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# Advancing the use of passive sampling in risk assessment and management of sediments contaminated with hydrophobic organic chemicals: Results of an international ex situ passive sampling inter-laboratory comparison

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48 **Abstract**

49 This paper presents the results of an international inter-laboratory comparison on ex situ  
50 passive sampling in sediments. The main objectives were to map the state of the science in  
51 passively sampling sediments, identify sources of variability, provide recommendations and  
52 practical guidance for standardized passive sampling, and advance the use of passive  
53 sampling in regulatory decision making by increasing confidence in the use of technique.  
54 The study was performed by a consortium of 11 laboratories and included experiments with  
55 14 passive sampling formats on 3 sediments for 25 target chemicals (PAHs and PCBs). The  
56 resulting overall inter-laboratory variability was large (a factor of ~10), but standardization  
57 of methods halved this variability. The remaining variability was primarily due to factors not  
58 related to passive sampling itself, i.e., sediment heterogeneity and analytical chemistry.  
59 Excluding the latter source of variability, by performing all analyses in one laboratory,  
60 showed that passive sampling results can have a high precision and a very low inter-method  
61 variability (< factor of 1.7). It is concluded that passive sampling, irrespective of the specific  
62 method used, is fit for implementation in risk assessment and management of contaminated  
63 sediments, provided that method setup and performance, as well as chemical analyses are  
64 quality-controlled.

65 **Introduction**

66 Traditional methods for assessing risks and managing contaminated sediments are based on  
67 total, solvent-extractable concentrations of sediment-associated chemicals, following  
68 normalization to the sediment organic carbon content.<sup>1</sup> Within the environmental scientific  
69 community it is generally accepted that this approach does not lead to a realistic assessment  
70 of actual risks at field-contaminated sites.<sup>2</sup> Therefore, several methods for estimating the  
71 ‘bioavailable’ concentration or fraction of a chemical have been developed during the past  
72 decades. These methods aim to determine the concentration or fraction that is available for  
73 causing ecotoxicological effects and more closely reflects actual or potential exposure.  
74 Among these methods, partitioning-based, non-depletive extractions with polymers  
75 (colloquially referred to as “passive sampling methods”, even though often active mixing of  
76 the polymer and the sediment is applied) are considered the best developed and have the  
77 most solid scientific basis.<sup>3</sup> Through passive sampling, the freely dissolved concentration  
78 ( $C_{\text{free}}$ ) of a chemical in sediment pore water is determined, which is a good metric of the  
79 driving force behind accumulation and toxicological effects in organisms.<sup>4</sup> The technique  
80 involves direct exposure of a polymer phase to sediment, either *in situ* or *ex situ*.  
81 Hydrophobic organic chemicals present in the sediment system partition into the polymer  
82 and the resulting polymer-sorbed equilibrium concentration is used to calculate  $C_{\text{free}}$ . Several  
83 different polymers have been applied as a sampling phase, including polydimethylsiloxane  
84 (PDMS), polyethylene (PE), polyoxymethylene (POM), polyacrylate (PAc), and silicone  
85 rubber (SR), with the polymers being available in different formats.<sup>5</sup>  
86 Despite the multitude of sampler formats and application possibilities, passive sampling is  
87 currently primarily used for scientific purposes and as an indicator of sediment remediation  
88 performance, rather than to design sediment management approaches. Acceptance in the risk  
89 assessment and regulatory community has been slow, among other reasons because so many

90 different types of passive samplers are applied and the lack of standardized methods. There  
91 is a perception outside the scientific community that no scientific consensus exists on which  
92 is the best method to use.<sup>2</sup> Although guidelines for selection of specific polymers have been  
93 proposed,<sup>5</sup> and the application of different passive samplers and (calculation and analysis)  
94 methods should theoretically yield identical  $C_{\text{free}}$  values, it is currently unknown if this  
95 actually holds true and the inter-method variability has not yet been adequately quantified.  
96 This information is crucial, however, when implementing passive sampling in risk  
97 assessment practices for contaminated sediments, as recently suggested by the US EPA.<sup>6</sup>  
98 In November 2012, a SETAC workshop on passive sampling in sediments was held in Costa  
99 Mesa (CA, USA), with the goal of advancing the application of passive sampling in the risk  
100 assessment and management of contaminated sediments.<sup>2</sup> During the workshop, several  
101 research needs and bottlenecks for implementation were identified, including the above-  
102 mentioned issue and the necessity for a round-robin inter-laboratory study, standardization  
103 of methods, and characterization of sources of uncertainty.<sup>2,5</sup> In response, an international  
104 inter-laboratory comparison study was initiated, with the main objectives to: (i) map the  
105 state of the science in *ex situ* passive sampling in sediments, and the inter-laboratory and  
106 inter-method variability in  $C_{\text{free}}$  determinations; (ii) identify the sources of variability in  $C_{\text{free}}$   
107 as determined with passive sampling; (iii) propose measures to reduce variability and to  
108 provide practical guidance (standardized methods); and, (iv) increase the overall confidence  
109 in passive sampling to advance its use outside the scientific domain, i.e., in regulatory  
110 decision making. The results of the inter-laboratory comparison are presented in this paper.  
111 Practical guidance (i.e., a proposed standard method) and polymer-water partition  
112 coefficients ( $K_{\text{pw}}$ ) needed to calculate  $C_{\text{free}}$  will be presented in separate, forthcoming papers.

113

## 114 **Study Design**

115 Eleven research laboratories from four different countries (USA, The Netherlands, Norway,  
116 and the Czech Republic) participated in the study. The Utrecht University laboratory acted  
117 as coordinating laboratory. Each participating laboratory had a proven track record in  
118 passive sampling in sediments and contributed to the study by applying their own passive  
119 sampling procedures (i.e., format, experimental setup), previously published in the peer-  
120 reviewed literature. In total, 14 passive sampling formats were included, which differed in  
121 polymer material, source, form (i.e., polymer sheet vs. coating on a glass (SPME) fiber), or  
122 thickness. Five of the 11 laboratories applied multiple formats. Passive sampling  
123 experiments were performed with three sediments, including two field-contaminated  
124 sediments and one unpolluted sediment that was spiked in the coordinating laboratory.  
125 Target chemicals included 12 polychlorinated biphenyls (PCBs) and 13 polycyclic aromatic  
126 hydrocarbons (PAHs).  $C_{\text{free}}$  values of these chemicals were determined in five-fold for each  
127 sediment in the following set of tiered experiments. In the first experiment, each laboratory  
128 followed its own procedure(s). The resulting  $C_{\text{free}}$  values were reported to the coordinating  
129 laboratory, along with the  $K_{\text{pw}}$  values used in the calculations and a description of the  
130 methods applied. This experiment mapped the overall variability in passive sampling  
131 methods. In the second experiment, participants were asked to redo the measurements, but to  
132 strictly apply a ‘standard’ protocol that was dictated by the coordinating laboratory. This  
133 experiment was performed in duplicate: one set of sample extracts was analyzed by the  
134 respective participant, to quantify the contribution of employing different protocols to the  
135 overall variability; the other set was shipped to, and analyzed by the coordinating laboratory,  
136 in order to evaluate the contribution of analytical chemistry to the overall variability. All  
137 participants were also provided with a standard solution of the target chemicals, of which the  
138 reported concentrations yielded a direct measure of the analytical (instrumental calibration)  
139 variability. In the third experiment, the coordinating laboratory applied the ‘standard’

140 protocol to all 14 passive sampling formats (as shared by the participants) in order to  
141 identify the inter-method variability. Finally, supplementary tests were performed to map  
142 any additional sources of variation in  $C_{\text{free}}$ , including polymer mass determination, sediment  
143 heterogeneity, and sediment storage time.

144

## 145 **Materials and Methods**

### 146 **Passive Samplers**

147 An overview of the applied passive samplers (polymer types, thicknesses, suppliers) is given  
148 in the Supporting Information (Table S1).

149

### 150 **Target Chemicals**

151 Target chemicals were the PAHs phenanthrene, anthracene, fluoranthene, pyrene,  
152 benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene,  
153 benzo[*a*]pyrene, benzo[*ghi*]perylene, dibenz[*ah*]anthracene, and indeno[123,*cd*]pyrene; and  
154 PCB congeners 18, 28, 52, 66, 77, 101, 118, 138, 153, 170, 180, and 187.

155

### 156 **Analytical Standard Solution**

157 A standard solution was prepared for each participant, by adding 50  $\mu\text{L}$  of an acetone spike  
158 containing the 25 target chemicals to 950  $\mu\text{L}$  of the participant-specific injection solvent  
159 applied during chemical analyses by the respective laboratory (either *n*-hexane, *n*-heptane, *n*-  
160 hexane/acetone (1:1), dichloromethane, or acetonitrile). Nominal concentrations (not shared  
161 with the participants) were about 50  $\mu\text{g/L}$  for PCBs and 100  $\mu\text{g/L}$  for PAHs.

162

### 163 **Sediments**



164 The three testing sediments differed in degree of complexity by passive sampling  
165 application. The ‘least complex’ sediment (“SP sediment”) was an unpolluted, sandy  
166 sediment, sampled from the small river ‘Kromme Rijn’, near Werkhoven, the Netherlands. It  
167 was sieved through a 1 mm sieve, yielding a 20-kg dry weight (dw) sample, which was  
168 intensively mixed for 30 min with a mechanical mixer. Ten 2 kg (dw) portions of the  
169 sediment were successively spiked in 5 L glass beakers with relatively high levels of the  
170 target chemicals, by adding drop-wise 4 mL of an acetone solution containing the target  
171 chemicals (PAHs at ~250 mg/L each; PCBs at ~150 mg/L each), while intensively  
172 mechanically stirring (30 min). All portions were finally pooled in a 110 L concrete mixer,  
173 which subsequently mixed this spiked (SP) sediment continuously for 4.5 weeks. The  
174 sediment of ‘intermediate complexity’ (“BB sediment”) originated from the “Biesbosch”, a  
175 Dutch sedimentation area. This sediment has been used in a previous study in outdoor  
176 ditches,<sup>7</sup> and the sediment used in the present study was sampled from that site. It contained  
177 relatively low native concentrations of the target chemicals, but was known to be  
178 homogeneous. Therefore, it was mixed in a concrete mixer for a shorter period of time, i.e.,  
179 1.5 week. The most complex sediment (“FD sediment”) was a sediment composed by  
180 combining (2:1) a French and a Dutch sediment. The French sediment was sampled from the  
181 river Tillet (Aix les Bains, Savoie), was very sandy, and contained hardly any PAHs. PCBs  
182 were however present at high concentrations, and originated from a former electric  
183 transformer manufacturing facility 2 km upstream. The Dutch sediment was sampled from  
184 the river Hollandsche IJssel and has been previously studied.<sup>8</sup> It contained no detectable  
185 PCBs, but PAHs were present at intermediate concentrations, mostly originating from an  
186 upstream diesel-powered water pumping station. This sediment also contained non-aqueous  
187 phase liquids (NAPLs). The composited sediment was mixed in a concrete mixer for 4  
188 weeks nonstop. Before mixing, a quantity of the biocide sodium azide ( $\text{NaN}_3$ ) was added to

189 all sediments, producing a concentration of 100 mg/L water. After mixing, the sediments  
190 were divided among amber-colored glass jars in portions sufficient to meet each  
191 participant's requirement to complete the tests (different procedures by different participants  
192 required different sediment masses). All jars were closed with aluminum foil-lined lids and  
193 shipped in cooled containers to the participants, along with the standard solution and coded  
194 autosampler vials and glassware for the standardized experiments. Dry weight and organic  
195 carbon content, as well as total concentrations of the target chemicals in the sediments were  
196 determined by the coordinating laboratory as previously described.<sup>9</sup> The results are provided  
197 in Table S2. This information was shared with the participants before initiating the  
198 experiments.

199

#### 200 **Determination of $C_{\text{free}}$ based on the Participants' Own Procedures**

201 In this first experiment, all participants performed  $C_{\text{free}}$  determinations according to their  
202 own procedure(s) and analyzed the resulting extracts themselves. Each measurement was  
203 performed five-fold. A summary of the materials used and methods applied by all 11  
204 participants is (anonymously) listed in Table S3. Procedures clearly differed in terms of type  
205 of exposure (i.e., static vs. dynamic), exposure duration, verification of equilibrium  
206 conditions (i.e., use of performance reference compounds (PRCs), multiple sampler  
207 thicknesses, or multiple time points), sampler mass, sampler/sediment/water ratio, washing  
208 and extraction of samplers, and solvents used.

209

#### 210 **Determination of $C_{\text{free}}$ based on Standardized Procedures**

211 After completing the above experiment, participants received a standardized protocol and  
212 were asked to repeat the five-fold  $C_{\text{free}}$  determinations, strictly adhering to the prescribed  
213 procedure. The protocol was method-, sediment-, and participant-specific, but all aspects and

214 steps (except the chemical analysis) were standardized, including sampler/sediment and  
215 sediment/water ratio, sampler washing, glassware, composition of the added water, exposure  
216 duration (6 weeks), method of shaking and shaking speed, and sampler cleaning and  
217 extraction procedures after finishing the exposures. The sampler/sediment ratio was  
218 dependent on the sediment properties and the polymer used, and the sampler washing and  
219 extraction procedures were specific for different polymers. Furthermore, the sampler  
220 extraction was tuned to the solvent used during chemical analysis by the particular  
221 participant. A general description of the standardized protocol is presented on pages S20-  
222 S21 of the Supporting Information. As outlined under ‘Study Design’, this experiment was  
223 performed in duplicate. One set of extracts was analyzed by the participant, the other set was  
224 shipped in a cooled container to the coordinating laboratory, where internal standards were  
225 added and the extracts analyzed. The standardized protocol was also applied by the  
226 coordinating laboratory to all 14 sampler types (as provided by the participants), in order to  
227 quantify the inter-method variability.

228

### 229 **Supplementary Tests**

230 Supplementary tests focusing on additional sources of variation in  $C_{\text{free}}$  (polymer mass  
231 determination, sediment heterogeneity, and sediment storage time) are described in the  
232 Supporting Information.

233

### 234 **Chemical and Data analysis**

235 Target chemicals were analyzed by the participants as described in Table S3. GC-MS or GC-  
236 ECD was used for PCB quantification, whereas PAHs were analyzed by either GC-MS or  
237 HPLC-FLD. Concentrations in the sampler extracts were converted to concentrations in the  
238 sampler material ( $C_s$ ), using the sampler’s mass (sheets) or polymer volume (SPME fibers).

239  $C_{\text{free}}$  was then obtained by dividing  $C_s$  by a polymer- and chemical-specific  $K_{\text{pw}}$ . In the first  
240 experiment (participants' own procedures), participants applied their own  $K_{\text{pw}}$ s (measured  
241 themselves or taken from the literature) and some used PRCs in their calculations. In the  
242 standardized experiment, a fixed set of  $K_{\text{pw}}$  values as measured by the coordinating  
243 laboratory according to previously-published methods<sup>10</sup> was applied. Variability in each  
244 experiment was quantified by averaging the five-fold  $C_{\text{free}}$  measurements of each participant  
245 and subsequently calculating a variation factor ( $VF$ ) for each target chemical. This factor  
246 was calculated by assuming the experimentally-determined concentrations exhibited normal  
247 distributions and then taking the ratio of the 95th percentile ( $PCTL$ ) value of the averaged  
248  $C_{\text{free}}$  values per target chemical, to the 5th percentile value:

$$VF = \frac{95th\ PCTL}{5th\ PCTL}$$

252 Using this statistic, the range in  $C_{\text{free}}$  was quantified and expressed intuitively as a factor,  
253 while excluding outliers. In order to compare experiments and sediments in a simple way,  
254 the chemical-specific  $VF$  values were averaged per sediment for each experiment ( $VF_{\text{av}}$ ).

## 256 **Results and Discussion**

### 257 **State of the Science in Passive Sampling Sediment Pore Water**

258 The results of the first experiment, in which all participants performed  $C_{\text{free}}$  determinations  
259 according to their own procedures, are presented in panels A1-3 of Figure 1. In these three  
260 figures (one for each sediment), the averaged  $C_{\text{free}}$  data for all target chemicals are plotted  
261 against  $C_{\text{free}}$  values obtained by averaging all chemical-specific data produced by the  
262 coordinating laboratory (referred to as Lab UU in Figure 1; all passive sampling formats;  
263 standardized protocol. Note that using these values as independent variables does not imply

264 they are the target or actual values; they are solely used as reference). This way, the data are  
265 presented in a straightforward and understandable manner, without any data manipulation,  
266 yet clearly demonstrating the data variability. Additionally, in Figure S1, box plots are  
267 presented per chemical. Nearly all data points fall within the 10:1 and 1:10 interval, but there  
268 is a clear tendency towards under-predicting the averaged data of the coordinating  
269 laboratory. Overall, the observed inter-laboratory variation is quite large; larger than the  
270 variability reported for a previous small-scale inter-laboratory passive sampling comparison  
271 (i.e., a factor of 2).<sup>11</sup> Note, however, that in ref 11 fewer samplers and target analytes (3 and  
272 8, respectively) were tested, using a single sediment. Figure 1 may be also somewhat  
273 misleading as the apparent concentration ranges in some cases seem to cover a factor of 100,  
274 whereas they are actually composed of data for more than one chemical. The largest  
275 variation in the present study was observed for PCB-77 in the BB and FD sediments, where  
276 the concentration ranges did indeed span a factor of 100 and even 2400, respectively (see  
277 Figure S1 and Table S4, in which ranges for all chemicals are presented). The cause for the  
278 deviating behavior of this particular chemical is as follows. PCB-77 was a target chemical,  
279 which was added to the SP sediment, but it was not present at detectable concentrations in  
280 the field-contaminated BB and FD sediments (Table S2), as revealed by dedicated GC-MS  
281 analyses at the coordinating laboratory. Nevertheless, several participants reported  
282 considerable  $C_{\text{free}}$  values for the chemical in these sediments. The large concentration ranges  
283 observed can thus be explained by the different detection (MS; ECD) and separation (GC  
284 columns) approaches applied by different participants, which will have resulted in  
285 inconsistencies in interfering/mis-identified peaks. Because the coordinating laboratory did  
286 not report a value, the  $C_{\text{free}}$  of PCB-77 as reported by one of the participants was used as x-  
287 axis value in Figure 1, in order to be able to visualize the variability of this chemical. Since  
288 the data for PCB-77 in the BB and FD sediments obscure the average variability, they were

289 excluded from the data analysis when calculating  $VF_{av}$  values. These  $VF_{av}$  values are listed  
290 in Table 1. Values for the first experiment are  $9.7\pm 4.1$ ,  $9.4\pm 6.3$ , and  $10.8\pm 4.5$  for the BB,  
291 FD, and SP sediment, respectively. Apparently, when omitting the PCB-77 data, there are no  
292 obvious differences in variability among the three sediments, even though they were  
293 selected/composed based on differences in complexity for passive sampling. This may imply  
294 that passive sampling produces results, which are independent of the type of sediment  
295 studied, but it should be stressed that the overall variability is so large that any subtle  
296 differences between results for the various sediments may be fully obscured.  
297 Note that the variation observed in Figures 1 A1-3 includes variability as introduced by: (i)  
298 different laboratories, applying different protocols carried out by different people (inter-  
299 laboratory variability), (ii) the use of different  $K_{pw}$  values by different participants, (iii)  
300 different ways of analyzing the chemicals, (iv) potential sediment heterogeneity and  
301 contaminant instability; and, (v) the use of different passive sampling approaches (inter-  
302 method variability). The contribution of each of these sources will be discussed in a semi-  
303 quantitative manner in the subsequent sections.

304

### 305 **Impact of Standardizing $K_{pw}$ values**

306 Since most of the measurements performed by the participants involved equilibrium passive  
307 sampling, and inaccuracies in the  $K_{pw}$  of target analytes under equilibrium conditions are  
308 considered “a major source of concern”,<sup>12</sup> one would expect a clear contribution to reducing  
309 the overall variability by standardizing the  $K_{pw}$ s used for calculating  $C_{free}$  values. After all,  
310 the participants applied  $K_{pw}$  values measured in their own laboratory or values taken from  
311 the literature. As such, there were considerable differences between the values that were  
312 used. For PDMS, the largest difference between the lowest and the highest chemical-specific  
313  $K_{pw}$  values was a factor of 7, whereas for PE and POM this was even a factor of 13 and 20,

314 respectively. The impact of standardizing  $K_{pwS}$  was investigated by using  $K_{pw}$  values that had  
315 been determined for each sampler/chemical by the coordinating laboratory (manuscript in  
316 preparation). Remarkably, the impact of using  $K_{pw}$  values from a single source on the overall  
317 variability was negligible, as shown in Figure S2. The  $VF_{av}$  values did not significantly  
318 change after recalculating the  $C_{free}$  data as reported by the participants, using  $K_{pw}$  values  
319 from the single source (see Table 1). The position of the data points, however, did change in  
320 many cases, which makes sense, as  $K_{pw}$  determines the absolute value for  $C_{free}$ . In other  
321 words, standardizing  $K_{pwS}$  does not reduce the variability of  $C_{free}$  measurements, but still is  
322 of utmost importance, because of the final accuracy of  $C_{free}$  data. Using inaccurate  $K_{pwS}$  will  
323 yield biased  $C_{free}$  data, which is an unwanted situation when applying passive sampling for  
324 assessing risks of contaminated sediments. Therefore, it is recommended that high-quality,  
325 accurate (standardized)  $K_{pw}$  values be used by the passive sampling community.<sup>5,13</sup>

326

### 327 **Impact of Standardizing Experimental Protocols**

328 Standardizing the experimental protocols, in addition to the  $K_{pw}$  values, had a clear impact  
329 on the  $C_{free}$  inter-laboratory variability. Figures 1 B1-3, Figure S1, and Table 1 demonstrate  
330 that the variability roughly halved, with the  $VF_{av}$  values being reduced to between 4 and 5  
331 for all tested sediments. This obviously implies that the methodology of passive sampling  
332 measurements influences the outcomes and that standardization of passive sampling  
333 methods is definitely desirable. Because multiple issues and steps were standardized in the  
334 protocols, it is not possible to attribute the variation reductions to a specific aspect of the  
335 protocols; there are several likely candidates. The most important aspects that were  
336 standardized (thus changed for certain participants) included the sampler/sediment and  
337 sediment/water ratios, sampler washing procedure, glassware used, exposure duration,  
338 method of shaking and shaking speed, and the sampler cleaning and extraction procedures

339 after finishing the exposures. Smedes et al.<sup>14</sup> showed that the sampler/sediment ratio may  
340 influence the equilibrium concentration in the sampler (and thereby the calculated  $C_{free}$ ), as it  
341 was observed to be inversely related to this metric, due to depletion of the system. Also for  
342 the presently-investigated sediments a similar relationship was observed (see Figure S3). In  
343 the standardized protocol, the ratio was set such that chemical depletion from the three  
344 sediments was always below 2% for all chemicals and samplers.<sup>14</sup> However, when  
345 performing the measurements according to their own procedure(s), some participants applied  
346 (much) higher ratios, which will have resulted in higher depletion ratios (theoretically up to  
347 about 70%). Therefore, standardization of this step most probably will have contributed to  
348 the variation reduction. Likewise, Smedes et al.<sup>14</sup> demonstrated that the sediment/water ratio  
349 can affect the system's kinetics. Higher ratios yielded faster equilibration. Optimization of  
350 this ratio, together with a sufficient equilibration time and shaking regime, assured (near)  
351 equilibrium in all cases during the standardized experiment, as illustrated in Figure S4. In  
352 the first experiment in which the participants followed their own procedures, several  
353 participants (presumably) did not achieve equilibrium for all chemicals. PRCs were used to  
354 correct for this in several cases, following different calculation approaches, but such a  
355 correction may introduce uncertainties and inaccuracies.<sup>15-16</sup> This particularly applies to the  
356 more hydrophobic chemicals, for which the correction by some participants was based on  
357 extrapolation from released fractions of less hydrophobic PRCs only. It should be stressed  
358 though that correction for the degree of non-equilibrium based on PRCs does not necessarily  
359 introduce substantial error, as demonstrated by the experiments from one participant (Figure  
360 S5). Whereas the standardized protocol prescribed thorough mixing and no PRCs, the  
361 procedure of this particular participant involved static exposures and included PRC  
362 corrections. Results of both approaches agreed within a factor of about 2 for all chemicals  
363 and sediments.



364 Standardization of some of the other aspects of the protocols may also have contributed to  
365 the variability reduction, but their contributions are probably less substantial. Sampler  
366 extraction after the exposures to sediments may be an exception, as the specific solvent used  
367 or the handling of samplers/extracts (e.g. cleanup or evaporation steps) by participants may  
368 have introduced variability through, for instance, variable extraction recoveries or losses of  
369 contaminants.

370

### 371 **Contribution of Analytical Chemistry to the Variability**

372 Even after standardizing  $K_{pw}$  values and experimental protocols, considerable variability in  
373 the inter-laboratory  $C_{free}$  data remained (Figures 1 B1 to B3). This variability again roughly  
374 halved when all passive sampling extracts were analyzed by one laboratory (see Figures 1  
375 C1 to C3 and Figure S1). The  $VF_{av}$  decreased to about 2.5 for all three sediments (Table 1).  
376 As such, chemical analyses had a substantial contribution to the overall variability. A similar  
377 conclusion was also drawn for other inter-laboratory comparison studies on passive  
378 sampling in surface waters,<sup>17-18</sup> but certainly is not restricted to passive sampling  
379 measurements. Each experiment involving chemical analyses will suffer from errors  
380 introduced through inaccuracies in the identification, integration, and calibration of  
381 compounds. The case of PCB-77, as discussed above, already demonstrated that  
382 identification is the first crucial step and, if not performed correctly, can result in huge inter-  
383 laboratory variability. Peak area quantification generally may not be considered as the step  
384 that contributes most to the overall variability introduced through chemical analysis.  
385 However, in complex chromatograms with co-eluting peaks, baseline selection is subjective  
386 and poor integrations may add from a few percent of error to perhaps a factor of two or  
387 more. Any error will strongly depend on the sediment, the chemical, the analytical  
388 separation power, the selectivity of identification, the integration approach (i.e.,

389 quantification based on peak area or height), and the efficacy of any clean-up procedure. The  
390 major source of error introduced by analytical chemistry is likely related to calibration.  
391 Apart from correct application of internal standards, final concentrations quantified in the  
392 analyzed extracts are directly related to the accuracy of calibration standards. Even for PAHs  
393 and PCBs, i.e., compounds that are often routinely analyzed, this accuracy may be  
394 insufficient. The analysis of the standard solution in the present study demonstrated that the  
395 variation in PCB concentrations was characterized by a  $VF$  of 2 to 3, while for PAHs it was  
396 3 to 4.5 (see Figure 2). From Figure 2 and the difference between Figures 1B and 1C, it can  
397 thus be concluded that a major part of the present inter-laboratory variability in  $C_{\text{free}}$  data  
398 originates from a step that basically has nothing to do with passive sampling measurements,  
399 but is part of every experiment involving the measure of chemicals, and is often overlooked  
400 as a source of error in experimental results. Therefore, including a standard solution in inter-  
401 laboratory comparison studies involving chemical quantification is a prerequisite.

402

### 403 **Other Sources of Variability**

404 Figure 1 C shows the variability in the results of experiments that were standardized and of  
405 which the extracts were analysed by one laboratory. The observed variability will therefore  
406 only be caused by (i) inter-method variability, which will be discussed below, (ii) variability  
407 in the performance of the standardized procedure by different laboratories, and (iii) other  
408 sources of variability. Two other sources of variability were investigated in the present  
409 study: the accuracy of sampler mass and fiber coating volume (i.e., analytical weighing and  
410 the use of nominal fiber coating thicknesses), and sediment heterogeneity (originating from  
411 insufficient mixing and different storage times). Generally, sheet samplers are weighed on a  
412 balance and the concentrations quantified in polymers are expressed on a sampler mass  
413 basis. Hence, an inaccurate balance or weighing procedure may introduce error and

414 consequently increase data variability. The results of the weighing test, however  
415 demonstrated that sampler weights generally were within 1% of the weights recorded by the  
416 coordinating laboratory. Only one participant reported weights deviating up to 4.7%. These  
417 differences are small and, consequently, weighing did not contribute significantly to the  
418 experimental variability in the present study.

419 When deriving the coating volume of a SPME fiber, product specifications provided by the  
420 manufacturer are rarely questioned, although it often remains unsure how these were  
421 established. A comparison of coating volumes calculated based on nominal, manufacturer-  
422 provided thicknesses versus measured ones (Table S5) demonstrated considerable  
423 differences, which amounted up to 16%. As such, fiber coating volumes may be a potential  
424 source of variability in  $C_{free}$ . However, two of the fibers showing the largest deviations (S30-  
425 1 and PAc) were used by the coordinating laboratory only, which used actual volumes  
426 throughout the different experiments. Therefore, in the present study, the use of nominal  
427 coating volumes may only have been a potential source of variability for the S10-1 fiber,  
428 albeit not in the experiments where the chemical analyses (and subsequent calculations)  
429 were performed by the coordinating laboratory.

430 Results of the sediment heterogeneity experiment showed that even after mixing for several  
431 weeks, sediment heterogeneity may also have contributed to the observed overall variability  
432 in  $C_{free}$ .  $VF_{av}$  values of 1.1 to 1.4 for the field-contaminated BB and FD sediments and 1.2 to  
433 even 2.4 for the spiked SP sediment were calculated (see Table S6). The  $VF$  values are  
434 rather chemical-independent for the BB and FD sediments, but for the SP sediment, they  
435 increase with chemical hydrophobicity (see Table S6). Apparently, mixing this spiked  
436 sediment for up to 4.5 weeks in a concrete mixer was insufficient to allow full chemical  
437 homogenization for the most hydrophobic compounds. Note that the results presented here  
438 were obtained by analyzing several sediment sub samples ( $n=10$ ) taken directly from the

439 concrete mixer. These samples do not necessarily perfectly represent the sediment samples  
440 as received by the participants, considering the large sediment volume that was contained in  
441 the mixers. After filling all the jars with sediment required by the participants, excess  
442 sediment was placed in spare jars. The  $VF_{av}$  values thus do not *per se* exactly quantify the  
443 actual variability caused by sediment heterogeneity in the experiments and cannot be  
444 directly deduced from the values in Table 1. They do indicate, however, that sediment  
445 heterogeneity potentially may have contributed to the variability observed in Figures 1A-C.  
446 Apart from that, sediment heterogeneity within a single sediment batch as received by a  
447 participant is expected to be much smaller, as will be shown below (intra-method  
448 variability).

449 Measurements performed with sediments stored for 4.5 months in the refrigerator, as  
450 compared to measurements initiated directly after sampling from the concrete mixers  
451 demonstrated that  $C_{free}$  of the target PAHs and PCBs decreased with about 20 % in the FD  
452 sediment and 10 % in the BB and SP sediments. This suggests that sediment storage also  
453 cannot be excluded as a source of variability. However, the time between the first participant  
454 starting the first experiment and the last participant starting this experiment, was only one  
455 month. Therefore, it is not very likely that storage time contributed significantly to the  
456 variability in Figure 1A. The first and last started standardized experiments were, however,  
457 three months apart and storage time thus may have been an additional source of variability in  
458 Figure 1B. It should be stressed though that the two measurements (i.e., before and after  
459 storage) were performed with two different sediment batches (jars); as such, sediment  
460 heterogeneity may also have caused (part of) the difference in  $C_{free}$ . Assuming the  
461 concentration decrease is a real phenomenon, progressive sorption (re-distribution) may be  
462 the underlying mechanism for the SP and FD sediment. However, for the field-contaminated

463 BB sediment this process is improbable. Degradation is unlikely in all cases (chemicals,  
464 sediments).

465

#### 466 **Intra-method and Inter-method Variability**

467 The last experiment included  $C_{\text{free}}$  measurements with all sampler formats by the  
468 coordinating laboratory. From this experiment, both the intra- and inter-method variability  
469 could be deduced. As observed before,<sup>19</sup> the intra-method variability appeared very low. For  
470 sheet samplers (PE, POM, SR), relative standard deviations (RSDs) of the five-fold  
471 measurements were generally  $< 5\%$  and for the (homogeneous) BB sediment, RSDs were  
472 often below 2 or even 1 %, indicating very high repeatability. Prerequisites for low RSDs are  
473 that the measurements are performed by skilled personnel, trained to work with passive  
474 samplers and to perform high-quality chemical analyses (including highly consistent  
475 integrations). For SPME fibers, RSDs of the five-fold measurements by the coordinating  
476 laboratory were somewhat higher, with the values increasing with decreasing coating  
477 thickness: RSDs  $S10 > S30 > S100 >$  sheets (see Table S7). The cause of this order most  
478 probably relates to (i) the fact that the uncertainty in the sampling phase volume increases  
479 with decreasing coating thickness (because of increased uncertainties in the actual coating  
480 thickness, inaccurate cutting of the fibers, or coating wear during equilibration) and (ii) the  
481 thinner the coating, the higher the probability for artifacts to occur through ‘fouling’ (i.e.,  
482 particles or NAPLs sticking to the coating), potentially causing over-estimation of the  
483 polymer-sorbed concentration.<sup>8</sup>

484 Owing to the high method precision, it was possible to accurately quantify the inter-method  
485 variability. The resulting  $VF_{\text{av}}$  values (see Table 1, last row) demonstrate that on average the  
486 results of all 14 passive sampling formats (both sheets and SPME fibers of different  
487 polymers, sources, and thicknesses) match within a factor of 1.7. Thus, differences in  $C_{\text{free}}$

488 determined with a suite of passive samplers were very small (see also Figure 1 D and Figure  
489 S1 D). The underlying  $VF$  values do slightly increase with target chemical hydrophobicity,  
490 in particular for the PCBs (Table S8). This increase is probably caused by the fact that  $K_{pw}$   
491 values become more uncertain for very hydrophobic chemicals, due to increasing  
492 experimental difficulties related to reduced solubilities and slow kinetics.<sup>10</sup> Lower  $C_{free}$   
493 values for the more hydrophobic chemicals cannot explain the observation, as the underlying  
494 measured concentrations in the extracts were not related to chemical hydrophobicity.

495 The data variability is practically identical for the different sediments, here indicating that  
496 passive sampling is a robust technique, with which  $C_{free}$  can be determined precisely,  
497 irrespective of the sediment under study. A comparison of the results of the different  
498 samplers shows that the highest  $C_{free}$  values generally were measured with the S100, S30-2,  
499 and S10 SPME fibers, whereas the lowest values generally were determined with POM, PE-  
500 6, and SR. However, because the differences are so small, in particular relative to the  
501 average (See Figure S1 D), it can be concluded that there are no specific polymers behaving  
502 substantially differently to all the others and that their usage should be avoided. Different  
503 methods do have their specific ‘pros’ and ‘cons’ though (e.g., practicability of handling, ease  
504 of  $K_{pw}$  determination, detection limits, etc.). A detailed discussion of these factors is beyond  
505 the scope of the present paper.

506 Overall, it can be concluded from the present study that passive sampling is ready for  
507 implementation in actual risk assessment and management practices of contaminated  
508 sediments. The technique is robust, as it produces results that are independent of the  
509 sediment studied and sampling polymer or format used. However, standard protocols should  
510 be applied (most importantly ensuring non-depletion, taking steps to deduce equilibrium  
511 concentrations in the polymers, and full sampler extraction) and the analytical chemistry  
512 element be carefully quality-controlled (e.g., by means of (certified) external standards). The

513 preparation and use of a passive sampling reference sediment may also be considered as a  
514 quality check in future work. Based on the standardized procedure, practical guidance and a  
515 proposed standard protocol for passive sampling in sediments will be presented in a follow  
516 up paper.

517

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532

## 533 **Supporting Information**

534 Description of supplementary tests; Tables listing sampling formats, sediment  
535 characteristics, participants' own procedures, concentration ranges, fiber volumes, *V<sub>F</sub>*s  
536 characterizing sediment heterogeneity and inter-method variability, and intra-method  
537 variability (RSDs); Figures showing box plots, the effects of *K<sub>pw</sub>* standardization and

538 sampler/sediment ratio, uptake kinetics in different samplers, and a static/dynamic exposure  
539 comparison. This material is available free of charge via the Internet at <http://pubs.acs.org>.

540

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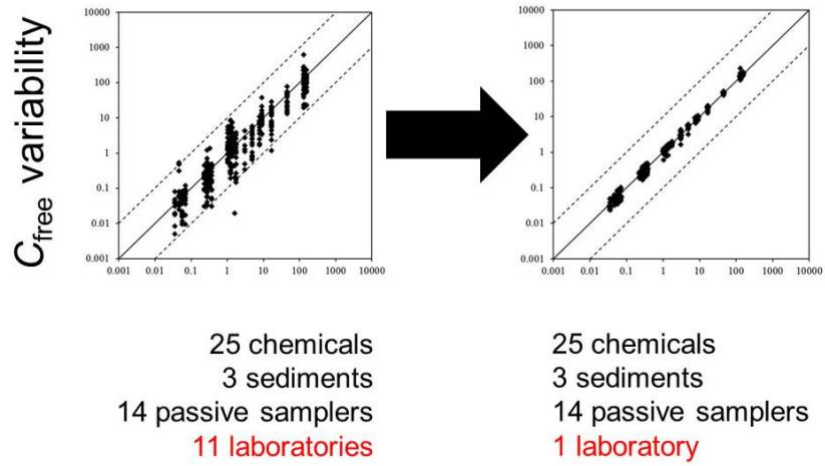
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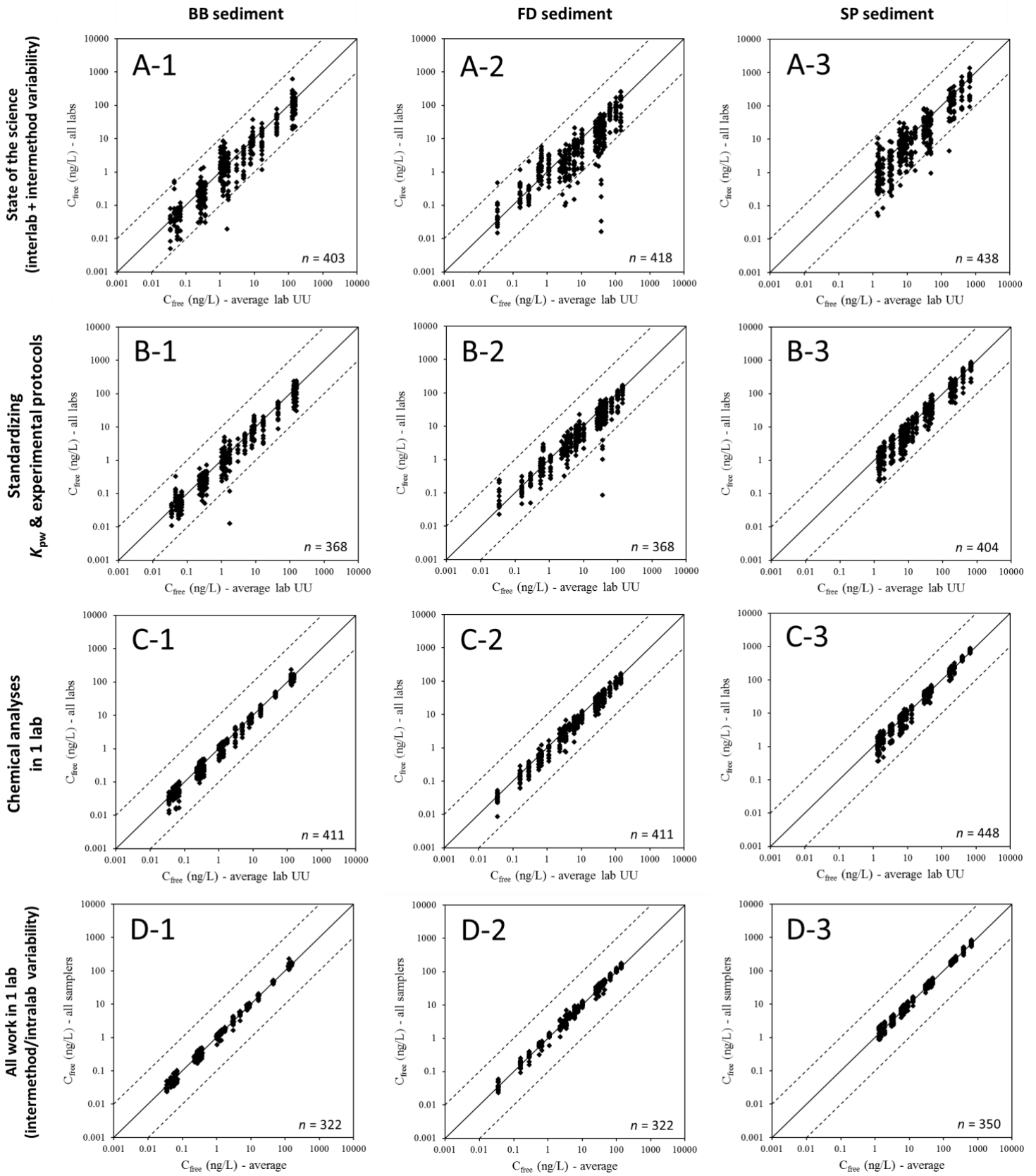
616 **Table 1.** Averaged Variation Factors ( $VF_{av}$ ;  $\pm$  standard deviations) per sediment and per  
 617 experiment.<sup>a</sup>  
 618

	BB sediment <sup>b</sup>	FD sediment <sup>b</sup>	SP sediment
Measurements based on own protocols	9.7 $\pm$ 4.1	9.4 $\pm$ 6.3	10.8 $\pm$ 4.5
Standardizing $K_{pw}$ values	8.9 $\pm$ 3.6	9.3 $\pm$ 4.6	10.8 $\pm$ 5.6
Standardizing protocols & $K_{pw}$ values	4.4 $\pm$ 1.4	4.6 $\pm$ 2.2	4.5 $\pm$ 1.2
Standardizing & chemical analyses in one lab	2.4 $\pm$ 0.89	2.4 $\pm$ 0.72	2.6 $\pm$ 0.82
All work performed in one lab	1.6 $\pm$ 0.35	1.7 $\pm$ 0.42	1.7 $\pm$ 0.31

619  
 620 <sup>a</sup> The  $VF_{av}$  values are calculated by averaging the  $VF$  values of all chemicals for one  
 621 sediment in a specific experiment. The number of chemicals included is 23 - 25, depending  
 622 on the sediment and experiment.

623 <sup>b</sup> Data for PCB-77 are excluded (see text for explanation).

Figure 1.



628 **Figure 1.** Variability in freely dissolved concentrations ( $C_{\text{free}}$ ) determined in three sediments  
629 as measured with passive sampling methods (A) when the participants of the inter-laboratory  
630 comparison followed their own protocols, (B) after standardization of  $K_{\text{pws}}$  and experimental  
631 protocols, (C) when, in addition to B, all chemical analyses were performed in one  
632 laboratory, and (D) when both experiments and analyses with all samplers were performed  
633 in one laboratory. Solid lines represent the 1:1 relationships; dashed lines indicate  $\pm$  a factor  
634 of ten. The  $n$  number in each plot indicates the number of data points.  
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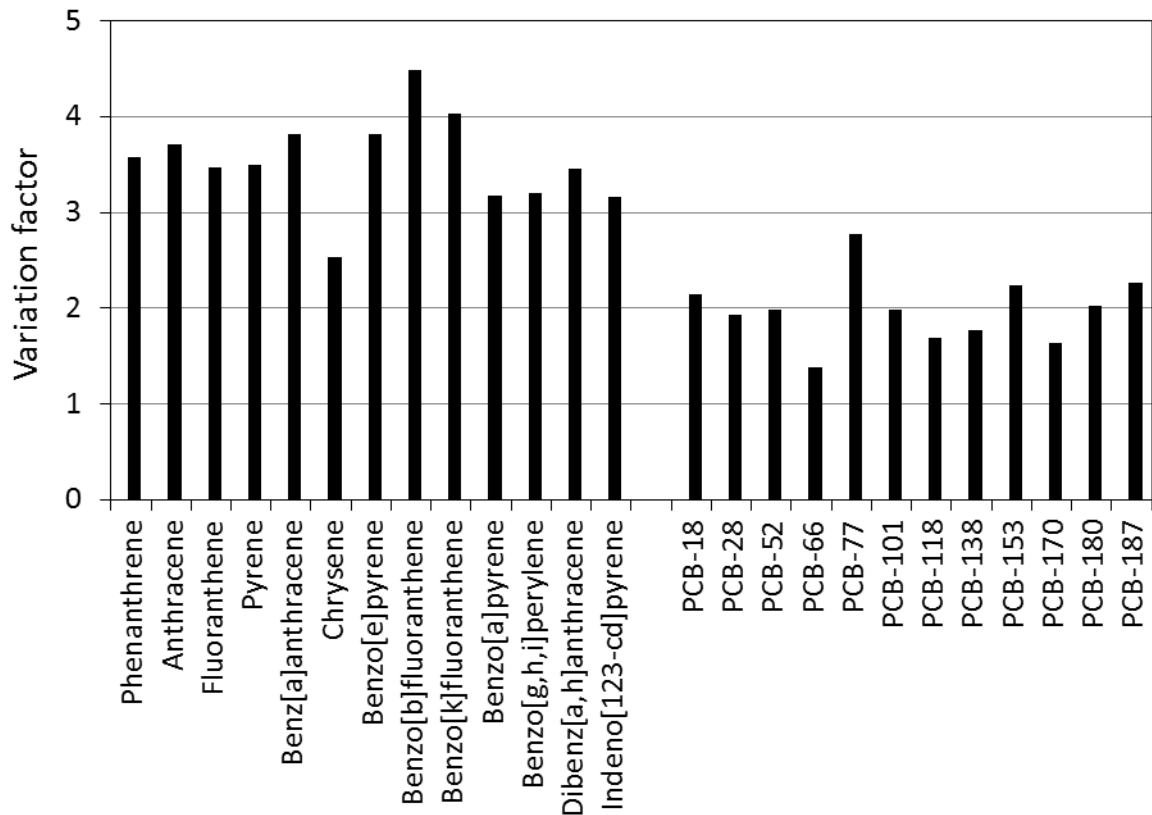
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Figure 2.

640



641

642 **Figure 2.** Variation factors (95<sup>th</sup> PCTL/5<sup>th</sup> PCTL) calculated based on the (range of)  
643 concentrations of the target chemicals in the analytical standard, as reported by the  
644 participants of the inter-laboratory comparison.

645