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Comparison of five integrative samplers in laboratory for the monitoring of indicator and dioxin-like polychlorinated biphenyls in water

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Abstract:

This study aimed at evaluating and comparing five integrative samplers for the monitoring of indicator and dioxin-like polychlorinated biphenyls (PCBs) in water: semi-permeable membrane device (SPMD), silicone rubber, low-density polyethylene (LDPE) strip, Chemcatcher and a continuous-flow integrative sampler (CFIS). These samplers were spiked with performance reference compounds (PRCs) and then simultaneously exposed under constant agitation and temperature in a 200 L stainless steel tank for periods ranging from one day to three months. A constant PCB concentration of about 1 $ng \cdot L^{-1}$ was achieved by immersing a large amount of silicone rubber sheets ("dosing sheets") spiked with the target PCBs. The uptake of PCBs in the five samplers showed overall good repeatability and their accumulation was linear with time. The samplers SPMD, silicone rubber and LDPE strip were the most promising in terms of achieving low limits of quantification. Time-weighted average (TWA) concentrations of PCBs in water were estimated from uptake of PCBs using the sampling rates calculated from the release of PRCs. Except for Chemcatcher, a good agreement was found between the different samplers and TWA concentrations ranged between 0.4 and 2.8 times the nominal water concentration. Finally, the influence of calculation methods (sampler-water partition coefficients, selected PRCs, models) on final TWA concentrations was studied.

Highlights

► We compare uptake kinetics for five integrative samplers applied for PCB in water. ► The method to calculate TWA concentrations strongly influences results. ► SPMD, SR and LDPE strip are the most efficient to accumulate PCB.

Keywords : Integrative samplers ; Polychlorinated biphenyls ; Water monitoring ; Time weighted average concentration ; Modeling

1. Introduction

Like many other hydrophobic organic contaminants, polychlorinated biphenyls (PCBs) have toxic effects on living organisms, including human beings (Carpenter, 2006). In aquatic environments, PCBs are principally adsorbed on particulate matter due to their hydrophobicity ($\log K_{OW} > 4.5$); hence, their concentration in the dissolved phase is therefore very low, typically in the ng/L to pg/L range. Monitoring such low concentrations with traditional bottle (or grab) sampling is challenging and requires sophisticated analytical methods such as isotopic dilution mass spectrometry. Furthermore, grab sampling only provides a snapshot of the contaminant concentration at a particular time without taking temporal variations into account.

Since two decades, several integrative sampling devices have been developed for the monitoring of organic contaminants in aquatic environments (Greenwood *et al*. 2009, Söderström *et al*. 2009, Lohmann *et al*. 2012). These samplers enable the improvement of limits of quantification (LOQ) by accumulation and concentration of contaminants over long-term exposure. Moreover, when they are used in the integrative phase of uptake (i.e. integrative samplers), time-weighted average (TWA) concentrations over the exposure period can be calculated, leading to a better representativeness of measurements.

Several integrative samplers, at different stages of development, are now available for monitoring non-polar organic contaminants. The semi-permeable membrane device (SPMD) is one of the most comprehensively studied integrative sampler; it consists of a low-density polyethylene (LDPE) lay-flat tubing filled with a small quantity of triolein. It was designed to sequester and concentrate freely dissolved organic contaminants with $\log K_{OW}$ ranging from three to eight and has already been extensively used for the monitoring of PCBs in water (Huckins *et al*. 2006). Next to biphasic sampling devices like SPMD, single-phase integrative samplers, such as LDPE strip and silicone rubber (SR), are gaining interest due to simpler modelling of contaminant transport processes and easier sample

processing. Numerous studies have shown the suitability of LDPE strips for the monitoring of hydrophobic organic contaminants, such as polyaromatic hydrocarbons (PAHs) or PCBs in various water bodies (Booij *et al*. 2003, Carls *et al*. 2004, Adams *et al*. 2007, Anderson *et al*. 2008). Silicone rubber was also found to be a suitable alternative to SPMD for the monitoring of hydrophobic contaminants (Rusina 2007). Indeed, SR sheets have been successfully used for the monitoring of PAHs and PCBs from 2002 in The Netherlands (Smedes 2007). Chemcatcher can house different combinations of receiving phases and membranes as appropriate for polar or non-polar contaminants monitoring (Greenwood *et al*. 2007). The first non-polar version of Chemcatcher, made of a C18 Empore disk and a LDPE membrane, aimed at sampling contaminants with logK_{OW} greater than three (Kingston *et al*. 2000). A recent optimization of the sampler, by adding a small volume of octanol between the receiving phase and the membrane, was proposed to decrease the internal sampler resistance to mass transfer of hydrophobic compounds with logK_{OW} above five (Vrana *et al*. 2005). Chemcatcher has already been used during field campaigns for the monitoring of PAH and organochlorine pesticides (Vrana *et al*. 2010). Finally, developed since 2008, CFIS (Continuous Integrative Flow Sampler) is a new active (i.e. using a pump) sampler designed for the determination of TWA concentrations of organic compounds in water (Llorca *et al*. 2009). Briefly, CFIS is a fully immersible device consisting of a small peristaltic pump powered by batteries and producing a constant water flow through the glass cell containing a PDMS sorbent. The main advantage of CFIS is that sampling rates are unaffected by water turbulence or velocity and thus, the use of performance reference compounds (PRCs) is not required. It has already been used for the monitoring of PAH and organochlorine pesticides in wastewater treatment plant effluent (Llorca *et al*. 2009).

Over the past 20 years, a variety of models has been developed to better describe the transfer kinetics of hydrophobic contaminants into integrative samplers (Booij *et al*.

100 2007). Whatever the integrative sampler and model considered, the calculation of TWA
101 concentrations of contaminants in water from amounts accumulated in the sampler
102 requires the knowledge of sampling rate (R_S) and sampler-water partition coefficient (K_{SW})
103 for each compound. Sampling rates are determined by laboratory calibration under
104 controlled exposure conditions. *In situ* R_s calibration is needed to take into account
105 differences between laboratory *vs. in situ* exposure conditions (i.e. flow velocity, biofouling
106 or temperature); it is achieved by the use of internal surrogates (performance reference
107 compounds, PRCs), spiked in samplers prior to exposure (Huckins *et al*. 2002). K_{SW} can
108 be determined experimentally (Smedes *et al*. 2009 for LDPE and SR) or estimated via
109 empirical relationships as a function of logK_{OW} (Huckins *et al*. 2006 for SPMD, Vrana *et al*.
110 2006 for Chemcatcher, Booij *et al*. 2003, Adams *et al*. 2007 and Lohmann and Muir 2010
111 for LDPE). Concerning CFIS, that is an “active” sampler, the use of PRC and K_{SW} is not
112 necessary. Indeed, a pump enables to control the water flow during exposure and the
113 temperature effect is known by previous calibration in laboratory (from 5°C to 35°C). By
114 this way, R_s estimated in laboratory for each PCB is corrected according to the average
115 temperature encountered during *in situ* exposure, to be directly used for the determination
116 of TWA concentrations (Llorca *et al*. 2009).

117 Very few intercomparison exercises on integrative samplers have been performed
118 until now. Allan *et al*. (2009) or Miège *et al*. (2012) tested *in situ* the performance of
119 several PSs (including non-polar Chemcatcher, LDPE, membrane enclosed sorptive
120 coating - MESCO, SR and SPMD) for the monitoring of hydrophobic compounds (among
121 PAHs, PCBs or organochlorine pesticides) in the river Meuse (The Netherlands) (Allan *et*
122 *al*. 2009) or the river Rhône (France) (Miège *et al*. 2012) respectively. Although different
123 integrative samplers and methods of calculation were used, relatively consistent TWA
124 concentrations were obtained (variation by a factor up to two). Allan *et al*. (2010)
125 compared under laboratory conditions the performances of six different integrative

samplers (non-polar Chemcatcher, SPMD, silicone rod and strip and two modified versions of MESCO), exposed in a flow-through calibration system with Meuse river water spiked with PAHs, PCBs and organochlorine pesticides (concentrations ranging from 20 to 700 ng/L). This laboratory experiment only lasting five days showed that the mass of contaminant absorbed normalized to the sampler surface area was comparable if uptake was controlled by diffusion through the water boundary layer.

In the context of the ECLIPSE project (2009-2011)[1], we have studied five integrative samplers that well represent the various types used nowadays for PCBs in term of receiving phase and configuration (dimensions, holders): SPMD, SR, LDPE strip, Chemcatcher (apolar version) and CFIS. After PRC spiking or not, samplers were exposed under constant agitation and temperature in water contaminated with 19 indicator and dioxin-like PCBs for periods ranging from one day to three months. A constant PCB concentration of about 1 ng/L was achieved by immersing a large amount of spiked silicone rubber sheets (Rusina *et al*. 2010). Using these five samplers allows comparing different strategies for integrative sampling: passive *vs*. active (with pump) sampling, use of PRC or not, use of different models and equations to assess TWA concentration. By exposing these five integrative samplers into the same experimental calibration system, a first objective was to compare their performances in accumulating PCBs (uptake, repeatability and linearity). Moreover, since there is no detailed guideline on integrative sampling, a second objective was to compare different methods of calculation of TWA concentrations (models, partition coefficients values and selected PRCs).

2. Materials and methods

2.1. Integrative samplers

[1] **EC**hantil**L**onneurs **I**ntégratifs pour la mesure de **P**CB dans la phase dis**S**oute de mili**E**ux aqueux, 2009-2011, coord. Irstea (C. Miège), funded by the French Axelera cluster

150 The main characteristics of the studied integrative samplers as well as the PRCs
151 tested and main steps of their processing are summarized in Table 1. Further details on
152 their characteristics, pretreatment and analysis are given in Supplementary data (S1).
153
154 *2.2. Target molecules*
155 The exposure of samplers was performed with 19 PCBs: PCB 18, indicator PCBs
156 (PCB 28, 52, 101, 118, 138, 153 and 180) and dioxin-like PCBs (PCB 77, 81, 105, 114,
157 118, 123, 126, 156, 157, 167, 169 and 189). All these PCBs were purchased from Cil
158 Cluzeau (Courbevoie, France) and delivered in a custom-made solution used to spike the
159 silicone rubber sheets (referred as “dosing sheets“ hereafter).
160
161 *2.3. Exposure device and strategy*
162 The exposure device was custom-made (PIC, Olivet, France) and consisted of a
163 tank (height = 120 cm, diameter = 47 cm), a stirrer and six holders; all these pieces being
164 made of stainless steel to minimize adsorption. A scheme of the exposure device is
165 presented in Supplementary data (S2). The tank was filled with 200 L of tap water agitated
166 with a stirrer (height = 100 cm, width = 18 cm) set in motion by an electronic engine
167 (Heidolph RZR 2102 control Z; VWR, Fontenay-sous-Bois, France). Rotation speed was
168 set at 33 rpm to obtain a water velocity of about 5 cm/sec near the samplers exposed in
169 the tank. To regulate water temperature, the exposure tank was placed in a 300 L
170 polyethylene tank (CVC series, Manutan, Gonesse, France) and water was cooled by an
171 aquarium chiller (Teco TR20, Europrix, Lens, France). The exposure tank contained six
172 holders (height = 100 cm, width = 20 cm) set along the wall. Two holders were used to
173 support the dosing sheets and the four other holders were used to fix four types of
174 integrative samplers: SPMD, SR, LDPE strip and Chemcatcher. Each holder had four

positions enabling the simultaneous exposure of four samplers at different depths. CFIS were installed outside the tank but were exposed to the tank water by use of glass tubes.

PCBs were dosed to the tank water by immersing a large amount of dosing sheets (Rusina *et al*. 2010). This allowed for maintaining a constant concentration of about 1 ng/L of each studied PCB throughout the experiment. Dosing sheets were first mounted in the exposure device and the tank was filled with tap water. Then, the exposure system was allowed to equilibrate under agitation and temperature regulation during two days, after which water was renewed. This step allowed for cleaning the system and eliminating traces of methanol that might have remained in the dosing sheets from spiking. After another two days of equilibration, samplers were deployed in the tank.

Exposures in the water tank lasted up to three months. SPMD, SR and LDPE strips were exposed during 1, 3, 7, 14, 21, 28 (in triplicate), 56 and 91 days. Chemcatcher and CFIS were exposed during 3, 7, 14 (in triplicate), 21, 28 and 56 days. Before and after exposure, samplers were stored at –20℃.

Temperature of the tank water was recorded every 6 h over the whole exposure duration. During the first month, water (1 L) was sampled weekly for determination of pH, conductivity and dissolved organic carbon (DOC) concentration. During the last two months, these measurements were performed every two weeks. The concentrations of PCBs in water were calculated from their concentration in dosing sheets (Rusina *et al*., 2010) and using their PDMS – water partition coefficients (Smedes *et al*. 2009). Dosing sheets were sampled every two weeks by cutting six small pieces at different depths in the tank obtaining a total amount of about 1 g of material. Further details about the preparation and analysis of dosing sheets are given in Supplementary data (S1).

2.4. Quality controls

2.4.1 Interlaboratory assay

In order to assess the interlaboratory variability in PCB analysis, a standard solution was prepared and sent for analysis by each of the five laboratories involved in this study with its own analytical method. This solution contained the 19 studied PCBs at concentrations ranging from 50 to 130 µg/L and was conditioned in amber glass vials prior to shipment. A good agreement was found between laboratories since the relative standard deviations (RSD) on measured concentrations ranged from 3 to 13 % depending on the congeners.

2.4.2. Blank samplers

After their preparation, several samplers were kept as procedural blanks in order to evaluate any possible contamination during fabrication, spiking, storage, processing and analysis. These procedural blanks were stored at –20°C until processing. Other samplers were used as “field” blanks and exposed to the ambient air during the handling of deployed samplers to take account for any possible contamination during deployment and retrieval. These “field” blanks were stored at -20°C until pro cessing. No contamination by PCB was measured in procedural and field blanks.

At last, for each type of sampler (except CFIS), a blank sampler (not spiked with PRC) was exposed in the tank during the whole exposure duration in order to assess any possible contamination with PRC between samplers. Only low amounts of rapidly releasing PRC were observed representing less than 4 % of the concentration in these exposed spiked samplers.

2.5. Calculations

Several models have been developed to describe the transfer of hydrophobic contaminants into the various available integrative samplers and to calculate the TWA concentrations in water from the accumulated amounts in the samplers (Booij *et al*. 2007).

In this work, for SPMD, SR, LDPE strip and Chemcatcher, TWA concentrations of PCBs in water were calculated from the following equation (Huckins *et al*. 2006):

$$C_W = \frac{N}{V_S K_{SW}\left(1-\exp\left(-\frac{R_S t}{V_S K_{SW}}\right)\right)} \quad (1)$$

where C_W is the TWA concentration of PCB in water (ng/L), N is the mass of PCB accumulated in sampler (ng), V_S is the volume of sampler (L), K_{SW} is the sampler-water partition coefficient of PCB (L/L), R_S is the sampling rate of PCB (L/day) and t is the exposure duration (day). For SR and LDPE, V_S is replaced by M_S, the mass of sampler (kg), and K_{SW} is expressed in L/kg.

For CFIS, TWA concentrations of PCBs were calculated from the following equation, which is a simplification of equation 1 for the sampling during the linear uptake phase (Huckins *et al*. 2006):

$$C_W = \frac{N}{R_S t} \quad (2)$$

More details on calculations of TWA concentrations of PCBs in water for each sampler are given in Table 2 and Supplementary data (S3).

3. Results and discussion

3.1. Exposure conditions

During the three months exposure, water temperature remained constant (22.6℃ ± 0.1℃) and pH only slightly varied (7.5 ± 0.2). In contrast, water conductivity slightly decreased from 380 to 310 µS/cm and DOC concentration showed an increase from around 1.5 to 5 mg/L (Supplementary data, S4). These variations of conductivity and DOC could be explained by the development of biofouling in the tank since no biocide was added. Another possible source of DOC could be the release of the octanol used in the Chemcatchers. The concentrations of the 19 PCBs in dosing sheets remained stable (RSD

between 3 and 11 %, n=7) and derived water concentrations ranged from 0.37 ng/L (PCB 189) to 3.80 ng/L (PCB 114), with a mean value of 1.29 ng/L. The exposure conditions were therefore considered as constant during the whole experiment.

3.2. Comparison of uptake curves and PRC candidates

To compare the uptake of the five studied integrative samplers, this uptake was normalized to a surface area of 100 cm^2 (N_A). Plotting N_A versus time showed that the uptake rate (slope) ranged within a factor five as depicted in Figure 1A for PCB 81 (4 Cl atoms), PCB 114 (5 Cl atoms), PCB 138 (6 Cl atoms) and PCB 180 (7 Cl atoms). With exception of PCB 81 (approaching equilibrium for LDPE), the N_A for SPMD and LDPE were quite similar, whereas SR was showing considerable higher uptake than SPMD. This could have been caused by the fact that SPMD and LDPE were both similarly fixed on a spider holder perpendicular to the flow, whereas SR was fixed in parallel with the flow (S2). The overall lower N_A for Chemcatcher is likely connected to the “beaker” shape configuration creating a longer diffusion path between sampler and bulk water. For CFIS, the N_A was not expected to be comparable as this sampler has its own flow regime; but by chance, this N_A was at the same level as that of the passive samplers. Remarkable is that CFIS showed the highest N_A (PCB 138 and 180) as well as the lowest (PCBs 81 and 114). It seems that for CFIS, the N_A for indicator PCBs were markedly higher than for dioxin-like PCBs, a phenomenon that was not observed for the other samplers.

Although, the N_A of most PCBs were linear with time for the whole exposure duration; there were some outliers, indicated by (a) in Figure 1. Indeed, the N_A for SPMD exposed for 91 days was similar to that at 56 days, and that even occurred for the most hydrophobic PCBs that could impossibly have obtained equilibrium. The low N_A of the SPMD at 91 days exposure however coincides with a reduced release of PRCs, as shown in Figure 1B for PCB 29. It is not clear whether the lower exchange for the SPMD

277 exposed during 91 days is caused by observed biofouling or different mounting position of
278 the spider holder giving a different flow regime. Anyway, these observations underline the
279 importance of PRC application. Figure 1B shows the release curves of some PRC
280 candidates spiked in samplers prior to exposure. PRCs were selected according to the
281 criteria reported in Table 2. The release rates of PRCs were used to calculate the TWA
282 concentrations of PCBs in section 3.4.1.

283 For LDPE strip, PCBs 18, 28 and 52 reached the equilibrium phase of uptake within
284 the 91 days of exposure and PCBs 77, 81 and 101 were in the curvilinear uptake phase,
285 as was PCB 18 in SPMD. With the exception of these less hydrophobic congeners, N_A in
286 LDPE strip, as well as in SR, Chemcatcher and CFIS, increased during the three months
287 of exposure with an overall good linearity. Linear uptake phase durations of all PCBs are
288 given in Supplementary data for SPMD, SR and LDPE strip (S5).

289

290 *3.3. Discussion on sampling rates*

291 When N_A is divided by (t x C_W), a R_{SA} ($L.d^{-1}.100\ cm^{-2}$) is obtained for the
292 compounds in linear kinetic phase (cf. equation 2). Figure 2 allows comparing the R_{SA} of
293 the different compounds and between the five samplers. It is important to note that R_{SA} for
294 SPMD, SR and LDPE are close with an average RSD of 21 % whereas that value
295 increases to 43 % when data of all samplers are considered. PCBs approaching
296 equilibrium (grey bars) were not included.

297 Figure 2 is based on the 28 days exposures for SPMD, SR and LDPE, and on the
298 14 days exposures for Chemcatcher and CFIS, because these exposures were performed
299 in triplicate and allowed an evaluation of the uptake repeatability (error bars in Figure 2).
300 Overall, repeatability of R_{SA} was very satisfying, with a mean value of RSD (combining all
301 the 19 PCBs) lower than 14 % (9 % for SPMD, 5 % for SR, 7 % for LDPE, 9 % for

302 Chemcatcher and 14 % for CFIS). This variability was only slightly higher than that
303 observed in the dosing sheets over time.

304 Despite the differences in materials (membranes, sequestering phases) and
305 configurations, SPMD, SR, LDPE strip and Chemcatcher exhibited similar patterns of R_{SA}
306 contrary to CFIS. Ignoring the compounds that were approaching equilibrium (PCB 18,
307 PCB 28 and PCB 52), the RSD of the R_{SA} ratios between two samplers (1 ratio per PCB,
308 n=16 to 19) can be used as a measurement for agreement between patterns. This
309 revealed that the pattern ratio between SPMD and SR showed a RSD of 10 % (average
310 ratio of 0.7) and excellent agreement. For both SPMD-LDPE and SR-LDPE, the RSD of
311 the pattern ratio was 16 %, with average ratios of 0.9 and 1.2 respectively. This larger
312 RSD for LDPE was due to relatively higher uptakes of PCBs 77, 81, 126 and 169, i.e. of
313 non-ortho substituted PCBs. For SPMD-Chemcatcher and SPMD-CFIS, the pattern
314 agreement was much lower with RSD of 40 % and 50 % and average ratios of 2.1 and 1.2,
315 respectively. For SPMD-Chemcatcher, leaving PCB 189 out reduced the RSD of the
316 pattern ratio to 23 %. The different level of R_{SA} for the CFIS sampler can be explained by
317 the different flow regime in the cell (outside the tank) compared to that inside the tank, but
318 we cannot explain the much higher R_{SA} of the indicator PCBs compared to those of the
319 dioxin-like PCBs. The RSD of pattern ratios for the membrane samplers were consistent
320 and only about a factor two higher than the repeatability of R_{SA} for each triplicate samplers;
321 this indicates that uptake processes of the different compounds were similar for SPMD, SR
322 and LDPE.

323 Between compounds, R_{SA} values were quite scattered (20 to 50 % RSD). To
324 explain this scatter between compounds, the origin of C_W should be considered. The
325 calculation of R_{SA} in the evaluation above was actually done according to:
326

$$R_{SA} = \frac{N_A}{t\ C_W} = \frac{N_A\ K_{SW}}{t\ C_{Dose}} \quad (3)$$

where C_{Dose} is the concentration in the sheets dosing the water phase. Equation 3 clearly shows that R_{SA} is proportional to K_{SW} and any uncertainty in the K_{SW} is included in C_W and, subsequently in the value of R_{SA}. The K_{SW} has a considerable uncertainty (Difilippo and Eganhouse 2010) and can easily be in the same range as the between compound variation of 32, 31 and 41 % observed for SPMD, SR and LDPE respectively. The K_{SW} uncertainty can also explain why the expected decrease of R_{SA} with increasing hydrophobicity (and Mw) (Booij *et al*. 2003, Huckins *et al*. 2006 Rusina *et al*. 2010) is not visible.

3.4. Evaluation of TWA concentrations

3.4.1. Comparison of TWA concentrations

The TWA concentrations of PCBs in water were calculated from PCB uptake and PRC release (except for CFIS) measured for triplicate samplers exposed during 14 days for Chemcatcher and CFIS and during 28 days for SPMD, SR and LDPE strip. The calculations of TWA concentrations were first carried out as indicated by the developer of the sampling system as listed in Table 2 and Supplementary data (S3). For Chemcatcher, the model used for calculations was stated to be only applicable for compounds with logK_{OW} ranging from 3.7 to 6.8 (Vrana *et al*. 2007) but was applied also for more hydrophobic PCBs. For SPMD, LDPE strip and Chemcatcher, TWA concentrations of PCBs in water were calculated using only PRCs whose dissipation was between 20 and 80 % in order to prevent quantification problems due to insignificant release or concentrations close to LOQ. In contrast, all PRCs spiked in SR were used (Booij and Smedes, 2010). PRC-based sampling rates for SPMD, SR and LDPE strip are given in Supplementary data (S6). Required logK_{SW} for SR and LDPE strip were available in the

353 literature, mostly experimentally determined and modeled for six of the dioxin-like PCBs
354 (Smedes *et al*. 2009). For SPMD and Chemcatcher, logK_{SW} were determined from
355 empirical relationships as a function of logK_{OW} (Huckins *et al*. 2006, Vrana *et al*. 2006). For
356 CFIS, with no PRC used, TWA concentrations of indicator PCBs were computed with R_S
357 previously determined in laboratory calibration experiments (Llorca *et al*. 2009). Sampling
358 rates of dioxin-like PCBs were extrapolated from R_S of indicator PCBs having the same
359 number of chlorine atoms.

360 For Chemcatcher, repeatability between triplicate samplers was satisfying (12-22
361 %) but TWA concentrations of PCBs in water were up to 12 times higher than the average
362 of the four other samplers, suggesting that the use of the model (Vrana *et al*. 2006, 2007)
363 for hydrophobic compounds was not applicable for PCBs. Chemcatcher results were
364 therefore not included in the comparison between samplers.

365 Figure 3 shows the ratios of the TWA concentrations of PCBs calculated from the
366 four samplers and the nominal concentrations of PCBs in water derived from
367 concentrations in dosing sheets. Overall, concentrations computed from the four samplers
368 were reasonably close. The highest difference was observed for PCB 153 with a factor of
369 eight between the lowest calculated concentration (0.5 ng/L for LDPE strip) and the
370 highest (4.0 ng/L for CFIS). For SPMD, calculated TWA concentrations of the 19 PCBs
371 were between 0.8 and 2.1 times (average 1.5) the nominal concentrations in water.
372 Repeatability between triplicate samplers was between 8 and 26 % (average 15 %). The
373 same tendency was observed for SR, with calculated TWA concentrations between 1.5
374 and 2.8 times (average of 2.1) higher than the nominal concentrations in water, and with
375 RSD for triplicate samplers between 10 and 27 % (average 18 %). In contrast, for LDPE
376 strip, TWA concentrations were found between 0.4 and 1.2 times (average of 0.7) the
377 nominal concentrations in water with RSD between 7 and 22 % (average 13 %). Finally,
378 for CFIS, TWA concentrations were between 0.5 and 5.0 times (average 1.5) the nominal

379 concentrations in water and RSD between 2 and 80 % (average 21 %). For CFIS, PCBs
380 180 and 153 were mainly responsible for high mean RSD and TWA concentration, as
381 illustrated in Figure 3.

382 In summary, except for Chemcatcher, TWA concentrations of PCBs computed from
383 the different samplers were in agreement with concentrations in water calculated from
384 dosing sheets and good repeatability was found. These results are very satisfying
385 considering that they were obtained from different samplers, processed in different
386 laboratories and obtained with different calculations methods (i.e. different models,
387 different selection criteria of PRCs and logK_{SW} either experimentally determined or
388 extrapolated from empirical relationship function of logK_{OW}).

389

390 *3.4.2. Influence of the data treatment method (PRC and K_{SW}) for SPMD, SR and LDPE*
391 *strips*

392 The method of calculation (the model used, the selection and the use of PRCs, the
393 choice of the partition coefficients) influences the TWA concentration results for a given
394 sampler. In order to observe the influence of these parameters, TWA concentrations for
395 the 28 days exposures were calculated again for SPMD, SR and LDPE with alternative
396 methods.

397 For SPMD, initial logK_{SW} used in part 3.4.1., obtained from the empirical model of
398 Huckins *et al*. (2006), was replaced by new logK_{SW} according to Booij and Smedes (2011).
399 For SPMD and LDPE, we also tested to use all the PRCs spiked (see Table 1), following
400 the method of Booij and Smedes (2010). At the opposite, for SR, instead of using all the
401 PRCs, we considered only PRCs whose release after 28 days were between 20 and 80 %;
402 three PRCs (i.e. PCBs 2, 3 and 10) were then retained. TWA concentration from SR were
403 then calculated with PCBs 2, 3 and 10 and were found similar (RSD < 7 %), we only
404 present results obtained with PCB 10 because of a smaller RSD.

405 The ratios of the TWA concentrations on the concentrations of PCBs in water
406 calculated from dosing sheets are illustrated in Figure 4. For SPMD, in spite of using a
407 different relation for logK_{SW}, the differences on TWA concentrations were relatively small
408 (slight decrease with Ksw from Booij and Smedes, 2011). Indeed, the relation mainly
409 affects the more hydrophobic PCBs but not the PRCs (low hydrophobic PCBs).
410 Consequently, the sampling rate used to calculate C_W for the more hydrophobic PCBs is
411 slightly affected. Besides, the use of all the PRCs spiked in SPMD, instead of only one,
412 resulted in a very slight increase of TWA concentrations. For SR, the change in PRC used
413 induced a slight decrease of the TWA concentrations. Indeed, by using only one PRC,
414 these concentrations were between 1.1 and 2.1 times higher than the concentrations in
415 water (with an average of 1.6), instead of 2.1 found with all PRCs. For LDPE, the use of all
416 PRCs instead of only one resulted in slight increase of TWA concentrations.
417 Note that the variations in PRC choice above are for illustration. We recommend
418 using all PRCs for R_S estimation as no information is lost and uncertainties in logK_{SW} of the
419 PRC may be averaged out. However uncertainty in logK_{SW} remains an issue also for target
420 compounds. Measurement of accurate logK_{SW} is very difficult, experimental logK_{SW} values
421 are scarce and can be considerably scattered (Difilippo and Eganhouse, 2010). Models
422 predicting the logK_{SW} from logK_{OW} can have typical uncertainties ranging from 0.13-0.36
423 log unit (factor 1.4-2.4) (Booij and Smedes 2010). Moreover, the selection of other logK_{OW}
424 sources than those used for creating the predictive relations, may contribute to further
425 variability. Considering the above, the results reported here for the three membrane
426 samplers with a general variation of about a factor two are very satisfying, as they were
427 based on logK_{SW} either experimentally determined or from an empirical relationship with
428 logK_{OW}, different calculations models, different selection criteria of PRCs, and obtained
429 from different samplers, processed in different laboratories.
430

4. Conclusions

The designed calibration system for the simultaneous exposure of the five integrative samplers enabled to maintain sufficiently constant exposure conditions up to three months and PCB uptake in samplers showed overall good linearity with time and repeatability. The three membrane samplers (SR, LDPE and SPMD) are efficient to accumulate large amounts of PCBs and have great potential for low LOQ when used in water monitoring programs. TWA concentrations of PCBs in water calculated from the different samplers were in good agreement, except for Chemcatcher whose model for hydrophobic compounds (Vrana *et al*., 2006, 2007) was not proven to be suitable for PCBs in this study. For the four other samplers, despite the variety of materials, geometries and calculation methods, TWA concentrations were generally between 0.5 and 3 times the nominal water concentrations calculated from dosing sheets, which is quite satisfying in the domain of ultra-trace (ng/L level) micropollutants analysis in aquatic environments.

At last, it must be underlined that TWA concentrations in water can be calculated through the use of various models, PRCs and logK_{SW} values. For the transfer of these sampling tools to water basin managers, it is therefore of crucial importance that protocols detail the calculation methods. Moreover, any results on TWA concentration (from the literature or *in situ* monitoring programs) should be accompanied with detailed information on calculation method used (i.e. model and equations, PRCs and logK_{SW} values).

Intercomparison exercises on sampling and processing, but also the determination of partition coefficients K_{sw}, should enable to progress on the knowledge and harmonization of practices for the use of integrative sampling, especially for priority chemical monitoring and regulatory programs in compliance with the Water Framework Directive and the Marine Strategy Framework Directive. To be noted that the challenge of PRC strategy is even more crucial for integrative samplers used for hydrophilic compounds (i.e. POCIS, polar Chemcatcher, …), since very few PRC candidates have

been found up to date. Further outputs of the ECLIPSE project should follow dealing on the application and comparison of these five integrative samplers *in situ*.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found in the online version.

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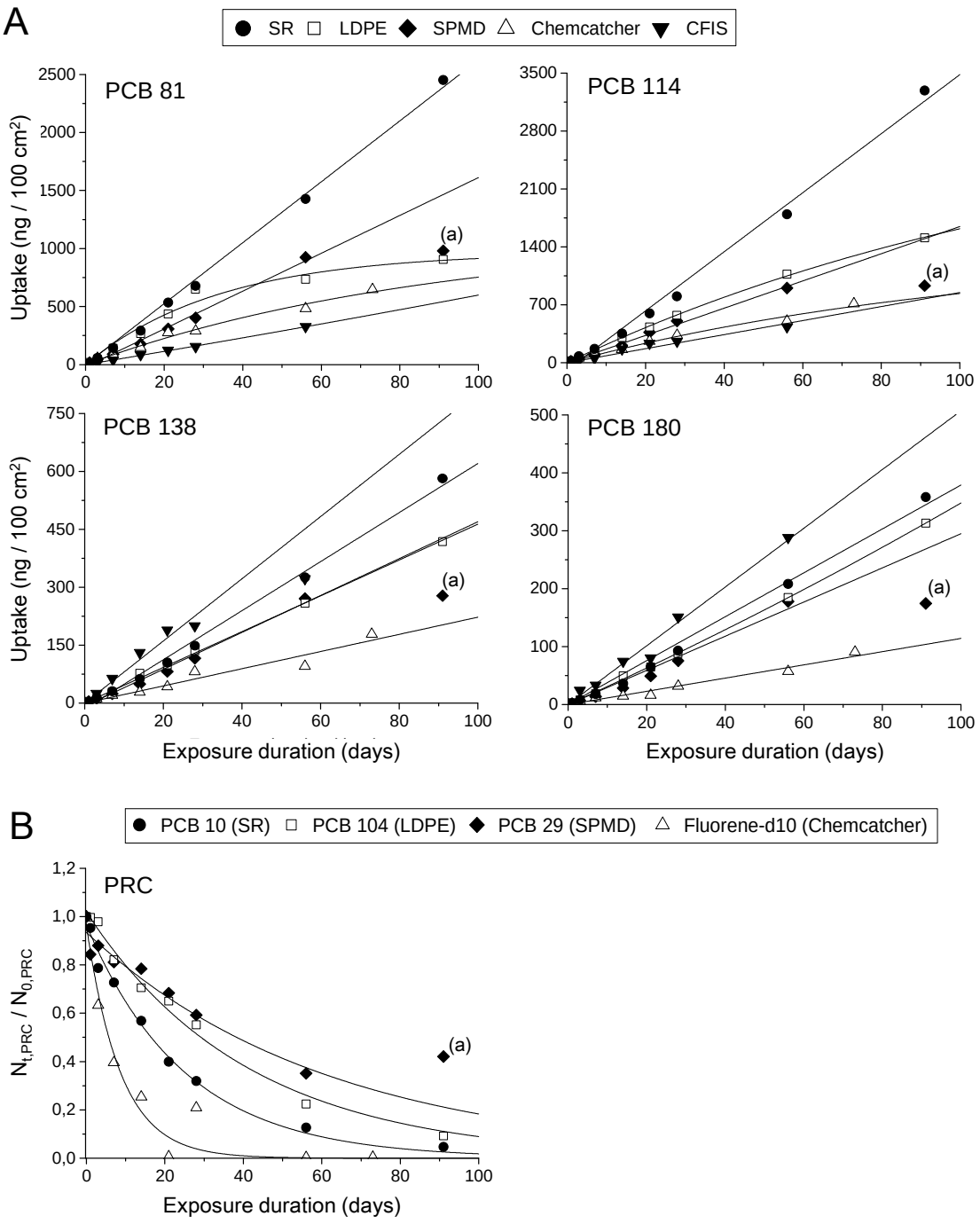
590

Figures

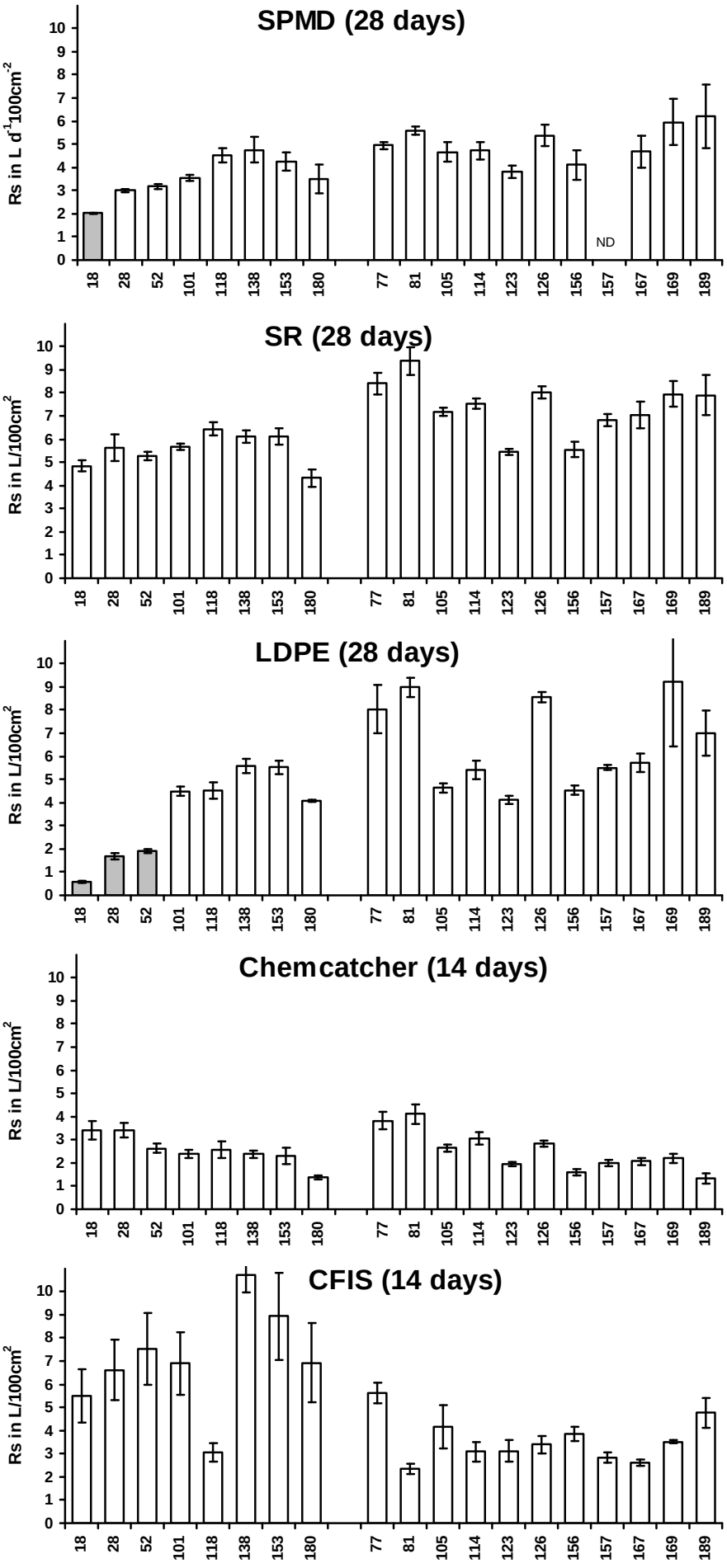
Fig. 1. Surface area normalized uptake (N_A) plotted versus time (panel A) for PCB 81 (4 Cl atoms), PCB 114 (5 Cl atoms), PCB 138 (6 Cl atoms) and PCB 180 (7 Cl atoms) in the five integrative samplers. Uptake was normalized to a membrane surface area of 100 cm^2. Panel B shows release curves of some selected PRCs.

(a) data not used for curve fitting



599 **Fig. 2.** Surface area normalized sampling rates (R_{SA}, $L.d^{-1}.100\ cm^{-2}$) of PCBs in the five
600 integrative samplers. Error bars represent the standard deviations (n=3). R_{SA} was
601 normalized to a membrane surface area of 100 cm^2. PCB congeners are on the x-axis.
602 PCBs approaching equilibrium are represented with grey bars.
603 PCB 157 could not be quantified in SPMD because of co-eluting peaks (ND).
604
605

606


SPMD (28 days)
Rs in L d-1100cm-2
ND
SR (28 days)
Rs in L/100cm2
LDPE (28 days)
Rs in L/100cm2
Chemcatcher (14 days)
Rs in L/100cm2
CFIS (14 days)
Rs in L/100cm2
18 28 52 101 118 138 153 180 77 81 105 114 123 126 156 157 167 169 189

607 **Fig. 3.** Ratios of the time-weighted average (TWA) concentrations of PCBs calculated from
608 integrative samplers on the PCB water concentrations calculated from dosing sheets. The
609 TWA concentrations were calculated as indicated in Table 2. PCB congeners are on the x-
610 axis.
611
612

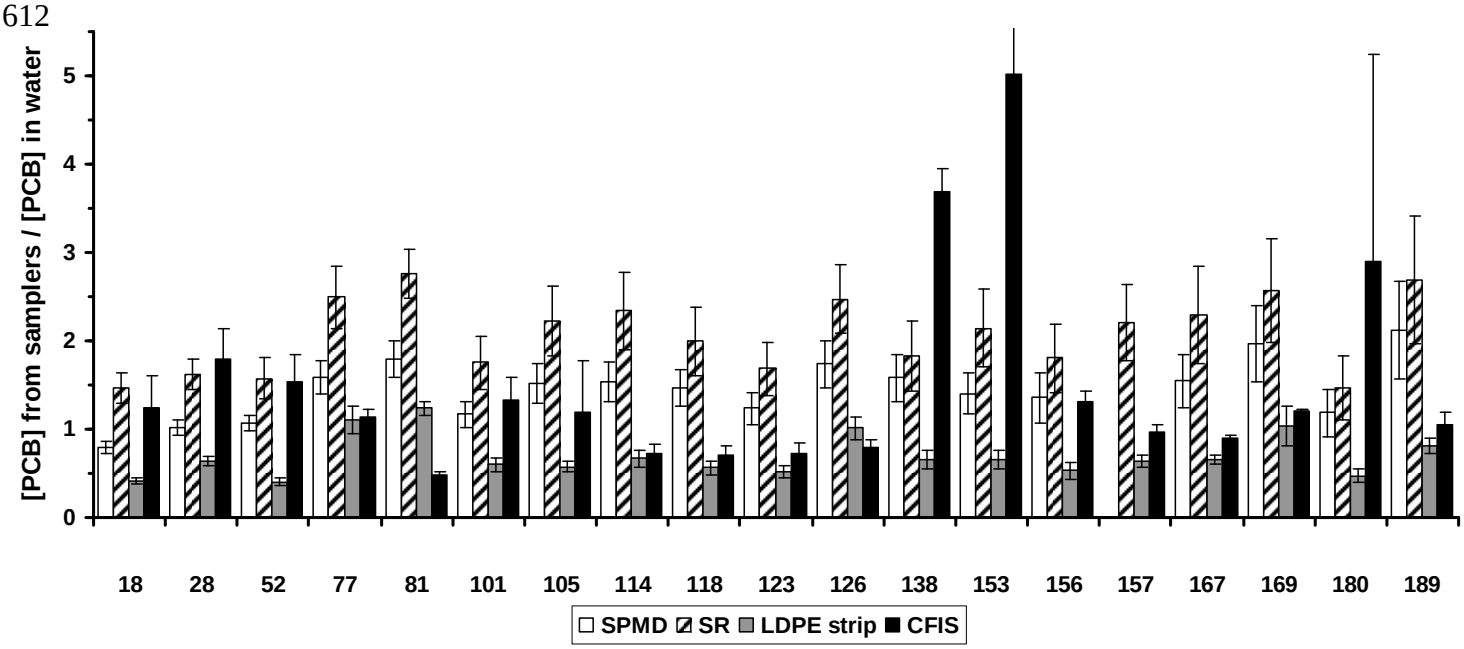
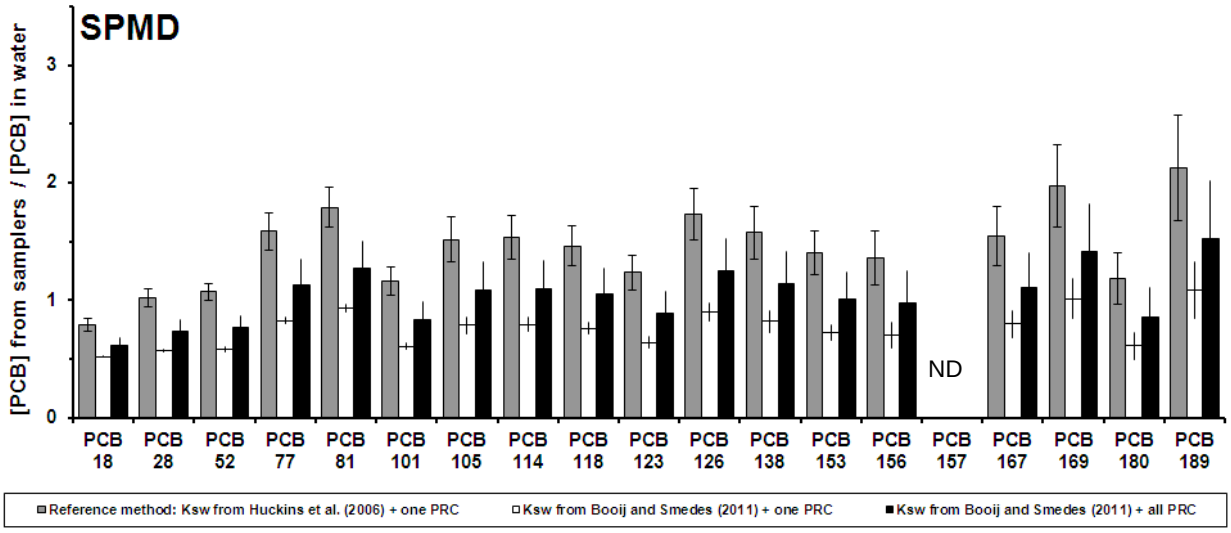


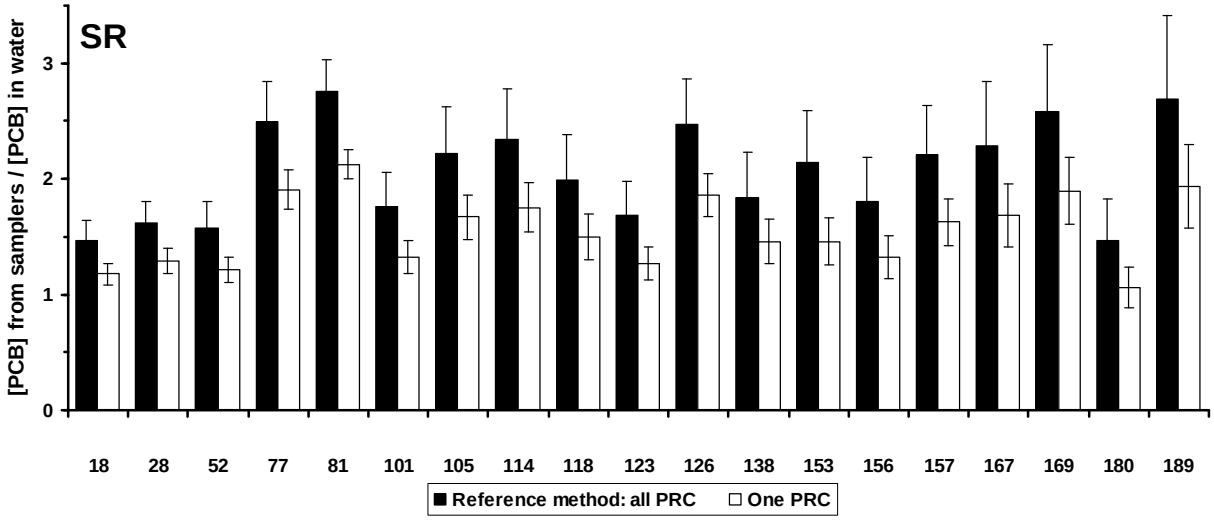
Fig. 4. Ratios of the time-weighted average (TWA) concentrations of PCBs calculated from integrative samplers on the concentrations of PCBs in water. The TWA concentrations were calculated as indicated in Table 2 (reference method) and by changing SPMD-water partition coefficient values (for SPMD) and selection criteria of PRCs (for SPMD, SR and LDPE strip). PCB congeners are on the x-axis.

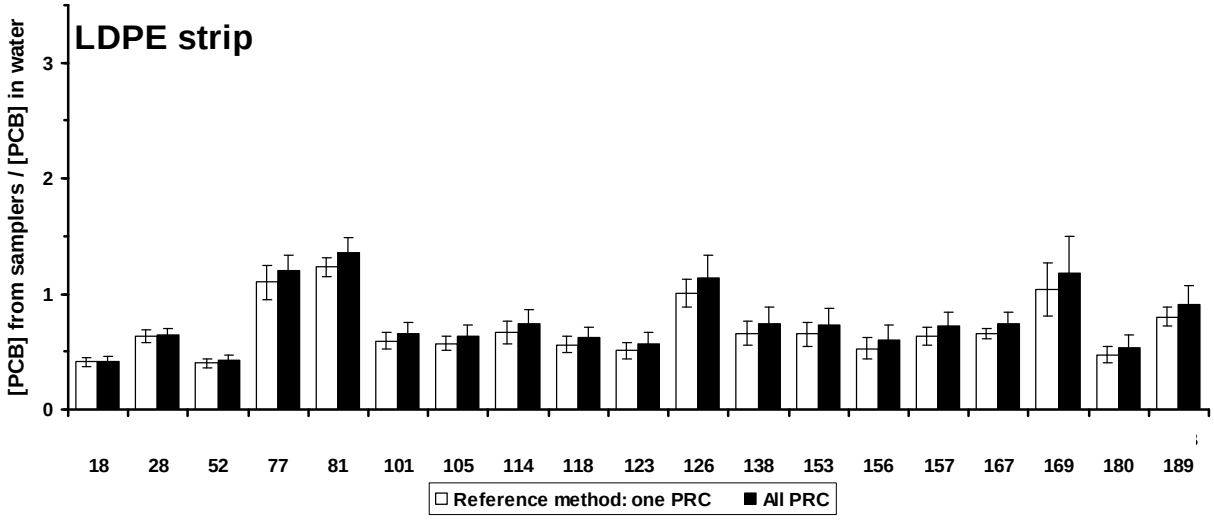
ND: not determined (PCB 157 could not be quantified in SPMD because of co-eluting peaks).


SPMD
[PCB] from samplers / [PCB] in water
0
1
2
3
ND
PCB 18
PCB 28
PCB 52
PCB 77
PCB 81
PCB 101
PCB 105
PCB 114
PCB 118
PCB 123
PCB 126
PCB 138
PCB 153
PCB 156
PCB 157
PCB 167
PCB 169
PCB 180
PCB 189
Reference method: Ksw from Huckins et al. (2006) + one PRC
Ksw from Booij and Smedes (2011) + one PRC
Ksw from Booij and Smedes (2011) + all PRC

636

637


SR
[PCB] from samplers / [PCB] in water
0
1
2
3
18
28
52
77
81
101
105
114
118
123
126
138
153
156
157
167
169
180
189
Reference method: all PRC
One PRC


LDPE strip
[PCB] from samplers / [PCB] in water
0
1
2
3
18
28
52
77
81
101
105
114
118
123
126
138
153
156
157
167
169
180
189
Reference method: one PRC
All PRC

638 **Tables**

639 **Table 1.** Main characteristics and processing steps of the five integrative samplers

	SPMD[a]	SR[b]	LDPE strip[c]	Chemcatcher[d]	CFIS[e]
Suppliers	Exposmeter	Altec Products Limited	Brentwood plastics	University of Portsmouth	LABAQUA
Receiving phase (membrane[f] , solid or liquid phase)	LDPE + Triolein	PDMS	LDPE	LDPE + C18 Empore disk + 450 µL of n-octanol	PDMS
Surface area (cm^2)	457	138	100	17	8
Weight (g)	4.5	4.1	0.39	0.62	0.144
Total volume (cm^3)	4.95	3.4	0.425	0.6	0.147
PRC spiking method	Syringe injection of isooctane solution	Soaking in water / methanol solutions	Soaking in water / methanol solutions	Percolation of aqueous solution	No PRC
PRC[g]	PCB 3, 10, 14, 29, 37, 55, 78, 104, 155, 166, 201, 204	Bip-d10, PCB 1, 2, 3, 10, 14, 21, 30, 50, 55, 78, 104, 145, 204	PCB 10, 14, 29, 104, 112, 204	Bip-d10, Ace-d10, Flu-d10, Phe-d10, Pyr-d10, B[a]a-d12	/
Extraction	Dialysis in cyclohexane	Soxhlet with methanol	Soaking in cyclohexane	Ultrasonic bath in acetone and ethyl acetate / isooctane	Thermodesorption
Analytical surrogate	PCB 34, 119, 141, 209	^{13}C labeled indicator PCB, PCB 143	PCB 30, 198, 209, TCN[h]	None	Flu-d10, Chry-d12
Purification	Florisil	None	Silica and alumina	None	None
Analytical technique	GC-ECD	GC-MS	GC-ECD for PCB_i GC-HRMS for PCB_{dl}	GC-MS	GC-MS

Chromatographic column	Restek RTX-PCB and RTX-5	Alltech AT-5MS	Agilent DB-5 and SGE HT8 for PCB_i SGE HT8 for PCB_{dl}	Varian CP-Sil 8 CB	Teknokroma TRB-5ms

[a] SPMD: semipermeable membrane device, membrane length = 91.4 cm, width = 2.5 cm, thickness = 70-95 µm ; triolein volume = 1 ml, weigth = 0.915 g.

[b] SR: silicone rubber, length = 12.5 cm, width = 5.5 cm, thickness = 500 µm.

[c] LDPE strip: low-density polyethylene strip, length = 20 cm, width = 2.5 cm, thickness = 80 µm.

[d] Chemcatcher: non-polar version, membrane diameter = 4.7 cm, thickness = 40 µm ; C18 Empore disk diameter = 4.7 cm, volume = 0.6 mL (i.e. 0.45 mL octanol + 0.15 mL C18).

[e] CFIS: continuous flow integrative sampler, 90 PDMS pieces with length = 2 mm, width = 2 mm, thickness = 400 µm or 3 Twisters® with length = 2 cm, diameter = 2 mm.

[f] LDPE: low density polyethylene, PDMS: polydimethylsiloxane.

[g] PRCs: performance reference compounds, Bip: biphenyl, Ace: acenaphthene, Flu: fluorene, Phe: phenanthrene, Pyr: pyrene, B[a]a: benzo[a]anthracene.

[h] TCN: 1,2,3,4-tetrachloronaphthalene

640 **Table 2.** Strategies (models, criteria to select PRCs and methods to evaluate logK_{SW})
641 used for the calculation of TWA concentrations of PCBs in water for each integrative
642 sampler.
643

	Model	Criteria to select PRC	Methods to evaluate $LogK_{SW}$
SPMD	Huckins et al. 2006 (water boundary layer - controlled uptake model)	PCB, used when dissipation was between 20% and 80%	empirical relationship function of $logK_{OW}$ [Huckins et al. 2006]
SR	Rusina et al. 2010 (water boundary layer - controlled uptake model)	PCB, all used with unweighted nonlinear least-squares regression [Booij and Smedes 2010]	measured and modeled [Smedes et al. 2009]
LDPE strip	Huckins et al. 2006 (water boundary layer - controlled uptake model)	PCB, used when dissipation was between 20% and 80%	measured and modeled [Smedes et al. 2009]
Chemcatcher	Vrana et al. 2007 (applicable for compounds with $3.7 < logK_{OW} < 6.8$)	PAH, used when dissipation was between 20% and 95%	empirical relationship function of $logK_{OW}$ [Vrana et al. 2006]
CFIS	none, use of predetermined R_S for PCB_l and extrapolated R_S for PCB_{dl}	none, not required	none, not required

644

Title

Comparison of five integrative samplers in laboratory for the monitoring of indicator and dioxin-like polychlorinated biphenyls in water

Authors

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Supplementary data (available online)

S1. Additional information about materials and methods

S1.1. SPMD

SPMD were purchased from Exposmeter (Tavelsjö, Sweden) and had the standard configuration, as defined by Huckins et al. (2006): an area-to-volume ratio of about 460 cm^2/ml of triolein (purity ≥ 95%), an approximate lipid-to-membrane mass ratio of 0.25 and a 70-95 µm wall thickness.

Prior to their exposure, SPMD were spiked with several PRC (Table 1). The membrane was perforated at one end and 25 µl of isooctane containing 4 mg/L of each PRC was injected with a 50 µl syringe. Membrane was then heat-sealed and SPMD were stored in air tight cans at -20℃ until exposure.

After exposure and retrieval, SPMD were stored in air tight cans at -20℃ until processing. Prior to extraction, mounting loops were cut and SPMD membranes were cleaned with Milli-Q water, wiped with paper and measured to determine their exact surface area. Recovery of accumulated PCBs was carried out by dialysis in 125 ml of cyclohexane at 15℃ during 24h in darkness. This operation was repeated one time. Dialysis was performed at 15℃ in order to reduce the amount of co-extracted material (Meadows et al. 1993). Both dialysates were combined and after addition of internal surrogates (100 ng of PCBs 34, 119, 141 and 209), the solvent was evaporated to 1 ml. Then, extracts were diluted (100 µl completed to 1 ml with cyclohexane) and purified on disposable Florisil cartridges (6 ml, 1 g) conditioned with 10 ml of cyclohexane. Extracts were loaded on the cartridges and allowed to soak during 5 min after which elution was performed with 10 ml of cyclohexane/methylene chloride 95/5 (v/v). After evaporation under nitrogen with 10 µl of n-dodecane, used as keeper, extracts were reconstituted in 1 ml of isooctane

containing 10 µg/L of 2,4,5,6-tetrachloro-m-xylene (TCX) and octachloronaphtalene (OCN), used as internal standards.

Analysis of SPMD extracts were performed with a Varian (Les Ulis, France) 3800 GC-ECD using two chromatographic columns purchased from Restek (Lisses, France), a RTX-PCB column (30 m x 0.25 mm x 0.25 µm) and a RTX-5 column (30 m x 0.25 mm x 0.25 µm). Both columns were equipped with 10 m of uncoated guard-columns. PCB 157 could not be quantified because of co-eluting peaks on both columns. All results were corrected for recovery of internal surrogates.

S1.2. Silicone rubber (SR)

Silicone rubber sheets of 60 x 60 cm and 0.5 mm thickness were purchased from Altec Products Limited (Cornwall, UK). From this large sheets sampler were prepared by cutting them at a size of 12.5x5.5 cm and were soxhlet extracted with ethylacetate for 100 h prior to use.

To measure of the exchange rate through the release of PRC, 27 exposure sheets were spiked with PRC (Table 1). Spiking was done by soaking the sheets in methanol containing the PRC and followed by adding portions of water to gradually increase the water content (Smedes and Booij, 2012). The procedure is similar to that for the dosing sheets, but starting with 300 ml of methanol. Time periods and methanol percentages were equal to the procedure described for dosing sheets (S1.6). After spiking, the sheets were washed with Milli-Q water, individually packed in diffusion closed glass jars numbered from 1 to 27 and stored at -20℃ when not exposed in the tank. After thawing, sheets were carefully wiped dry with a tissue before exposure.

Prior to analysis of the bulk samples, a one day exposure sheet was analyzed to allow estimation of appropriate dilutions ensuring later extracts to fit the calibration curve. Prior to extraction, each sheet was spiked with internal surrogates: 1000 ng of PCB 143 and up to 28 days exposure, 10 ng of ^{13}C labeled indicator PCB were added. One and three days exposures, that were performed four and two times, respectively, were considered as single exposures and extracted together. Exposed and unexposed sheets were soxhlet extracted by 120 ml of methanol for 16 hours. Extracts were Kuderna-Danish evaporated until 2 ml and 20 ml of hexane were added. By Kuderna-Danish evaporation, the methanol was azeotropically removed and consequently the extract was transferred to hexane. Hexane extracts were further concentrated to 1 ml using a gentle stream of nitrogen for short exposures and gradually diluted for longer exposures, up to 15 ml of hexane for a 90 d exposure. To each extract TCN was added to obtain a concentration at 100 ng/ml.

Extracts were analysed on an Agilent (Palo Alto, CA, USA) HP 6890 Series GC-MS with an Agilent HP 5973N mass selective detector. The column was an Alltech AT-5MS (30 m x 0.25 mm x 0.25 µm) from Grace (Deerfield, IL, USA). Selected Ion Monitoring (SIM) mode was applied for quantification using appropriate masses and two masses were monitored for each PCB. All calculations were done based on TCN as an internal standard.

S1.3. LDPE strips

LDPE strips were prepared from additive-free LDPE lay-flat tubing purchased from Brentwood plastics (MO, USA). Single layered strips were obtained by cutting sections of the tubing twice along the side edges. A mounting loop was prepared at each extremity of the strips and removed before the whole analytical treatment.

Prior to use, LDPE strips were pre-extracted twice by soaking in cyclohexane overnight and then spiked with six PRC (Table 1) following the method described by Booij et al. (2002). Briefly, LDPE strips were soaked overnight in a PRC solution in methanol/water 80/20 (v/v). Spiked strips were stored at -20℃ until exposure.

After exposure, LDPE strips were kept in the dark at -20℃ until further treatment. The mounting loops were removed and strips were rinsed with Milli-Q water. Strips were then extracted twice by soaking overnight in cyclohexane. Surrogate standards (PCBs 30, 198, 209 and TCN) were spiked into cyclohexane at the beginning of the extraction. After extraction, strips were removed from cyclohexane and allowed to dry for weight determination. The combined cyclohexane extract was concentrated to 4 ml and an aliquot of 200µl was taken for dioxin-like PCB analysis. The exact volume was controlled gravimetrically by weighting both extracts. The analytical protocols for cleanup and analysis of indicator PCBs and PRCs have been described previously (Johansson et al. 2006). Briefly, the clean-up and fractionation of all extracts were made by adsorption chromatography on a two layer silica/alumina column. The first fraction eluted with hexane was analysed for PCB by GC-ECD according to the procedure described earlier (Johansson et al. 2006). For dioxin-like PCB analysis, separation of coplanar (non-ortho) PCB from non-planar PCB was achieved on an activated mixture of Florisil/Carbopack C/Celite 545.

Analysis of LDPE extracts for indicator PCBs were performed with a Varian (Les Ulis, France) 3800 GC fitted with two electron capture detector and two columns of different polarities: a DB-5 column (60 m x 0.25 mm x 0.25 µm) from Agilent (Palo Alto, CA, USA) and a HT8 column (50 m x 0.25 mm x 0.25 µm) from SGE Europe Ltd (Milton Keynes, UK). All PCB congeners were quantified on both columns and the

reported result was chosen for each non-coeluting congener on the appropriate column. Dioxin-like PCB analysis were conducted at LABERCA laboratory (Nantes, France) according the method of Costera et al. (2006). Separation of coplanar (non-ortho) PCBs from non-planar PCBs was achieved on an activated mixture of Florisil/Carbopack C/Celite 545. Analyses were performed by GC-HRMS (gas chromatograph (HP-7890) from Hewlett Packard -Palo Alto, CA, USA; mass spectrometer (JMS-800D) from Jeol - Japan) equipped with a a HT8-PCB capillary column (60 m x 0.25 mm x 0.25 µm) from SGE Analytical Science (Australia).

S1.4. Chemcatcher

Chemcatchers were purchased from the University of Portsmouth and were prepared according to their own protocol (University of Portsmouth, 2009).

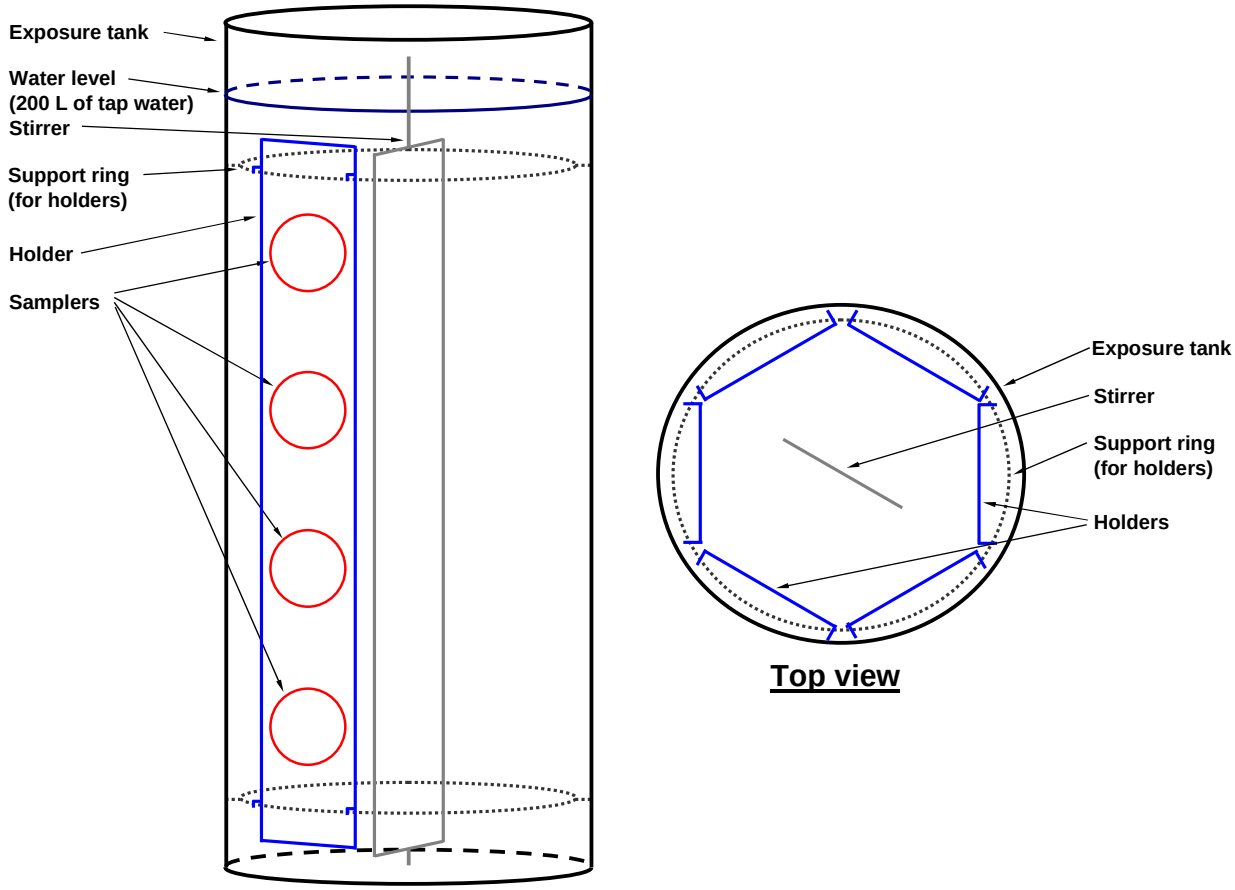
Before use, C18 Empore disks were soaked in methanol overnight in a clean glass beaker. Then, they were placed on a 47 mm diameter disk vacuum manifold platform and 50 ml of methanol were slowly passed through the disks, followed by 150 ml of ultrapure water. Then 250 ml of water spiked with 300 µl of PRC (Table 1) standard solution at 2 µg/ml in methanol was filtered through the disks. The Empore disks were then dried under vacuum during 30 min and put on the sampler PTFE supports. Then, 1 ml of 45% (v/v) n-octanol in methanol was applied evenly to the surface of each C18 Empore disk. The resulting volume of n-octanol was 450 µl. The LDPE membranes (pre-cleaned by soaking in n-hexane during 24h and dried) were put on the top and any air bubbles were smoothed away from between the two layers by gently pressing the top surface of the membrane using a clean paper tissue. The PTFE supporting disks were placed in the sampler bodies and fixed in place to form

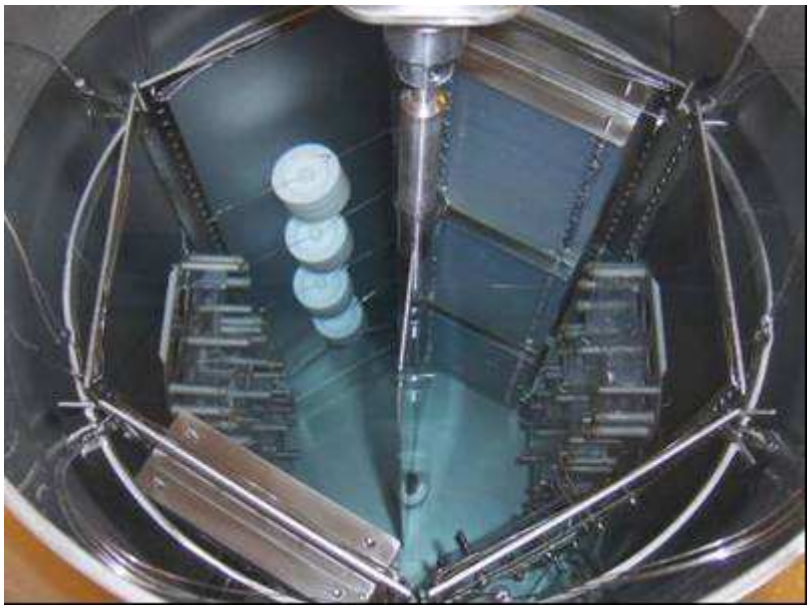
141 a watertight seal between the membrane and the top section of the sampler (Vrana
142 et al. 2005; Vrana et al. 2006). Chemcatchers were stored at -20℃ until exposure.
143 After exposure, samplers were rinsed with ultrapure water, carefully
144 disassembled and LDPE membranes were removed and rinsed with acetone. PCBs
145 were extracted from the Empore disks with 5 min of ultrasonic bath in acetone
146 followed by 5 min in ethyl acetate/2,2,4-trimethylpentane 50/50 (v/v). The disks were
147 then removed and the solvent extracts, combined with the LDPE membrane rinsates,
148 were filtered through a drying cartridge containing sodium sulfate. Extracts were
149 reduced under nitrogen at 450 µl and transferred to 2 ml vials prior to analysis with a
150 solution of chrysene-d12 (internal standard) in n-octanol. The final volume was
151 adjusted to 500 µl with n-octanol (University of Portsmouth, 2009; Vrana et al. 2005).
152 Sampler extracts were analysed with a Varian (Les Ulis, France) 240 GC-
153 MS/MS system using a Varian CP-SIL 8 CB (50 m x 0.25 mm x 0.25 µm) capillary
154 column equipped with a guard-column.
155
156 *S1.5. CFIS*
157 The CFIS device was developed by Labaqua and was prepared with PDMS
158 pieces or PDMS in Twister® format from Gerstel (Mülheim an der Ruhr, Germany).
159 The PDMS pieces were obtained by cutting a PDMS tubing in pieces of 2 x 2 mm.
160 Every device contains 90 PDMS pieces or 3 Twisters®. Prior to use, Twisters® were
161 conditioned in an empty thermodesorption tube at 300ºC for 4 h with an helium flow
162 of 75 ml/min.
163 After exposure, the Twisters® or PDMS pieces were removed from the CFIS,
164 gently dried with a paper tissue and finally introduced in glass desorption tubes.

165 Analysis were performed by thermodesorption-GC-MS using an Agilent (Palo
166 Alto, CA, USA) 6890 GC - 5973 MS system equipped with a Gerstel thermal
167 desorption unit TDS-2 and connected to a Gerstel programmed-temperature
168 vaporization (PTV) injector CIS-4 Plus by a heated transfer line. Analysis were
169 carried out using an TRB-5ms column (30 m x 0.25 mm x 0.25 µm) from Teknokroma
170 (Barcelona, Spain).
171
172 *S1.6. Dosing sheets*
173 Silicone rubber sheets of 60 x 60 cm purchased from Altec Products Limited
174 (Cornwall, UK) were cut in pieces of 5 x 15 cm and four holes were pinched in the 4-
175 12 cm middle part. A total of 1.1 kg of dosing sheets, corresponding to a surface area
176 of around 3.5 m^2, were prepared this way. Prior to use, sheets were soxhlet extracted
177 with ethylacetate for one week and subsequently, the ethylacetate was extracted
178 from the sheets by two times 4 h with 2 L of methanol. Then the dosing sheets were
179 immersed in 1.6 L of methanol and the custom-made spiking solution obtained from
180 CIL Cluzeau (Courbevoie, France) was added. This solution contained PCB 18 (0.34
181 mg), PCB 28 (0.60 mg), PCB 52 (0.9 mg), PCB 77 (2.2 mg), PCB 81 (3.3 mg), PCB
182 101 (2.28 mg), PCB 105 (2.6 mg), PCB 114 (9.6 mg), PCB 118 (2.6 mg), PCB 123
183 (2.7 mg), PCB 126 (3 mg), PCB 138 (6 mg), PCB 153 (5 mg), PCB 156 (5 mg), PCB
184 157 (7 mg), PCB 167 (8 mg), PCB 169 (10 mg), PCB 180 (10 mg), PCB 189 (7 mg)
185 in 5 ml of ethylacetate. After 6 h of shaking, water was added to obtain a 90%
186 methanol solution that was shaken for 32 h. Dilution with water was continued by
187 10% steps as follows: 36 h at 80%, 48 h at 70%, 56 h at 60% and 80 h at 50%
188 methanol. Then the water/methanol mixture was discarded and sheets were washed

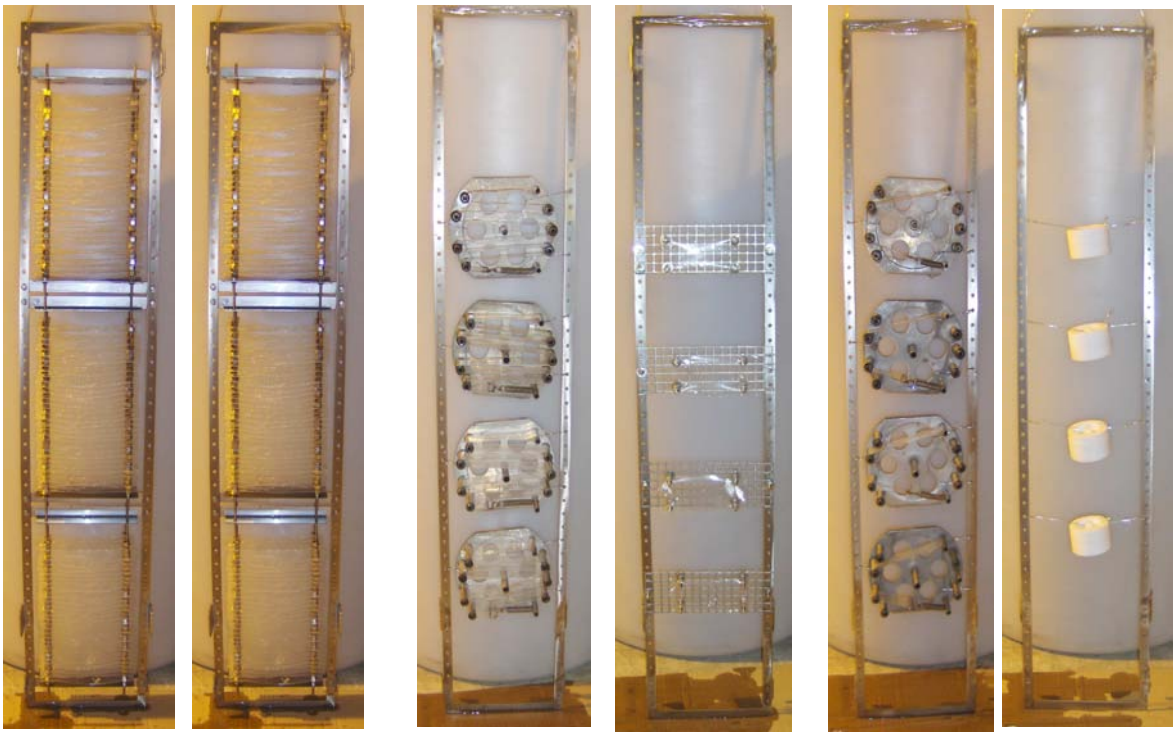
189 once with milli-Q water. Two quality control samples were taken just after spiking and
190 another one after the mounting of dosing sheets in the tank.
191 Before analysis, samples of dosing sheets were stored in glass jars at –20℃.
192 For each analysis, about 1 g of dosing sheet was extracted with 50 ml of methanol in
193 a glass jar with an aluminum foil lined lid shaked overnight at 100 rpm. Prior to
194 extraction, 1000 ng of PCB 143 was added as an internal surrogate. The extraction
195 was repeated and the combined extract was Kuderna Danish evaporated to about 2
196 ml followed by addition of 20 ml of hexane and Kuderna Danish evaporation was
197 repeated. The obtained hexane extract was transferred to a 15 ml vial and brought to
198 10 ml on weight basis. From the extract, 1 ml (on weight basis) was transferred to a
199 vial and 100 ng of TCN (1,2,3,4-tetrachloronaphtalene) were added. Further, a
200 dilution was made by measuring 100 µl into a vial with 100 ng of TCN and adding
201 hexane to 1 ml. Extracts were analysed as described for silicone rubber exposure
202 sheets (S1.2).
203

S2. Scheme and pictures of the exposure device (height = 120 cm, diameter = 47 cm).





Top view



The six holders with passive samplers (from the left to the right : 2 dosing sheets as source of contamination, 1 SPMD, 1 SR, 1 LDPE, 1 Chemcatcher)

CFIS outside the tank

S3. Detailed calculations of TWA concentrations of PCBs in water

$N_{t,i}$: amount of compound i accumulated in the sampler at time t

V_s : volume of sampler

V_i : molecular volume of compound i

M_s: mass of the sampler

$K_{ow,\,i}$: octanol-water partition coefficient of compound i

A_s : surface area of the sampler

MW_i: molecular weight of compound i

S3.1. SPMD

1. Calculation of PRC release rate constant, $k_{e,PRC}$ (day^{-1}):

$$k_{e,PRC} = -\frac{\ln\left(N_{t,PRC} / N_{0,PRC}\right)}{t}$$

2. Calculation of SPMD-water partition coefficient, $K_{sw,i}$ [Huckins et al. 2006]:

$$\log K_{SW,i} = -2.61 + 2.321 \log K_{OW,i} - 0.1618\left(\log K_{OW,i}\right)^2$$

3. Calculation of PRC sampling rate, $R_{S,PRC}$ (L.day^{-1}):

$$R_{S,PRC} = V_S\, K_{SW,PRC}\, k_{e,PRC}$$

4. Calculation of analyte i sampling rate, $R_{S,i}$ (L.day^{-1}):

$$R_{S,i} = R_{S,PRC}\left(\frac{V_{PRC}}{V_i}\right)^{0.39}$$

5. Calculation of analyte time-weighted average concentration in water, $C_{W,i}$ (ng/L):

$$C_{W,i} = \frac{N_{t,i}}{V_S \; K_{SW,i} \left(1 - \exp\left(- \frac{R_{S,i} \; t}{V_S \; K_{SW,i}} \right) \right)}$$

6. Calculation of analyte linear uptake phase duration, $t_{1/2,i}$ (day):

$$t_{1/2,i} = \frac{\ln 2 \; V_S \; K_{SW,i}}{R_{S,i}} = \frac{\ln 2}{k_{e,i}}$$

S3.2. SR

1. Estimation of F through nonlinear regression by fitting the measured release of PRC with modeled data as a function of K_{pw} and $MW^{0.47}$. [Booij and Smedes, 2010]

$$N_{t,PRC} / N_{0,PRC} = \exp\left(- \frac{A_S \; MW_{PRC}^{-0.47} \; F \; t}{M_S \; K_{PW}} \right)$$

2. Calculation of analyte time-weighted average concentration in water, $C_{W,i}$ (ng/L):

$$C_{W,i} = \frac{N_{t,i}}{M_S \; K_{PW} \left(1 - \exp\left(- \frac{A_S \; MW_i^{-0.47} \; F \; t}{M_S \; K_{PW}} \right) \right)}$$

3. Calculation of analyte linear uptake phase duration, $t_{1/2,i}$ (day):

$$t_{1/2,i} = \frac{\ln 2 \; M_S \; K_{PW,i}}{A_S \; MW^{-0.47} F} = \frac{\ln 2}{k_{e,i}}$$

S3.3. LDPE

1. Calculation of PRC release rate constant, $k_{e,PRC}$ (day^{-1}):

$$k_{e,PRC} = -\frac{\ln\left(N_{t,PRC} / N_{0,PRC}\right)}{t}$$

2. Calculation of LDPE-water partition coefficient, $K_{PW,i}$ [Smedes et al. 2009]:

$$\log K_{PW,i} = 0.0141\ MW_i + 0.90\ MPF_i + 1.06\ \left(+ 0.21\ \textit{for tetra–ortho substituted PCB}\right)$$

(with $MPF = \frac{\textit{number of } (\textit{meta} + \textit{para}) \textit{chlorine atoms}}{\textit{total number of chlorine atoms}}$, meta-para chlorine fraction)

3. Calculation of PRC sampling rate, $R_{S,PRC}$ (L.day-1):

$$R_{S,PRC} = M_S\ K_{PW,PRC}\ k_{e,PRC}$$

4. Calculation of analyte i sampling rate, $R_{S,i}$ (L.day-1):

$$R_{S,i} = R_{S,PRC}\left(\frac{V_{PRC}}{V_i}\right)^{0.39}$$

5. Calculation of analyte time-weighted average concentration in water, $C_{W,i}$ (ng/L):

$$C_{W,i} = \frac{N_{t,i}}{M_S\ K_{PW,i}\left(1 - \exp\left(-\frac{R_{S,i}\ t}{M_S\ K_{PW,i}}\right)\right)}$$

6. Calculation of analyte linear uptake phase duration, $t_{1/2,i}$ (day):

290 $$t_{1/2,i} = \frac{\ln 2 \; M_S \; K_{PW,i}}{R_{S,i}} = \frac{\ln 2}{k_{e,i}}$$

291

292

293 *S3.4. Chemcatcher*

294

295 1. Calculation of PRC release rate constant, $k_{e,PRC}$ (day^{-1}):

296 $$k_{e,PRC} = -\frac{\ln\left(N_{t,PRC} / N_{0,PRC}\right)}{t}$$

297

298 2. Calculation of Chemcatcher-water partition coefficient, $K_{DW,i}$ [Vrana 2006]:

299 $$\log K_{DW,i} = 1.382 \log K_{OW,i} - 1.77$$

300

301 3. Calculation of PRC sampling rate, $R_{S,PRC}$ (L.day-1):

302 $$R_{S,PRC} = V_S \; K_{DW,PRC} \; k_{e,PRC}$$

303

304 4. Calculation of analyte sampling rate, $R_{S,i}$ (L.day-1) [Vrana 2007]:

305 $$\log R_{S,i} = P_i + 22.755 \log K_{OW,i} - 4.061 \left(\log K_{OW,i}\right)^2 + 0.2318 \left(\log K_{OW,i}\right)^3$$

306 *Pi* : a factor taking into account environmental conditions and determined from R_s of

307 PRC [Pi = log $R_{S,\ PRC}$ -22.775 log $K_{ow,PRC}$ +4.061 (log $K_{ow,PRC}$)^2 -0.2318 (log

308 $K_{ow,PRC}$)^3]

309

310 5. Calculation of analyte time-weighted average concentration in water, $C_{W,i}$ (ng/L):

311 $$C_{W,i} = \frac{N_{t,i}}{V_S\ K_{DW,i}\left(1-\exp\left(-\frac{R_{S,i}\ t}{V_S\ K_{DW,i}}\right)\right)}$$

312

313 6. Calculation of analyte linear uptake phase duration, $t_{1/2,i}$ (day):

314 $$t_{1/2,i} = \frac{\ln 2\ V_S\ \ K_{DW,i}}{R_{S,i}} = \frac{\ln 2}{k_{e,i}}$$

315

316

317 *S3.5. CFIS*

318

319 1. Calculation of analyte time-weighted average concentration in water, $C_{W,i}$ (ng/L):

320 $$C_W = \frac{N_{t,i}}{R_{S,i}\ t}$$

321

322 2. Calculation of analyte linear uptake phase duration, $t_{1/2,i}$ (day):

323 $$t_{1/2,i} = \frac{\ln 2\ V_S\ \ K_{SW,i}}{R_{S,i}} = \frac{\ln 2}{k_{e,i}}$$

324

S4. Results of the physicochemical analysis of water sampled during exposure

Day	Temperature (℃)	pH	Conductivity (µS/cm)	DOC[a] (mg/L)
D0	22.61	7.7	380	1.50
D3	22.61	7.3	380	1.20
D7	22.61	7.8	375	1.90
D17	22.61	7.5	375	1.35
D21	22.63	7.5	380	1.80
D28	22.60	7.7	375	3.25
D42	22.60	7.2	355	4.50
D56	22.59	7,0	325	5.15
D70	22.65	7.5	320	5.15
D91	22.65	7.6	310	4,70

[a] DOC: dissolved organic carbon

330 S5. PRC-based linear uptake phase durations of PCBs (days)

331

	Log K_{OW}[a]	SPMD	SR	LDPE strip
PCB 18	5.24	27	43	3
PCB 28	5.67	46	84	5
PCB 52	5.84	57	159	12
PCB 77	6.36	86	318	34
PCB 81	6.36	86	318	34
PCB 101	6.38	90	473	47
PCB 105	6.65	103	661	70
PCB 114	6.65	103	610	70
PCB 118	6.74	106	653	70
PCB 123	6.74	106	610	70
PCB 126	6.89	110	819	107
PCB 138	6.83	112	1306	170
PCB 153	6.92	114	1459	170
PCB 156	7.18	117	1305	239
PCB 157	7.18	117	1649	239
PCB 167	7.27	116	1649	239
PCB 169	7.42	114	2108	338
PCB 180	7.36	118	2437	589
PCB 189	7.71	108	4395	795

332 [a] values from Hawker and Connell (1988)

333

334 S6. PRC-based sampling rates of PCBs (L/day/100cm2)

335

	Log K_{OW}[a]	SPMD	SR	LDPE strip
PCB 18	5.24	3.6 ± 0.3	4.2 ± 0.7	10.0 ± 1.2
PCB 28	5.67	3.6 ± 0.3	4.2 ± 0.7	10.0 ± 1.2
PCB 52	5.84	3.5 ± 0.3	4.0 ± 0.6	9.6 ± 1.2
PCB 77	6.36	3.5 ± 0.3	4.0 ± 0.6	9.6 ± 1.2
PCB 81	6.36	3.5 ± 0.3	4.0 ± 0.6	9.6 ± 1.2
PCB 101	6.38	3.4 ± 0.3	3.8 ± 0.6	9.4 ± 1.2
PCB 105	6.65	3.4 ± 0.3	3.8 ± 0.6	9.4 ± 1.2
PCB 114	6.65	3.4 ± 0.3	3.8 ± 0.6	9.4 ± 1.2
PCB 118	6.74	3.4 ± 0.3	3.8 ± 0.6	9.4 ± 1.2
PCB 123	6.74	3.4 ± 0.3	3.8 ± 0.6	9.4 ± 1.2
PCB 126	6.89	3.4 ± 0.3	3.8 ± 0.6	9.4 ± 1.2
PCB 138	6.83	3.3 ± 0.3	3.6 ± 0.6	9.1 ± 1.2
PCB 153	6.92	3.3 ± 0.3	3.6 ± 0.6	9.1 ± 1.2
PCB 156	7.18	3.3 ± 0.3	3.6 ± 0.6	9.1 ± 1.2
PCB 157	7.18	3.3 ± 0.3	3.6 ± 0.6	9.1 ± 1.2
PCB 167	7.27	3.3 ± 0.3	3.6 ± 0.6	9.1 ± 1.2
PCB 169	7.42	3.3 ± 0.3	3.6 ± 0.6	9.1 ± 1.2
PCB 180	7.36	3.2 ± 0.3	3.4 ± 0.6	8.9 ± 1.2
PCB 189	7.71	3.2 ± 0.3	3.4 ± 0.6	8.9 ± 1.2

a values from Hawker and Connell (1988)

336

337

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