fraction (Fig. 1A and B). Two to three of the quantified PCB congeners in both the particulate and dissolved fractions had frequently a concentration of less than three times the blank (predominantly PCB congeners #180, #194 and #199). Such data points were consistently excluded from consideration and are not presented in any of the figures (except Fig. 3). The measured levels of total congener concentrations in surface water in the Baltic Sea are of the same magnitude as previous field measurements in this region [6,8]. The observed organic-carbon normalised solid–water distribution coefficients (K_{oc}(obs)) clearly demonstrate the influence of compound hydrophobicity on the phase distribution (Fig. 1C). Such high log K_{oc}(obs) values, even above log K_{ow}, have previously been observed for several HOC compound classes in various aquatic systems [19, for a recent review]. This observation and potential mechanistic explanations will be evaluated in detail in a separate publication (Sobek & Gustafsson, manuscript in prep).

Constraints on Contamination: Absolute Values, Sources and Trends

Due to the low concentrations of PCBs in environmental samples, the risk of contamination during sampling and analysis is significant. Determination of blank levels is therefore crucial in order to diagnose the resolution and reliability of the data. It has been shown in previous studies that elevated PCB concentrations in indoor air of laboratory buildings cause contamination during sample preparation [20]. Individual congener data on filter- and adsorbent-blanks as well as analytical blanks (no filter or adsorbent extracted) are shown in Fig. 2. Average amounts of congeners #28, #101 and #180 were 12, 10 and 8 pg in the blank PUF adsorbents and 15, 13 and 10 pg respectively in the blank GFF filters. The filter blanks had consistently the highest

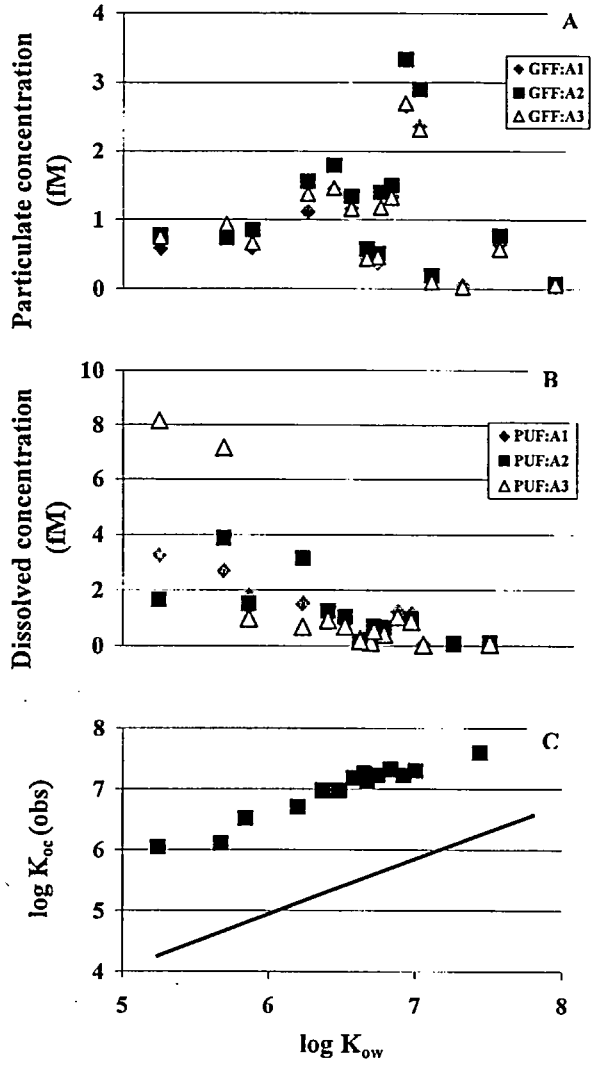

FIGURE 1 Three observations of the PCB concentrations (fM) for system A ('best system'; see text and Table I) in the particulate fraction (Fig. 1A) and the dissolved fraction (Fig. 1B) as a function of congener hydrophobicity (log K_{ow}). Fig. 1C shows the observed organic-carbon normalised partition coefficient log K_{oc}(obs) for PCBs relative to log K_{ow} obtained with system A. The regression line shows the predicted log K_{oc}(obs) [22]. Congeners with concentrations lower than three times the blank values were excluded (predominantly congeners #199 and #194, in total nine concentration data points).

degree of contamination, while PUF blanks and method blanks showed lower contamination levels. There were no general differences between filter blanks generated either in the field or just exposed to the laboratory (data not shown), supporting our sampling methodology as not adding any significant contamination.

Normalisation of sample concentrations to blank concentrations (signal-to-noise ratio; S–N) provides an index of the reliability of the data with respect to blank contamination. The average S–N values for all congeners and all sampling systems, in both particulate and dissolved fractions, are shown in Fig. 3A, and the corresponding

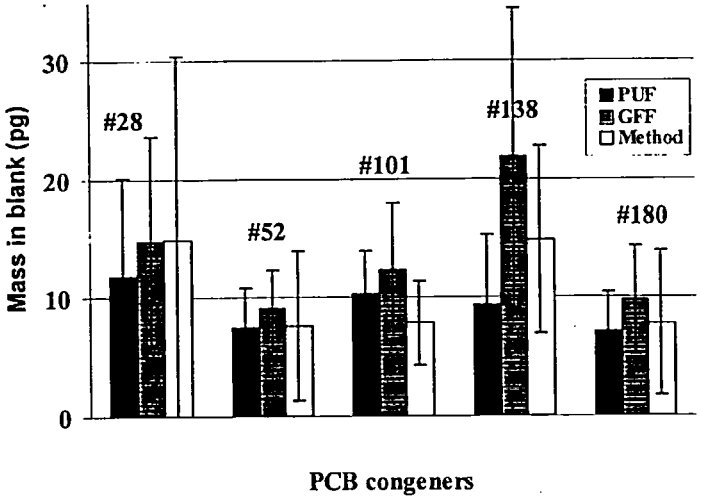

FIGURE 2 Mass (pg) of PCB congeners in filter blanks ($n=12$), PUF blanks ($n=8$) and method blanks ($n=13$) (method blank: only solvent was extracted) for a set of selected congeners spanning a range in hydrophobicity. The error bars represent 1 S.D.

S–N for the 'best' system (System A) is shown in Fig. 3B. The congener hydrophobicity ($\log K_{ow}$) is presumably the factor explaining most of the trends seen in Fig. 3A and B. Congeners with a high $\log K_{ow}$ are more likely to be found in the particulate phase in contrast to congeners with a low hydrophobicity that are more water soluble and thus more inclined to dissolve in the water phase. Hence, the S–N was high for less hydrophobic congeners in the dissolved phase. In accordance with this reasoning, there was an increasing trend in S–N values in the particulate fraction, relative to the dissolved counterpart, with increasing $\log K_{ow}$. Above $\log K_{ow}$ of 7, low S–N values were observed in both fractions. The same trends were observed for S–N in System A (Fig. 3B, note differences in scales in Fig. 3A and B), but system A had an overall higher S–N than the average for all systems. Hydrophobic organic contaminants with high hydrophobicity are to a large extent absorbed to particles and organic material of different matrices. Parts of the organic material in surface water with absorbed HOCs are exported from the mixed surface water to deeper water layers and sediments, e.g. [7]. There might therefore be a fractionation in favour of less hydrophobic PCBs found in surface water. Congeners with $\log K_{ow}$ between 6 and 7 had the highest S–N ratios of 8–25 for both fractions. This makes these congeners suitable candidates as model compounds in, for instance, calculations of partition coefficients such as K_d and K_{oc} where both fractions are equally important.

Elucidation of Possible Sample Fractionation

To facilitate the comparison of congener distribution patterns between the four different sampling systems, concentration data sets were normalised in each sample to PCB#110. Thereafter, the PCB#110-normalised fingerprints were plotted relative to the PCB#110-normalised pattern of System A (Eq. (1)). System A was in this comparison

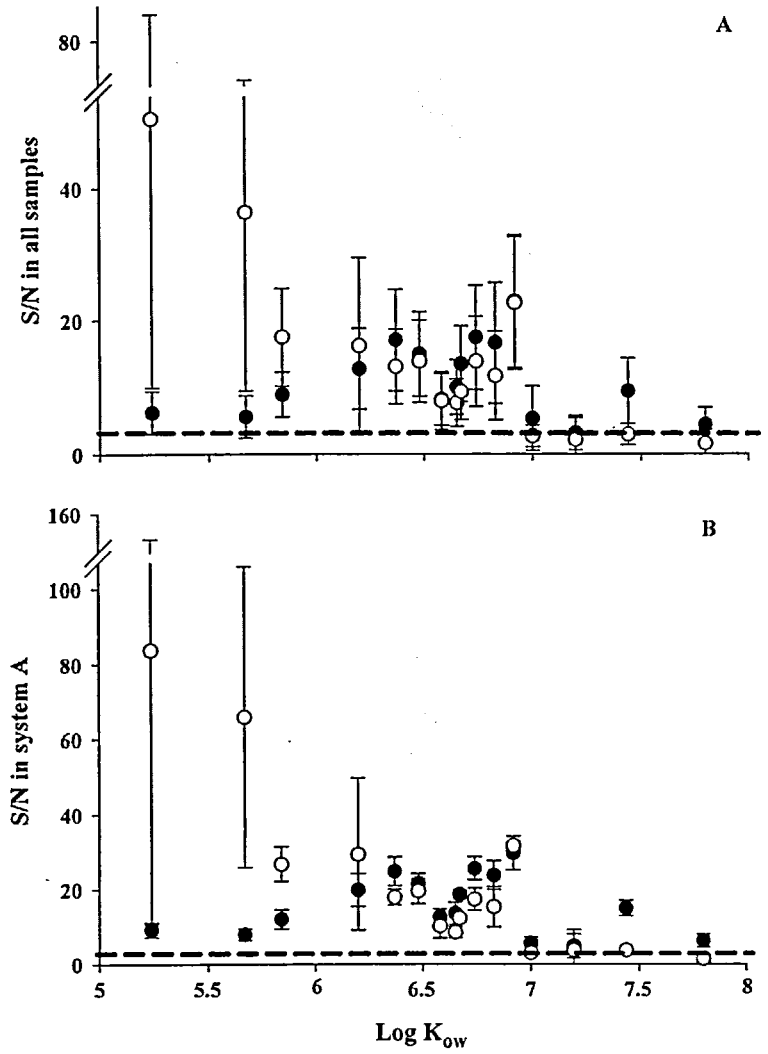

FIGURE 3 Concentrations measured in sampled seawater relative to blank concentrations (S–N) as a function of congener hydrophobicity (log K_{ow}) for GFF (closed circles) and PUF (open circles) samples. In Fig. 3A, average S–N values of all samples and systems are shown, in Fig. 3B the S–N values of System A are shown. The error bars represent 1 S.D. The hatched lines represent S–N ratios of 3.

considered to be the 'best system', since it had three replicates, was sampled with stainless steel tubing and was the system with the largest S–N (Fig. 3).

$$V(i)_x = \frac{C(i)_x / C(110)_x}{C(i)_A / C(110)_A} \quad (1)$$

In Eq. (1), $C(i)_x$ is the concentration of PCB congener #i sampled with system x. For instance, $C(110)_x$ is the concentration of congener #110 sampled with system x. The $V(i)_x$ is thus the value derived from the normalisation of a specific congener to PCB#110 and System A.

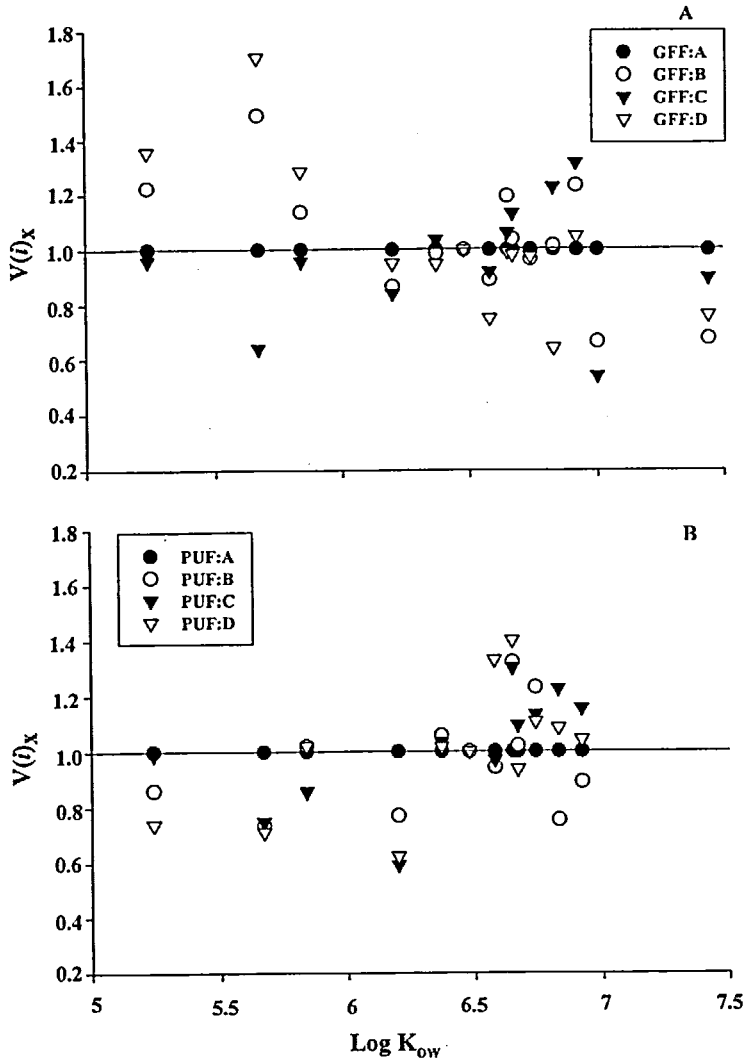

FIGURE 4 The PCB congener fingerprints for the four different sampling systems in particulate (Fig. 4A) and dissolved (Fig. 4B) fractions. All congeners were normalised to the concentration of PCB#110 in each system and are shown ($V(i)_x$) relative to the PCB#110-normalised pattern of System A. Congeners with concentrations lower than three times the blank were disregarded (predominantly congeners#199 and #194, in total nine concentration data points excluded).

The relative PCB congener fingerprints for particulate matter (Fig. 4A) showed no significant dissimilarities between the four systems (F-test between slopes suggested no significant differences). Particle-absorbed PCBs are expected to be less affected by the choice of sampling equipment compared to congeners dissolved in water, which potentially may sorb to hydrophobic plastic polymers. In the dissolved phase, PCB congeners sampled with System D showed an increasing relative trend towards higher hydrophobicity (F-test between slopes; slope of System D significantly positive with $p < 0.05$) compared to the other three systems (Fig. 4B). This pattern suggests a possible fractionating process of PCB congeners sampled with System D (PVC tubing). Since

sorption kinetics is limited by diffusion, it is likely that the data reflects the higher diffusion coefficients for the smaller molecules as they associate with the PVC tubing material. Systems B and C showed no significant difference in slope to that of System A, supporting the absence of any significant fractionation, losses or contamination in those systems.

Variance of the Sampling Step

The precision that a sampling system produces is an important analytical quality parameter. The overall variation introduced to the data from sampling, laboratory cleanup procedures and quantification is crucially important to quantify and to keep low for a correct interpretation of the data. Since all samples were treated equally during the sample cleanup stages and quantification, it is only the sampling step that differs between the four groups of samples.

In Fig. 5 the 'total' precision is expressed as relative standard deviation (RSD) for each system and averaged for all congeners. From this figure it appears that System C (silicone tubing) had the lowest RSD for dissolved congeners (9%). However, System C was sampled only with duplicates, which might increase the apparent precision for that system. Among the other three systems the PUF RSDs spanned between 35 and 45%. For the particulate fraction the difference between tested sampling systems was not as large; System A had a mean total variance of 13% and System D had 36%. The sampling volume (Table I) could also be a factor affecting the total RSD. However, both Systems A and C had large volumes in each of the triplicates (> 370 L).

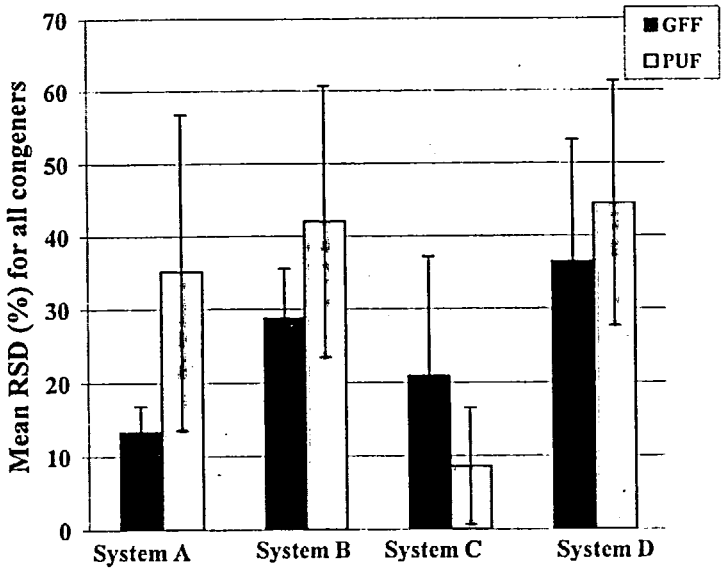

FIGURE 5 The total sampling and analytical precision (mean relative standard deviation; RSD) for the average of all congeners, illustrated for both particulate (black bars) and dissolved (grey bars) fractions for the different systems. Congeners with concentrations below three times the blank values were disregarded (on average two congeners in the particulate fraction and three in the dissolved fraction; predominantly congeners #180, #190 and #194). The error bars represent 1 S.D. of the means from the relative standard deviations.

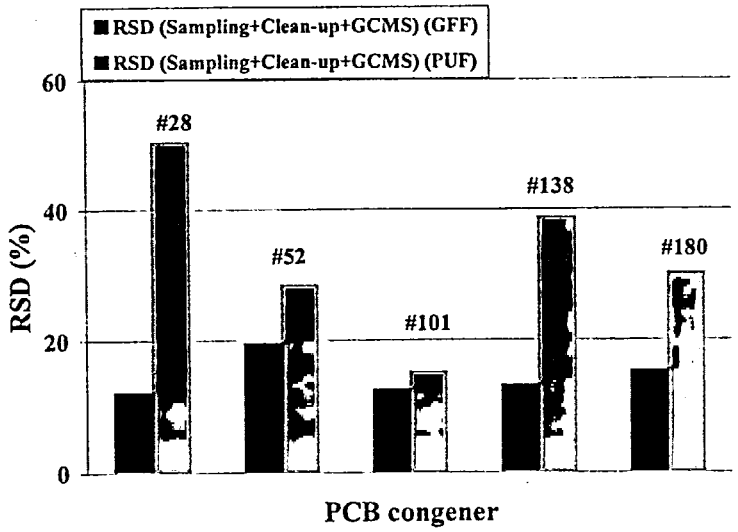

FIGURE 6 The precision (RSD) produced by System A (stainless steel) for PCB congeners #28, #52, #101, #138 and #180 (PUF and GFF shown separately).

Few studies are available where the sampling variance is reported and related to the variance from the laboratory based cleanup procedures and quantification steps. However, in one study where sediments were sampled in the Baltic Sea it was shown that the sampling procedure and spatial variation introduced significantly more error to the total variability than the chemical analysis [21]. Sediment sampling is complicated due to the heterogeneity that sediments pose, but the issue of sampling variance appears highly significant also for sampling of water.

Potential losses of PCB congeners during the analytical cleanup procedures and GCMS quantification are not reflected in the reported concentrations, since ^{13}C-labelled internal standards were used. Hence, the non-natural variances in the concentration data originates from the sampling step. The field sampling step contributed in System A (to five selected congeners) a variance for PUF of 30% (range 15–50%) and GFF of 15% (range 13–20%) (Fig. 6). As espoused above, there was a hydrophobicity-driven trend in relative variance between GFF and PUF (Fig. 6). It is encouraging that the total variance is as small as what has here been constrained. An implication of the elucidated sampling and thus total variances is that natural variations in concentrations for several PCB congeners exceeding about 50% can be resolved and interpreted using the described analytical sampling and cleanup methods. Further, this study demonstrated that the tubing material does not have a major impact on the derived concentration data even of hydrophobic chemicals. Thus, awkward stainless steel tubing can safely be replaced by silicone or HDPE materials.

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References

[1] J.W. Farrington, *Environ. Health Persp.*, **90**, 75–84 (1991).
[2] H. Iwata, S. Tanabe, N. Sakai and R. Tatsukawa, *Environ. Sci. Technol.*, **27**, 1080–1098 (1993).
[3] P. Mayer, B. Halling-Sörensen, D.T.H.M. Sijm and N. Nyholm, *Environ. Toxicol. Chem.*, **17**, 1848–1851 (1998).
[4] J.J. Stegeman, J. Schlezinger, J.E. Craddock and D.E. Tillitt, *Environ. Sci. Technol.*, **35**, 54–62 (2001).
[5] H.G. Petersen, C.Boutin, P.A. Martin, K.E. Freemark, N.J. Ruecker and M.J. Moody, *Aquatic Toxicol.*, **28**, 275–292 (1994).
[6] J. Axelman, D. Broman and C. Näf, *Ambio*, **29**, 210–216 (2000).
[7] Ö. Gustafsson, P.M. Gschwend and K.O. Buesseler, *Environ. Sci. Technol.*, **31**, 3544–3550 (1997).
[8] D.E. Schulz-Bull, G. Petrick, N. Kannan and J.C. Duinker, *Mar. Chem.*, **48**, 245–270 (1995).
[9] D.E. Schulz-Bull, G. Petrick, R. Bruhn and J.C. Duinker, *Mar. Chem.*, **64**, 101–114 (1998).
[10] J.I. Gómez-Bellinchón, J.O. Grimalt and J. Albaigés, *Environ. Sci. Technol.*, **22**, 677–685 (1988).
[11] M.B. Yunker, F.A. McLaughlin, R.W. Macdonald, W.J. Cretney, B.R. Fowler and T.A. Smyth, *Anal. Chem.*, **61**, 1333–1343 (1989).
[12] G. Bremle and P. Larsson, *Environ. Sci. Technol.*, **31**, 3232–3237 (1997).
[13] D. Broman, C. Näf and Y. Zebuhr, *Environ Sci. Technol.*, **25**, 1850–1864 (1991).
[14] S.C. Lung, L.M. Altshul, T.E. Ford and J.D. Spengler, *Chemosphere*, **41**, 1865–1871 (2000).
[15] G. Petrick, D.E. Schulz-Bull, V. Martens, K. Scholz and J.C. Duinker, *Mar. Chem.*, **54**, 97–105 (1996).
[16] D. Broman, C. Näf, J. Axelman, C.Bandh, H. Pettersen, R. Johnstone and P. Wallberg, *Environ. Sci. Technol.*, **30**, 1238–1241 (1996).
[17] C. Bandh, I. Rasha. D. Broman, C. Näf, Y. Rönquist-Nii and Y. Zebuhr, *Environ. Sci. Technol.*, **30**, 214–219 (1996).
[18] L.M. Smith, *Anal. Chem.*, **53**, 2152–2154 (1981).
[19] T.D. Bucheli and Ö. Gustafsson, *Environ. Toxicol. Chem.*, **20**, 1450–1456 (2001).
[20] J.C. Wallance, I. Basu and R.A. Hites, *Environ. Sci. Technol.*, **30**, 2730–2734 (1996).
[21] H. Pettersen, J. Axelman and D. Broman, *Chemosphere*, **38**, 1025–1034 (1999).
[22] C.T. Chiou, P.E. Porter ad D.W. Schmedding, *Environ. Sci. Technol.*, **17**, 227–231 (1983).