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1       Effects of sampling techniques on physical  
2       parameters and concentrations of selected  
3       persistent organic pollutants in suspended matter

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6                                   **Abstract**

7           This study focusses on the effect of sampling techniques for suspended matter  
8           in stream water on subsequent particle-size distribution and concentrations of total  
9           organic carbon and selected persistent organic pollutants. The key questions are  
10          whether differences between the sampling techniques are due to the separation  
11          principle of the devices or due to the difference between time-proportional versus  
12          integral sampling. Several multivariate homogeneity tests were conducted on an  
13          extensive set of field-data that covers the period from 2002 to 2007, when up to  
14          three different sampling techniques were deployed in parallel at four monitoring  
15          stations of the River Rhine. The results indicate homogeneity for polychlorinated  
16          biphenyls, but significant effects due to the sampling techniques on particle-size,  
17          organic carbon and hexachlorobenzene. The effects can be amplified depending  
18          on the site characteristics of the monitoring stations.

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# 19 **1 Introduction**

20 The requirements regarding the data quality of existing and planned monitoring pro-  
21 grams for suspended matter (SPM) quality increased within the last decades. Currently,  
22 the collection of SPM in stream water for subsequent trace-analysis is fundamental  
23 for (i) the monitoring of the long-term development of SPM-quality regarding the ef-  
24 ficiency control of environmental policies, as well as the detection of land-use and  
25 climate change impact on SPM-quality<sup>1</sup>, (ii) process-oriented studies about sediment  
26 source apportionment<sup>2</sup>, (iii) the calibration and validation of hydrodynamic transport  
27 models<sup>3</sup>, (iv) the approval procedure and monitoring of sediment dredging activities in  
28 streams and impoundments, and (iv) forensic investigations to detect actual emitters.

29 The techniques for collecting SPM developed over the past decades: e.g. in the  
30 1980s, several hundreds of liters of water needed to be taken from the stream and  
31 SPM was consequently separated off-site by time-consuming sedimentation in specific  
32 tanks<sup>4,5</sup> or by centrifuges in laboratories<sup>6</sup>; modified plankton nets were used for SPM  
33 sampling under low-flow conditions in small streams<sup>7</sup>. Currently, sedimentation tanks  
34 are used in Germany in order to collect suspended matter in a time-integrated way for a  
35 retrospective analysis of contaminants in the German Environmental Specimen Bank<sup>8</sup>.  
36 Pioneering studies on the inter-comparison of several field and laboratory centrifuges  
37 for the suitability in nationwide or international SPM-quality monitoring programs date  
38 back to the early 1990s<sup>9,10</sup>. However, at this time only a limited set of data and sam-  
39 pling devices were available for the inter-comparison.

40 We therefore analyzed an extensive dataset that covers the period from 2002 to  
41 2007, when three different, well established sampling devices for the collection of SPM  
42 (i.e. continuous-flow centrifuge, floating collector and sedimentation tank) operated in  
43 parallel under field conditions, which has not been done before. The objective of our  
44 study is to test the aforementioned sampling devices for homogeneity with respect to  
45 the subsequently analyzed particle-size distribution and concentrations of both total  
46 organic carbon and selected persistent organic pollutants. We focus on two particular  
47 questions, i) are mean differences between the devices related to their separation prin-

48 ciple, or ii) are mean differences related to the difference between time-proportional  
49 sampling versus integral-composite sampling of SPM?

## 50 **2 Research Area**

51 The research area covers the main stretch of the River Rhine (Fig. 1.) between  
52 Weil (Rhine-km 174) and Bimmen (Rhine-km 865). The focus of this study is on  
53 the particle-size distribution (PSD), total organic carbon (TOC), hexachlorobenzene  
54 (HCB), pentachlorobenzene (PeCB), several PCB congeners (PCB-28, PCB-52, PCB-  
55 101, PCB-118, PCB-138, PCB-153) and the sum of the aforementioned PCB congeners  
56 ( $\Sigma$ PCB). We selected HCB and PCB-153 in particular because these compounds are  
57 relevant contaminants for SPM and sediments in the River Rhine. The environmental  
58 objectives for SPM-quality in terms of particle-bound concentrations ( $c$ ) that were in-  
59 troduced by the International Commission for the Protection of the River Rhine (ICPR)  
60 for HCB/ $\mu\text{g kg}^{-1}$  ( $c \leq 40$ ) and PCB-153/ $\mu\text{g kg}^{-1}$  ( $c \leq 4$ ) are frequently exceeded at  
61 several monitoring stations.

62 Contaminations of HCB in SPM of the River Rhine originated from historical direct  
63 inlets of a chemical plant located at Rheinfelden (High Rhine) during the 1970s and  
64 1980s<sup>11</sup>. Although direct emissions have stopped many years ago, the impounded  
65 river stretch of the Upper Rhine, where contaminated sediments are trapped, acts as a  
66 secondary source for particle-bound HCB due to flood events and dredging activities<sup>12</sup>.  
67 As opposed to HCB, PCBs are ubiquitous compounds in the River Rhine catchment,  
68 although the production and direct emission into the stream waters have stopped since  
69 the early 1980s.

## 70 **3 Sampling techniques**

### 71 **3.1 Centrifuges**

72 Continuous-flow centrifuges (CE) with single tubular chamber bowls (Fig. 2) are rou-  
73 tinely deployed to instantaneously take SPM-samples at the River Rhine. The sam-

74 pling is conducted at one single point (between 0.8 m and 1 m below the water surface)  
75 within the cross-section of the river. The CE is operated with a spin of  $16,000 \text{ min}^{-1}$   
76 and a flow rate of  $1,000 \text{ L h}^{-1}$  to ensure a high separation rate of 86% to 98%<sup>5,10</sup>.  
77 Sampling time of 10 to 12 hours is regulated in such a way, that a sufficient amount  
78 of SPM (i.e.  $\geq 20 \text{ g}$  of wet SPM) is collected for subsequent chemical analysis, and  
79 depends on the actual suspended sediment concentration (S) in the stream water. SPM  
80 is collected on the outer surface of the centrifuge bowl that is coated with a lining of  
81 polytetrafluorethylene (PTFE) to minimize decontamination and ease cleaning.

## 82 **3.2 Floating collector**

83 Floating collectors (FC) are integral samplers that are used in order to *in-situ* sample  
84 large amounts of composite SPM-samples (i.e.  $> 800 \text{ g}$  of wet SPM) within periods  
85 of several days to several weeks. A wide range of isokinetic and non-isokinetic FC-  
86 types are operated on an international level<sup>13</sup>, however, in this study we used the FC-  
87 type *Binnensammler* (Fig. 3) - a development by the Federal Institute of Hydrology  
88 (BfG)<sup>14</sup>. The body of this specific FC has a streamlined shape with a total length  
89 of 1050 mm and a diameter of 250 mm. The length and diameter of the inlet are  
90 104 mm and 8 mm, respectively. Two vertical fins at the bottom and the posterior of  
91 the FC ensure a stable position that is antipodal to the flow direction of the stream.  
92 The funnel-shaped interior of the FC serves as a sedimentation pan as the SPM/water  
93 mixture is diverted from a horizontal to a circular flow pattern which increases the  
94 retention time for sedimentation. The SPM is then trapped in a sampling flask that is  
95 located at the bottom of the FC, and the water leaves the FC through the orifices at the  
96 posterior. The separation rate of the FC is difficult to determine because this device is  
97 operated under unsteady flow conditions. Furthermore, a fractionation of SPM towards  
98 a collection of coarser particles is likely as the principle for separation of the FC is  
99 based on sedimentation and, thus, on the settling velocity of particles and flocs. For  
100 this study, the FC were fixed at buoys and landing stages at a single point within the  
101 cross-section in a sampling depth of 1 m below the water surface.

### 102 **3.3 Sedimentation tanks**

103 For this study, sedimentation tanks (ST) were installed *ex-situ* in two monitoring sta-  
104 tions. Similar as compared to FC, these integral samplers are designed for collecting  
105 SPM over periods from days to months. The ST comprises a cuboid tank (1 m × 1 m  
106 × 0.4 m) made of polymethyl methacrylate (PMMA) with a sloped bottom (Fig. 4).  
107 The constant low in-flow of the SPM/water mixture is facilitated with a continuously  
108 operating pump that is placed at one point within the cross-section of the river in a  
109 depth of 1 m. The pump ensures a constant water level of 800 mm in the sedimentation  
110 tank in order to collect large amounts of composite SPM-samples. As the separation of  
111 the SPM/water mixture is also based on sedimentation, with a reported separation rate  
112 of 20 % to 40 %<sup>15</sup>, a fractionation towards particle-sizes with higher settling velocities  
113 is likely. The mass of collected wet SPM using ST is comparable to the mass of wet  
114 SPM collected with FC.

### 115 **3.4 Time-proportional versus integral sampling**

116 As collected SPM in both integral samplers (ST and FC) is stored inside the devices for  
117 several days to weeks prior to the chemical analysis, a potential decay of chemical con-  
118 stituents of SPM (e.g. particulate macro-nutrients, TOC, volatile organic compounds,  
119 and hydrophilic organic compounds) is possible.

120 Furthermore, the final concentration of given contaminant  $\chi$  in a composite SPM  
121 sample collected under unsteady flow conditions is a mixture with unequal amounts  
122 of SPM (i.e. the composite sample does not comprise of daily aliquots; thus integral  
123 SPM-sampling is not time-proportional). As the amount of collected SPM in an inte-  
124 gral sampler increases with S in stream water, the concentration of  $\chi$  under high S will  
125 have a higher weight on the final concentration of  $\chi$  in the composite SPM-sample.  
126 Consequently, three effects are possible: i) If  $\chi$  and S are positively related, the final  
127 concentration of  $\chi$  in the composite SPM for a given period is higher than the arith-  
128 metic mean (i.e. temporal average) of  $\chi$  when SPM was instantaneously sampled at  
129 discrete dates within the same period. ii) If  $\chi$  and S are inversely related, then  $\chi$  in the

130 composite SPM is lower, than the temporal average of  $\chi$ . iii) No effects are expected  
131 if there is no significant correlation between  $\chi$  and S.

## 132 **4 Suspended matter quality data and statistical analy-** 133 **sis**

134 An extensive dataset with a total of  $n = 497$  records per parameter was compiled for  
135 this study using (i) published data from the existing Rhine-monitoring program of the  
136 ICPR ([www.iksr.de](http://www.iksr.de)) and (ii) SPM-quality data from additional monitoring programs  
137 that were conducted by the BfG within the period 2002 to 2008. Table 1 provides  
138 the selected locations and the equipment of the SPM-quality monitoring stations at the  
139 River Rhine.

140 Due to the configuration of parallel measurements, the entire dataset was divided  
141 into three sub-sets for further multivariate testing. Additionally, there was one short-  
142 term dataset available for the period 19. January 2005 to 26. March 2005 that covers  
143 a flood event at the SPM-monitoring station Koblenz, when CE, ST and FC operated  
144 in parallel. The integral samplers ST and FC consistently collected SPM on a monthly  
145 basis in these field experiments. Furthermore, one long-term dataset (1990-2008)  
146 of the routine SPM-quality monitoring program for the locations Weil, Karlsruhe-  
147 Lauterbourg, Koblenz and Bimmen was used for correlation analysis in order to test  
148 the impact of time-proportional versus integral sampling.

### 149 **4.1 Physico-chemical analysis of suspended matter**

150 The chemical analysis of particle-size distribution, total organic carbon, chloro-organic  
151 compounds and polychlorinated biphenyls (PCBs) was done extramural by certified  
152 laboratories on behalf of the maintainers of the SPM-quality stations (i.e. BfG and en-  
153 vironmental agencies of the German Federal States). The deployed analytical methods  
154 were in accordance to national standard procedures.

#### 155 **4.1.1 Granulometry**

156 The method for gravimetric determination of PSD in this study is equivalent to a stan-  
157 dard procedure for sediment fractionation in the BfG. 20 g of the freeze-dried bulk  
158 samples of SPM are repeatedly sieved through a cascade of sieves with mesh sizes of  
159 2000  $\mu\text{m}$ , 630  $\mu\text{m}$ , 200  $\mu\text{m}$ , 63  $\mu\text{m}$  and 20  $\mu\text{m}$  with the aid of agate pellets in an ultra-  
160 sonic bath. The percolate of the 20  $\mu\text{m}$  sieve is trapped with a flask and the remaining  
161 SPM/water mixture is de-watered with a laboratory centrifuge for 15 min. at 2000 -  
162 3000 g. The filter residues and centrifuge residues are then oven-dried at 105 °C and  
163 weighted<sup>16</sup>.

#### 164 **4.1.2 Total organic carbon**

165 TOC in the freeze-dried SPM sample was analyzed with an elemental analyzer after dry  
166 combustion with subsequent infrared detection<sup>17</sup>. Inorganic carbon of the sample is re-  
167 leased prior to the IR-detection through acidifying the SPM-sample with hydrochloric  
168 acid.

#### 169 **4.1.3 Chloro-organic compounds and polychlorinated biphenyls**

170 The analytical methods for the determination of chloro-organic compounds and poly-  
171 chlorinated biphenyls (PCBs) are in accordance to national standard procedures.<sup>18,19</sup>  
172 The bulk SPM-samples are first freeze-dried and subsequently pulverized to particle-  
173 sizes of  $D \leq 100 \mu\text{m}$ . Acceptable extraction methods that are deployed by the certified  
174 labs are the soxhlet, the accelerated solvent extraction, or the microwave method using  
175 a solvent of n-hexane/acetone of 2:1. Clean-up comprises treatment with concentrated  
176 sulfuric acid and cleaning with several different adsorbents in a chromatographic col-  
177 umn using n-hexane as eluent. Finally, the chemical analysis is done with coupled gas  
178 chromatography / mass spectrometry (GC/MS).



## 179 **4.2 Statistical methods**

180 The statistical analysis was conducted with the R-software package<sup>20</sup> in a stepwise  
181 fashion using descriptive summary statistics, two-way analysis of variance (two-way  
182 ANOVA) to globally test for homogeneity and the least significant difference test  
183 (LSD-test) as an *a-posteriori* test for the detection of significant differences between  
184 the SPM collection techniques. Interaction plots were constructed that aim to ease the  
185 interpretation of the empirical findings. The correlations (Spearman's rank correlation  
186 coefficient  $r_S$ ) between the parameters were calculated and tested for significance.

## 187 **4.3 Sub-sets of data**

### 188 **4.3.1 One sampling location and three sampling devices (Short-term period: 19. 189 January 2005 to 26. March 2005)**

190 During the period 19. January 2005 to 26. March 2005 three sampling devices - CE,  
191 ST and FC - operated in parallel at the SPM-quality monitoring station Koblenz. SPM-  
192 samples were taken with CE on a daily basis and analysed for TOC, PCBs, HCB and  
193 additionally PSD, which is usually not the case for CE-samples in routine measure-  
194 ments. Furthermore, data on daily mean flow (Q) were available for this period and  
195 location.

### 196 **4.3.2 Four sampling locations and two sampling devices (Period: 6. May 2005 to 197 31. December 2005)**

198 We conducted a two-way ANOVA with a  $4 \times 2$  layout in order to test the effects of four  
199 sampling locations and two sampling devices (main effects) as well as the combined  
200 effect (interaction term) for the period from 6. May 2005 to 31. December 2005  
201 ( $n = 424$ ). The first factor "location" comprises the monitoring stations Weil ( $k_1 =$   
202 220), Karlsruhe-Lauterbourg ( $k_2 = 143$ ), Koblenz ( $k_3 = 39$ ) and Bimmen ( $k_4 = 22$ )  
203 in downstream direction. It should be noted that at Karlsruhe-Lauterbourg the device  
204 FC was installed about 19 km upstream of the device CE (Table 1). However, we  
205 treated this configuration as one single location. The second factor "device" comprises

206 data grouped by the two devices CE ( $j_1 = 260$ ) and FC 164 ( $j_2 = 164$ ). The two-  
207 way ANOVA was separately conducted for particulate TOC and the aforementioned  
208 contaminants.

209 We favored the parametric two-way ANOVA because the test-power is higher than  
210 for non-parametric tests<sup>21</sup>. A further advantage is that the combined effect (i.e. inter-  
211 action: Location  $\times$  Device) can be tested as different concentrations of contaminants in  
212 SPM that are attributable to the sampling devices may only be present or amplified at  
213 specific locations. This aims to ease the interpretation and conclusion of the subsequent  
214 results.

#### 215 **4.3.3 Two sampling locations and two sampling devices (Period: 9. July 2002 to** 216 **4. June 2007)**

217 We conducted a two-way ANOVA with a  $2 \times 2$  layout using  $n = 310$  data collected in  
218 the period between 9. July 2002 to 4. June 2007 in order to test the replicability of the  
219 previous findings of the  $4 \times 2$  ANOVA (Sect. 4.3.2). The factor “location” comprises  
220 Weil ( $k_1 = 183$ ) and Karlsruhe-Lauterbourg ( $k_2 = 127$ ) and the factor “device” consists  
221 of CE ( $j_1 = 187$ ) and FC 164 ( $j_2 = 123$ ).

#### 222 **4.3.4 Two sampling locations and three sampling devices (Period: 19. January** 223 **2005 to 21. December 2005)**

224 Finally, we conducted a two-way ANOVA in order to test the effects of two “locations”  
225 Koblenz ( $k_1 = 49$ ) and Bimmen ( $k_2 = 31$ ), as well as three “devices” CE ( $j_1 = 37$ ), ST  
226 ( $j_2 = 21$ ) and FC ( $j_2 = 22$ ).

227 The LSD-test was used after each global homogeneity test (Sect. 4.3.2 to 4.3.4)  
228 to test for significant differences ( $p \leq 0.05$ ) of mean particle-bound concentrations per  
229 sampling device in order to rank the results.

#### 230 **4.3.5 Bi-variate correlations (Long-term period: 1990 to 2008)**

231 We compiled an additional dataset that covers the period 1990 to 2008 with bi-weekly  
232 records of flow (Q), S and concentrations of HCB, PCB-138 and PCB-153 in SPM

233 in order to test the bi-variate correlations after Spearman ( $r_S$ ) between the aforemen-  
234 tioned variables. It should be noted that these SPM-samples were taken instantaneously  
235 with CE at the monitoring stations Weil, Karlsruhe-Lauterbourg, Koblenz and Bim-  
236 men, which makes a correlation analysis between the aforementioned variables mean-  
237 ingful. This additional statistical analysis is used for the interpretation whether mean  
238 differences between the sampling techniques are likely due to the obtained composite  
239 SPM-sample using time-integral sampling (i.e. if  $|r_S| > 0.5$ ) or due to the separation  
240 principle of the devices.

## 241 **5 Results**

### 242 **5.1 Descriptive summary statistics**

243 The range of HCB is about one to two orders of magnitude higher as the range of PCBs  
244 in SPM of the River Rhine (Table 2). The analytical results for PeCB, PCB-28, PCB-  
245 52, PCB-101 and PCB-118 were frequently below the limit of quantification (Table 2).  
246 Thus, we excluded these parameters from further multivariate testing. In contrast, the  
247 concentrations of PCB-138 and PCB-153 in SPM were in a range that was adequate  
248 for chemical analysis and, hence, for further statistical testing.  $\Sigma$ PCB was calculated  
249 by summing up the concentrations of the analysed PCB-congeners. Half of the limit of  
250 quantification was taken into account for those cases, when concentrations were below  
251 this limit (Table 2).

### 252 **5.2 One sampling location and three sampling devices (Short-term 253 period: 19. January 2005 to 26. March 2005)**

254 The collected SPM (19. January 2005 to 17. May 2005 at Koblenz) mainly consists  
255 of silt, as the percent by weight ranges between 74% to 99% in the  $< 63 \mu\text{m}$  fraction  
256 for all devices (Fig. 5). According to the one-way ANOVA, the sampling devices  
257 have a highly significant effect on mean collected particle-size,  $D_{\text{Mean}}$ :  $F(2, 34) =$   
258  $37.10$ ,  $p < 0.01$ ,  $\eta^2 = 0.69$ . The devices can be ranked according to  $D_{\text{Mean}}/\mu\text{m}$  into

259 FC ( $58.2 \pm 2.89$ ) > ST ( $41.5 \pm 1.14$ ) = CE ( $42.1 \pm 0.69$ ), as indicated by the LSD-  
260 test on the level of  $p \leq 0.05$ . Furthermore, in the fraction of fine sand (63 – 200  $\mu\text{m}$ )  
261 the highest median percent by weight was present in SPM-samples of FC (16.3 %)  
262 followed by ST (6.3 %) and CE (1.0 %).

263 The daily variability of  $D_{\text{Mean}}$ , TOC, HCB, and  $\Sigma\text{PCB}$  within the period 19. Jan-  
264 uary to 26. March 2005 at Koblenz is low, as indicated by the daily SPM samples col-  
265 lected with a CE (Fig. 6). Although a flood event occurred (12. February to 5. March,  
266 Fig. 6 A) with a peak-flow of  $4000 \text{ m}^3 \text{ s}^{-1}$ , there is hardly any effect on the concentra-  
267 tions of the constituents in SPM that was collected with a CE. However,  $D_{\text{Mean}}$  in SPM  
268 collected with FC is higher (Fig. 6 B), and the HCB concentration of the composite  
269 sample of SPM increases during the rising limb of the aforementioned flood event (Fig.  
270 6 D).

### 271 **5.3 Four sampling locations and two sampling devices (Period: 6.** 272 **May 2005 to 31. December 2005)**

273 Only the first main-effect “location” is significant for  $\Sigma\text{PCB}$  ( $F(3, 75) = 32.6$ ,  $p <$   
274  $0.01$ ,  $\eta^2 = 0.56$ ; Table 3). The second main-effect (“device”) and the interaction effect  
275 are not significant. This is confirmed by the interaction plot for  $\Sigma\text{PCB}$  that clearly de-  
276 picts an increase of mean concentrations of  $\Sigma\text{PCB}$  in SPM from Weil to Bimmen (Fig.  
277 7 A), but there are no trend lines for “device” (Fig. 7 B). Hence, the sampling devices  
278 do not effect the results on the concentration of  $\Sigma\text{PCB}$  in SPM in the investigated range  
279 that is present in the River Rhine.

280 The main effect “device” is significant for TOC (Table 3) and accounts for  $\eta^2 =$   
281  $0.24$ . Additionally, the interaction effect (“location  $\times$  “device”) is also significant (Ta-  
282 ble 3) for TOC, though the proportion of explained variance is low ( $\eta^2 = 0.08$ ). As  
283 given by Fig. 8, there is a specific interaction of both factors: i.e. the effect of the “de-  
284 vice” decreases from the locations Weil, to Koblenz, and Bimmen (Fig. 8 B), which  
285 means that the effect of the sampling “device” can be amplified upon the “location”.

286 Both main effects, “location” and “device” as well as the interaction effect are sig-  
287 nificant for HCB concentration in SPM (Table 3). The proportion of explained variance

288 for the interaction effect accounts for  $\eta^2 = 0.11$ . As given by the interaction plot (Fig.  
289 9), there is no effect attributable to the devices at location Weil, but there are strong  
290 effects caused by the devices at the locations Karlsruhe-Lauterbourg and Koblenz.

291 The differences in subsequently analyzed mean concentrations of the chemical con-  
292 stituents of SPM that are attributable to the sampling devices CE and FC were tested  
293 *a-posteriori* with the LSD-test on the level of  $p \leq 0.05$ . TOC (%) differs significantly  
294 in the order CE ( $5.36 \pm 0.26$ ) > FC ( $3.54 \pm 0.24$ ). There are neither significant dif-  
295 ferences for the PCB congeners nor for the investigated  $\Sigma$ PCB, as indicated by PCB-  
296 138/ $\mu\text{g kg}^{-1}$ : CE ( $6.09 \pm 0.47$ ) = FC ( $6.09 \pm 0.64$ ), PCB-153/ $\mu\text{g kg}^{-1}$ : CE ( $6.35 \pm$   
297  $0.46$ ) = FC ( $6.79 \pm 0.76$ ) and  $\Sigma$ PCB/ $\mu\text{g kg}^{-1}$ : CE ( $26.19 \pm 2.09$ ) = FC ( $32.00 \pm 3.33$ ).  
298 However, HCB/ $\mu\text{g kg}^{-1}$  significantly differs by a factor of 3 between the devices:  
299 CE ( $12.26 \pm 1.50$ ) < FC ( $34.4 \pm 5.51$ ).

#### 300 **5.4 Two sampling locations and two sampling devices (Period: 9.** 301 **July 2002 to 4. June 2007)**

302 The main-effect “device” is significant for TOC, PCB-138, PCB-153 and HCB, and  
303 the explained variance accounts for  $\eta^2 = 0.21$ ,  $\eta^2 = 0.04$ ,  $\eta^2 = 0.03$  and  $\eta^2 = 0.02$ ,  
304 respectively. The parameter  $\Sigma$ PCB is not effected by the factor “device” (Table 4).

305 According to the LSD-test on the level of  $p \leq 0.05$ , TOC (%) differs by a factor of  
306 2 in the order CE ( $6.5 \pm 0.18$ ) > FC ( $3.08 \pm 0.13$ ). There are minor, though significant  
307 differences for PCB-138/ $\mu\text{g kg}^{-1}$ : CE ( $4.59 \pm 0.21$ ) > FC ( $3.77 \pm 0.18$ ) and PCB-  
308 153/ $\mu\text{g kg}^{-1}$ : CE ( $4.90 \pm 0.27$ ) > FC ( $4.16 \pm 0.23$ ). There are no significant differ-  
309 ences for  $\Sigma$ PCB/ $\mu\text{g kg}^{-1}$ : CE ( $20.24 \pm 0.94$ ) = FC ( $19.91 \pm 0.79$ ). However, HCB/ $\mu\text{g}$   
310  $\text{kg}^{-1}$  differs by a factor of 3 in the order CE ( $16.61 \pm 6.05$ ) < FC ( $54.36 \pm 8.78$ ). The  
311 results of the  $2 \times 2$  ANOVA are consistent with the findings of the previously conducted  
312  $4 \times 2$  ANOVA (Sect. 5.3).

313 **5.5 Two sampling locations and three sampling devices (Period:**  
314 **19. January 2005 to 21. December 2005)**

315 The factor “device” significantly affects TOC, HCB and  $\Sigma$ PCB and accounts for  $\eta^2 =$   
316  $0.21$ ,  $\eta^2 = 0.25$  and  $\eta^2 = 0.05$  of the explained variance, respectively (Table 5). There  
317 are no significant effects caused by the devices on PCB-138 and PCB-153. Further-  
318 more, the factor “location” does not significantly effect TOC and HCB, but concen-  
319 trations of PCB-138, PCB-153 and  $\Sigma$ PCB significantly differ between Koblenz and  
320 Bimmen (Table 5).

321 The findings for the  $2 \times 3$  ANOVA are in agreement with the findings in Sect.  
322 5.3 and Sect. 5.4. According to the LSD-test on the level of  $p \leq 0.5$ , TOC (%) is  
323 highest in CE-samples: CE ( $5.02 \pm 0.23$ ) > FC ( $4.0 \pm 0.18$ ) = ST ( $3.82 \pm 0.14$ ). There  
324 are no significant differences for PCB-138/ $\mu\text{g kg}^{-1}$ : CE ( $7.91 \pm 0.5$ ) = FC ( $8.08 \pm$   
325  $0.62$ ) = ST ( $8.07 \pm 0.75$ ), and PCB-153/ $\mu\text{g kg}^{-1}$ : CE ( $8.15 \pm 0.42$ ) = FC ( $9.36 \pm$   
326  $0.72$ ) = ST ( $9.77 \pm 0.78$ ). However,  $\Sigma$ PCB/ $\mu\text{g kg}^{-1}$  in CE-samples were moderately,  
327 but significantly lower as compared to ST-samples: CE ( $33.73 \pm 2.14$ )  $\leq$  FC ( $41.63 \pm$   
328  $3.47$ ) = ST ( $42.75 \pm 3.92$ ). As it was the case in the previous tests, HCB/ $\mu\text{g kg}^{-1}$  is  
329 lowest in CE-samples: CE ( $18.42 \pm 1.93$ ) < ST ( $40.55 \pm 5.33$ ) = FC ( $34.54 \pm 3.77$ ).

330 **5.6 Bi-variate correlations (Period: 1990 to 2008)**

331 The correlations ( $r_S$ ) between HCB (PCB-138, PCB-153) and S using SPM-samples  
332 that were only collected with CE decrease with increasing river reach length (Table  
333 6). At the SPM-quality monitoring station Weil, there are highly significant, inverse  
334 relations between the aforementioned contaminants and S. Furthermore, TOC is sig-  
335 nificantly, inversely correlated with S at each monitoring station, whereas TOC de-  
336 creases asymptotically with increasing S (data not shown). In contrast, HCB (PCB-138,  
337 PCB-153) is not correlated with S at the SPM-quality monitoring stations Koblenz and  
338 Bimmen. It is noteworthy, that PCB-138 and PCB-153 are strongly, linearly corre-  
339 lated ( $r_S = [0.81, 0.88]$ , Table 6), and there is a positive, power-function-type relation  
340 between Q and S at each SPM-quality monitoring station, though the correlations com-

341 prise a wider range ( $r_S = [0.37, 0.77]$ ).

## 342 **6 Discussion**

343 The tested effects are reproducible over different time-periods and different locations.  
344 TOC was always highest in CE-samples and no spatial trend was detectable. In con-  
345 trast, there is no effect due to “device” on  $\Sigma$ PCB, but there is an increasing trend of  
346  $\Sigma$ PCB with river reach length. This can be explained by the fact that secondary sources  
347 for PCBs emissions and re-mobilization are ubiquitous in the River Rhine catchment,  
348 although direct inputs into the streams have stopped many years ago. The most re-  
349 markable effects are present for concentrations of HCB in SPM that are highest in  
350 SPM-samples collected with FC and ST, followed by CE. This effect can be amplified  
351 depending on the location. Although HCB in SPM differs significantly between the  
352 locations (Tables 3 & 4), there is no general increasing trend with river reach length.  
353 Hence, HCB is a non-ubiquitous substance with locally relevant secondary sources  
354 and HCB-contaminated SPM is mixed with the SPM of tributaries further downstream,  
355 which dilutes the concentration of HCB. A further indication for both longitudinal  
356 dispersion and the mixing of SPM with tributaries are the decreasing correlation coef-  
357 ficients between HCB (PCB-138, PCB-153) and S with river reach length (Table 6).

### 358 **6.1 Effects due to the separation principle**

359 The two passive samplers FC and ST that separate the SPM/water mixture by sedimen-  
360 tation show a clear fractionation effect as it has been reported by others<sup>15,22</sup>.  $D_{\text{Mean}}$  and  
361 PSD in these SPM-samples differed significantly from SPM-samples collected with  
362 CE, in that coarser particles (i.e. particles with higher settling velocities) are present  
363 in SPM-samples that were taken with FC or ST. As the temporal course of daily  $D_{\text{Mean}}$   
364 does not show a high variability in instantaneously collected SPM with CE (Fig. 6  
365 B), this fractionation towards coarser particles can not be attributed to a mixing effect  
366 caused by integral sampling, but must rather be attributed to the separation principle of  
367 the passive samplers FC and ST.

368 The different sampling techniques lead to homogeneous subsequent  $\Sigma$ PCB concen-  
369 trations in SPM in each test. It is widely accepted that the concentrations of non-polar  
370 organic pollutants such as PCBs are inversely related with particle-size<sup>23</sup> in soils and  
371 sediments and the organic coating of the fines act as the sorbent. However, as there  
372 is no relevant effect caused by the sampling devices on the investigated PCB con-  
373 geners, although a clear fractionation towards coarser particles occurs for FC and ST,  
374 we hypothesize, that PCBs are almost equally distributed within the relevant range of  
375 particle-sizes ( $< 200 \mu\text{m}$ ) in collected SPM of the River Rhine.

376 In contrast to  $\Sigma$ PCB, the concentrations of HCB in SPM are three times higher in  
377 SPM-samples collected with FC than with CE. As FC also collects coarser particles  
378 in the fine sand fraction, we hypothesize that HCB concentration is positively skewed  
379 among the relevant particle-size fractions of collected SPM in the River Rhine. It is  
380 likely that HCB was historically emitted in granular form with particle-sizes in the  
381 range of coarse silt to fine sand.

382 Furthermore the interaction term (location  $\times$  device) for HCB is significant (Tables  
383 3 & 4), which means that the differences between the sampling techniques can be am-  
384 plified upon the “location”. This can be explained by the fact that the statistical factor  
385 “location” comprises the specific in-stream conditions (i.e. flow velocity,  $S$  and  $\chi$ ) at  
386 the corresponding sampling point of a sampling device. As each of these parameters  
387 differ along the river stretch (i.e. “location”), which in return effects the separation  
388 efficiency of the installed passive samplers (FC and ST) as well as the magnitude of  
389 fractionation, the discrepancies caused by the devices on HCB in SPM can be amplified  
390 upon the sampling location.

391 Throughout the field experiments, TOC was highest in SPM-samples collected with  
392 CE. Potential reasons for this are numerous, but one reason can be attributed to the  
393 separation principle: Not only humic substances that are attached to the mineral par-  
394 ticles, but also living algae and fresh detritus with low densities are separated from  
395 the SPM/water mixture by centrifugation. Furthermore, TOC is inversely related to  
396 decreasing particle-size and the maximum loading is attached to minerals in the fine-  
397 fraction (i.e.  $< 20 \mu\text{m}$ ). The fine-fraction, algae and detritus are collected to a much



398 lesser extend, when sedimentation is the separation principle. Thus, the subsequent  
399 TOC is higher in SPM-samples collected with CE as compared to SPM-samples col-  
400 lected with FC and ST. Other potential reasons are discussed in Sect. 6.2.

## 401 **6.2 Effects due to time-proportional versus integral sampling**

402 As the correlation coefficients between HCB (PCB-138, PCB-153) and S are not sig-  
403 nificant (Table 6) at most of the SPM-quality stations and the daily variability of the  
404 aforementioned parameters is low (Fig. 6 D & E), we conclude that integral sampling  
405 with its consequent unequal amounts of daily collected SPM can not be the reason for  
406 the higher HCB concentration in SPM that was collected with FC.

407 However, the elevated TOC concentrations in SPM that was collected with CE can  
408 not only be attributed to the different separation efficiencies of the devices, but must  
409 also be discussed in light of the significant inverse correlation of TOC with S that is  
410 present at each SPM-quality monitoring station. As the amount of collected SPM under  
411 high S is larger, the final TOC concentration in the composite SPM sample is likely to  
412 be lower than the temporal average. This is consistent with the findings that mean TOC  
413 concentrations in CE are highest at each SPM-quality monitoring station, and TOC  
414 is not significantly different between the SPM-samples of FC and ST. Furthermore, a  
415 decay of rapidly biodegradable organic compounds of TOC is possible, because the  
416 sampled SPM remained inside the FC for periods of four weeks.

## 417 **7 Conclusion**

418 In this study, we analyzed an extensive set of field data on the homogeneity of SPM-  
419 sampling techniques across several monitoring stations at the River Rhine. This brought  
420 new insights for the evaluation and implementation of SPM-quality monitoring pro-  
421 grams. As differences between the SPM collection techniques may be amplified de-  
422 pending on the location and the chemical parameter in focus, guidelines for SPM sam-  
423 pling techniques need to be revisited with an appropriate concept.

424 The sampling techniques FC, ST and CE provide homogeneous results with respect

425 to the relevant contaminants of PCB congeners in the River Rhine, but physical param-  
426 eters and HCB concentrations differ significantly between the sampling techniques.  
427 The general findings are reproducible over several collection periods and sampling lo-  
428 cations. We thus hypothesize that the relevant PCBs are equally distributed among  
429 the particle fractions  $< 200 \mu\text{m}$ . As HCB concentrations are highest in SPM-samples  
430 with coarser particles collected with FC, we hypothesize that HCB was likely emitted  
431 in granular form. Further chemical analysis (i.e. determination of PCBs and HCB in  
432 fractions of composite SPM and selected fluvial sediment samples) is required to test  
433 our hypothesis with respect to the distribution of PCBs and HCB among particle-size  
434 fractions.

435 We propose the following for the harmonization and implementation of SPM-  
436 quality monitoring programs that aim to quantify the concentration of particle-bound  
437 contaminants: If the SPM of the stream water mainly consists of fine material (silt and  
438 clay), as it is the case for the River Rhine, then integral samplers such as FC and ST  
439 are only adequate for the monitoring of those particle-bound contaminants, which are  
440 almost non-reactive (e.g. persistent organic pollutants, heavy metals), do not corre-  
441 late with the concentration of suspended sediments at the specific monitoring site, and  
442 are equally distributed within the particle-size fraction  $< 200 \mu\text{m}$ . In any other case,  
443 time-proportional instantaneous sampling with CE is superior.

444 If the stream water mainly transports large fractions of sand, then a less rigorous  
445 sampling technique might be possible. In this case, the fractionation effect of FC and  
446 ST is dampened and, thus, plays a minor role for the contaminant concentration in the  
447 composite SPM-sample. Furthermore, FC and ST samplers can be useful to detect  
448 qualitatively those contaminants, whose temporal courses are discontinuous (i.e.  $\chi$  is  
449 usually below the limit of quantification), provided that the compounds in focus are  
450 almost non-reactive.

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Table 1: Names of the monitoring stations (location), the installed devices, their corresponding river-kilometer index (RI, increasing order from source to mouth) and sampling period (SP). n.a. denotes not available.

Location		Centrifuge	Floating collector	Sedimentation tank
Bimmen	RI	Rhine-km 865.0	Rhine-km 865.0	Rhine-km 865.0
	SP	Since 1990	2005-01-19 to 2005-12-31	2005-01-19 to 2005-12-21
Karlsruhe-Lauterbourg	RI	Rhine-km 359.2	Rhine-km 340.3	n.a.
	SP	Since 1990	2002-07-09 to 2007-06-04	n.a.
Koblenz	RI	Rhine-km 590.3	Rhine-km 590.3	Rhine-km 590.3
	SP	Since 1990	2005-01-19 to 2005-12-31	2005-01-19 to 2005-12-21
Weil	RI	Rhine-km 174.0	Rhine-km 173.1	n.a.
	SP	Since 1990	2002-07-09 to 2007-06-04	n.a.

Table 2: Summary statistics of the investigated parameters in suspended matter. Limits of quantification are indicated by the “<”-sign.

Parameter	Median	Minimum	Maximum	n
TOC (%)	4.4	< 0.5	91.0	383
HCB/ $\mu\text{g kg}^{-1}$	10.0	< 2.0	985.0	497
PentCB/ $\mu\text{g kg}^{-1}$	2.0	< 1.0	21.0	361
PCB-28/ $\mu\text{g kg}^{-1}$	2.0	< 1.0	14.1	451
PCB-52/ $\mu\text{g kg}^{-1}$	2.0	< 1.0	23.1	451
PCB-101/ $\mu\text{g kg}^{-1}$	2.1	< 1.0	16.0	451
PCB-118/ $\mu\text{g kg}^{-1}$	2.0	< 1.0	15.0	451
PCB-138/ $\mu\text{g kg}^{-1}$	4.2	< 1.0	26.4	451
PCB-153/ $\mu\text{g kg}^{-1}$	2.7	< 1.0	21.4	451
$\Sigma\text{PCB}/\mu\text{g kg}^{-1}$	19.4	< 7.0	132.6	451

Table 3: Two-way ANOVA tables for  $\Sigma\text{PCB}$ , TOC and HCB for the period: 6. May 2005 to 31. December 2005. The factor “location” consists of the monitoring stations Weil, Karlsruhe-Lauterbourg, Koblenz and Bimmen, and the factor “device” comprises centrifuges and floating collectors.  $\phi$ , SSQ, MSSQ,  $F$ , and  $p$  indicate the degree of freedom, the sum of squared residuals, the mean SSQ, the  $F$ -value and the corresponding  $p$ -value. Note: due to incomplete TOC-series, Karlsruhe-Lauterbourg was not considered in the two-way ANOVA.

Parameter	Factor	$\phi$	SSQ	MSSQ	$F$	$p$
PCB-138	Location	3	484.8	161.6	25.51	0.000
	Device	1	2.8	2.8	0.44	0.509
	Location:Device	3	7.0	2.3	0.37	0.778
	Residuals	75	475.1	6.3		
PCB-153	Location	3	549.5	183.2	28.31	0.000
	Device	1	0.0	0.0	0.00	0.957
	Location:Device	3	69.5	23.2	3.58	0.018
	Residuals	75	485.2	6.5		
$\Sigma\text{PCB}$	Location	3	12195.4	4065.1	32.64	0.000
	Device	1	262.8	262.8	2.11	0.150
	Location:Device	3	761.8	253.9	2.04	0.116
	Residuals	75	9339.5	124.5		
TOC	Location	2	5.8	2.9	1.34	0.269
	Device	1	49.3	49.3	22.66	0.000
	Location:Device	2	17.9	9.0	4.12	0.021
	Residuals	60	130.6	2.2		
HCB	Location	3	12570.7	4190.2	17.69	0.000
	Device	1	8791.8	8791.8	37.11	0.000
	Location:Device	3	4614.6	1538.2	6.49	0.001
	Residuals	75	17767.9	236.9		

Table 4: Two-way ANOVA tables for PCB-138, PCB-153,  $\Sigma$ PCB, TOC and HCB for the extended period: 9. July 2002 to 4. June 2007. The factor “location” consists of the monitoring stations Weil and Karlsruhe-Lauterbourg, and the factor “device” comprises centrifuges and floating collectors. Same notation as Table 3.

Parameter	Factor	$\phi$	SSQ	MSSQ	$F$	$p$
PCB-138	Location	1	299.6	299.6	53.95	0.000
	Device	1	90.6	90.6	16.32	0.000
	Location:Device	1	10.7	10.7	1.92	0.167
	Residuals	300	1666.1	5.6		
PCB-153	Location	1	781.9	781.9	99.32	0.000
	Device	1	108.1	108.1	13.73	0.000
	Location:Device	1	77.1	77.1	9.80	0.002
	Residuals	300	2361.8	7.9		
$\Sigma$ PCB	Location	1	9900.0	9900.0	110.49	0.000
	Device	1	297.8	297.8	3.32	0.069
	Location:Device	1	1894.1	1894.1	21.14	0.000
	Residuals	300	26880.1	89.6		
TOC	Location	1	312.2	312.2	105.19	0.000
	Device	1	432.9	432.9	145.87	0.000
	Location:Device	1	6.2	6.2	2.08	0.151
	Residuals	243	721.1	3.0		
HCB	Location	1	327620.6	327620.6	49.63	0.000
	Device	1	58397.3	58397.3	8.85	0.003
	Location:Device	1	65566.4	65566.4	9.93	0.002
	Residuals	300	1980319.8	6601.1		

Table 5: Two-way ANOVA tables for PCB-138, PCB-153,  $\Sigma$ PCB, TOC and HCB for the period: 19. January 2005 to 21. December 2005. The factor “location” consists of the monitoring stations Koblenz and Bimmen, and the factor “device” comprises centrifuges, floating collectors and sedimentation tanks. Same notation as Table 3.

Parameter	Factor	$\phi$	SSQ	MSSQ	$F$	$p$
PCB-138	Location	1	235.7	235.7	35.47	0.000
	Device	2	0.2	0.1	0.01	0.987
	Location:Device	2	24.2	12.1	1.82	0.169
	Residuals	74	491.8	6.6		
PCB-153	Location	1	160.1	160.1	24.20	0.000
	Device	2	30.7	15.4	2.32	0.105
	Location:Device	2	90.0	45.0	6.81	0.002
	Residuals	74	489.5	6.6		
$\Sigma$ PCB	Location	1	5987.2	5987.2	38.97	0.000
	Device	2	1058.4	529.2	3.44	0.037
	Location:Device	2	1131.8	565.9	3.68	0.030
	Residuals	74	11370.0	153.6		
TOC	Location	1	0.4	0.4	0.31	0.579
	Device	2	23.9	11.9	9.44	0.000
	Location:Device	2	0.3	0.1	0.10	0.904
	Residuals	69	87.3	1.3		
HCB	Location	1	433.1	433.1	1.48	0.228
	Device	2	7981.6	3990.8	13.60	0.000
	Location:Device	2	1613.8	806.9	2.75	0.071
	Residuals	74	21720.1	293.5		

Table 6: Matrix of Spearman's rank correlation coefficients ( $r_S$ ) for the parameters flow ( $Q$ ), suspended sediment concentration ( $S$ ), HCB, PCB-138, PCB-153 and TOC concentration in suspended matter that was instantaneously collected with centrifuges at various River Rhine monitoring stations (1990-2008). Bold digits denote highly significant ( $p \leq 0.01$ ) values of  $r_S$ ; significant ( $p \leq 0.05$ ) values of  $r_S$  are marked with italics.

Location		S	HCB	PCB-138	PCB-153	TOC
Weil	$Q$	<b>0.73</b>	<b>-0.39</b>	<b>-0.41</b>	<b>-0.44</b>	<b>-0.62</b>
	$S$		<b>-0.48</b>	<b>-0.48</b>	<b>-0.52</b>	<b>-0.70</b>
	HCB			<b>0.58</b>	<b>0.69</b>	<b>0.50</b>
	PCB-138				<b>0.84</b>	<b>0.57</b>
	PCB-153					<b>0.60</b>
Karlsruhe-Lauterbourg	$Q$	<b>0.37</b>	<i>0.10</i>	<b>-0.27</b>	<b>-0.25</b>	n.a.
	$S$		-0.05	<b>-0.27</b>	<b>-0.26</b>	n.a.
	HCB			<b>0.25</b>	<b>0.24</b>	n.a.
	PCB-138				<b>0.88</b>	n.a.
	PCB-153					
Koblenz	$Q$	<b>0.77</b>	-0.09	<b>-0.32</b>	<b>-0.33</b>	<b>-0.28</b>
	$S$		0.03	-0.10	<i>-0.13</i>	<b>-0.43</b>
	HCB			<b>0.41</b>	<b>0.33</b>	-0.02
	PCB-138				<b>0.86</b>	<b>0.14</b>
	PCB-153					<b>0.13</b>
Bimmen	$Q$	<b>0.41</b>	<i>-0.11</i>	<b>-0.47</b>	<b>-0.40</b>	<b>-0.31</b>
	$S$		0.01	-0.06	0.02	<b>-0.21</b>
	HCB			<b>0.35</b>	<b>0.44</b>	-0.04
	PCB-138				<b>0.81</b>	<b>0.26</b>
	PCB-153					<b>0.12</b>

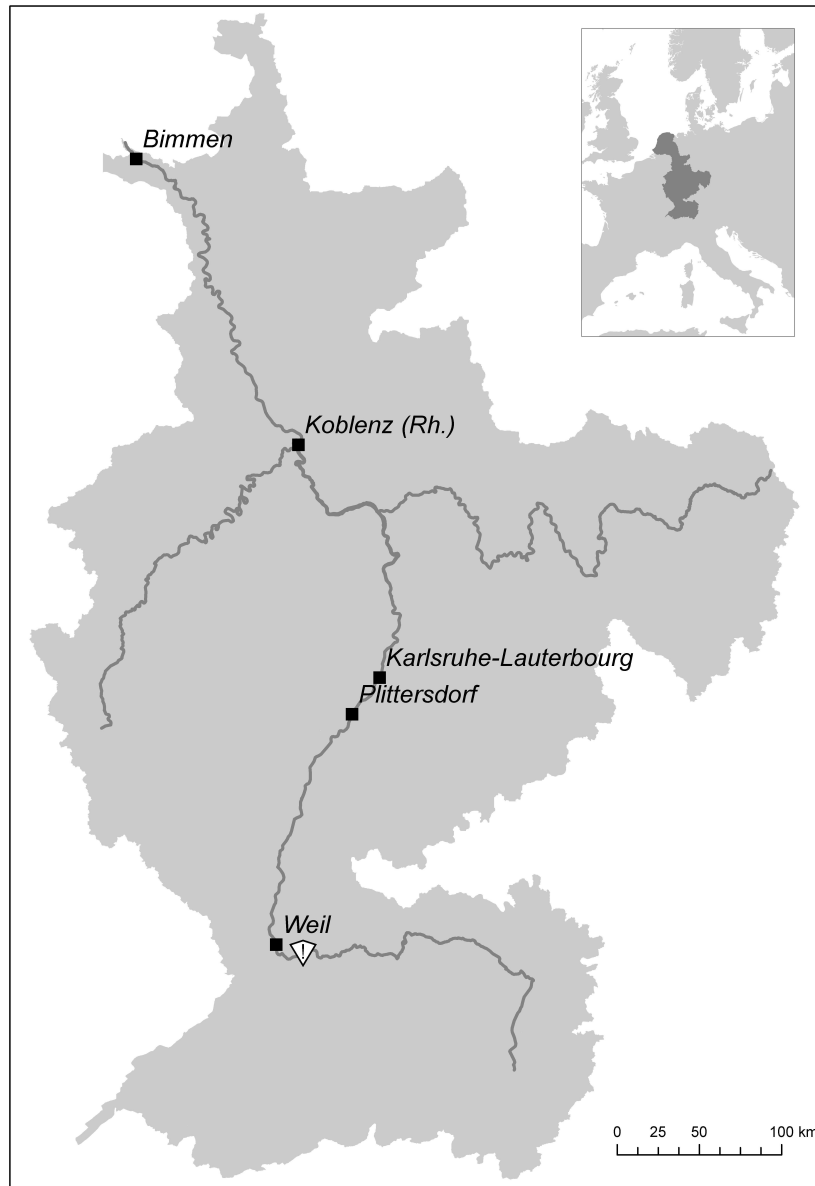


Figure 1: River Rhine catchment and locations of suspended matter quality stations. The historic emission site for HCB is located ca. 16 km upstream of the city of Weil. Note that Plittersdorf and Karlsruhe-Lauterbourg are treated as one single location in this study.

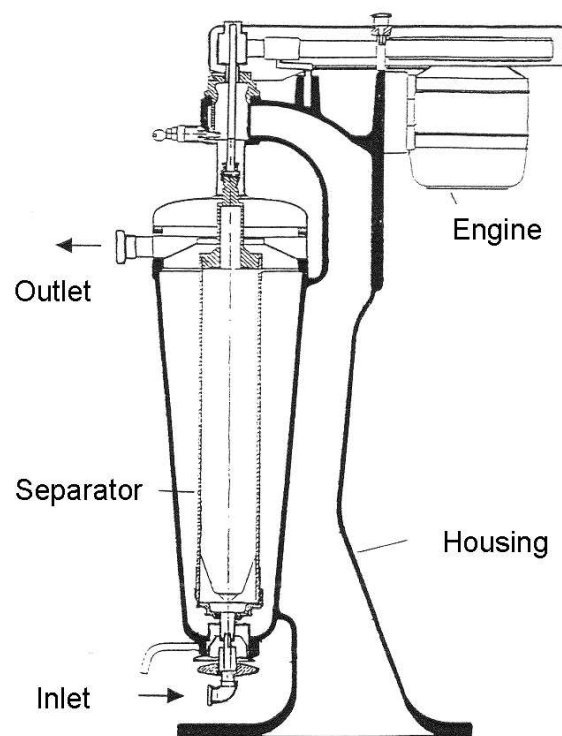


Figure 2: Sketch of a continuous flow centrifuge (modified after ISO 5667-17<sup>15</sup>).

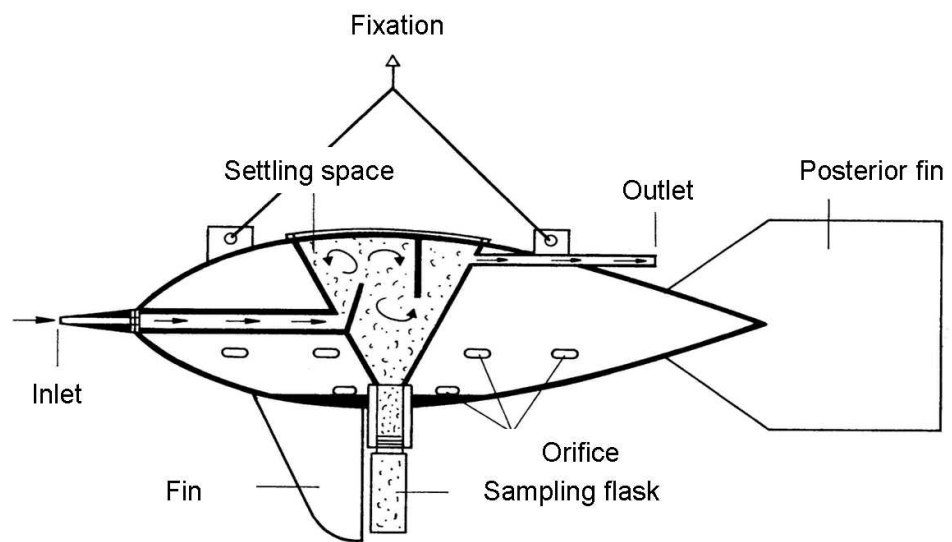


Figure 3: Sketch of the floating collector *Binnensammler* (modified after ISO 5667-17<sup>15</sup>).



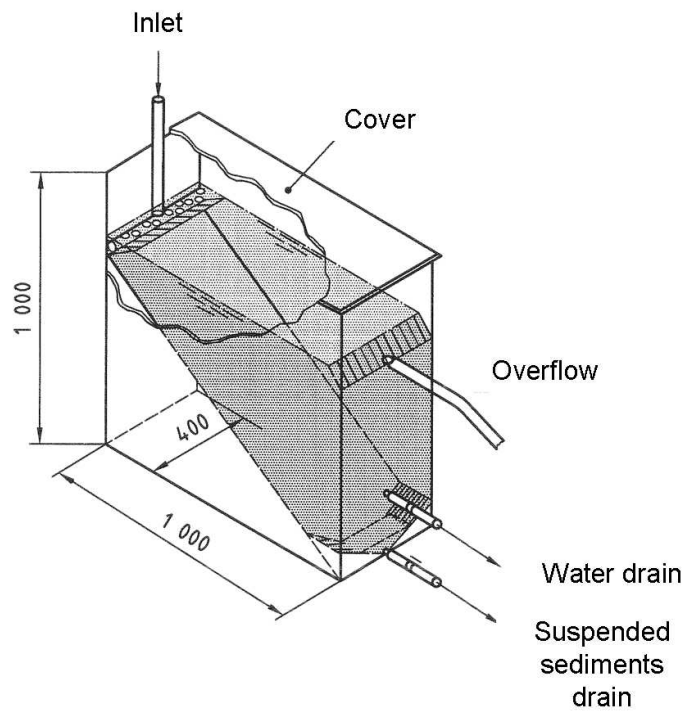


Figure 4: Sketch of a sedimentation tank (modified after ISO 5667-17<sup>15</sup>).

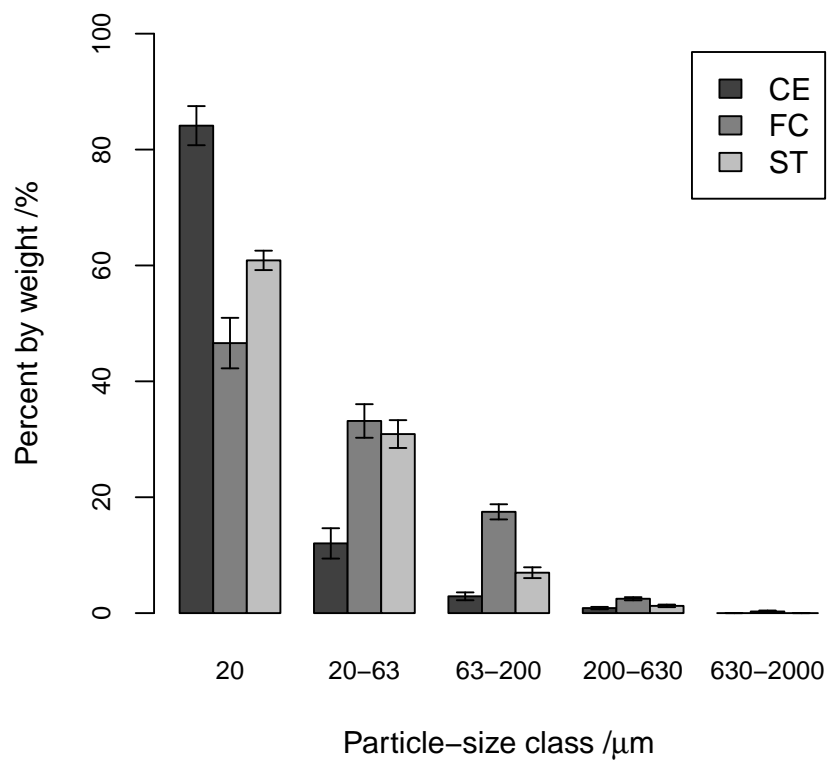


Figure 5: Particle-size distribution of SPM collected with centrifuges (CE), floating collectors (FC) and sedimentation tanks (ST) at Koblenz (19. January 2005 to 17. May 2005). Whiskers denote standard error of the mean.

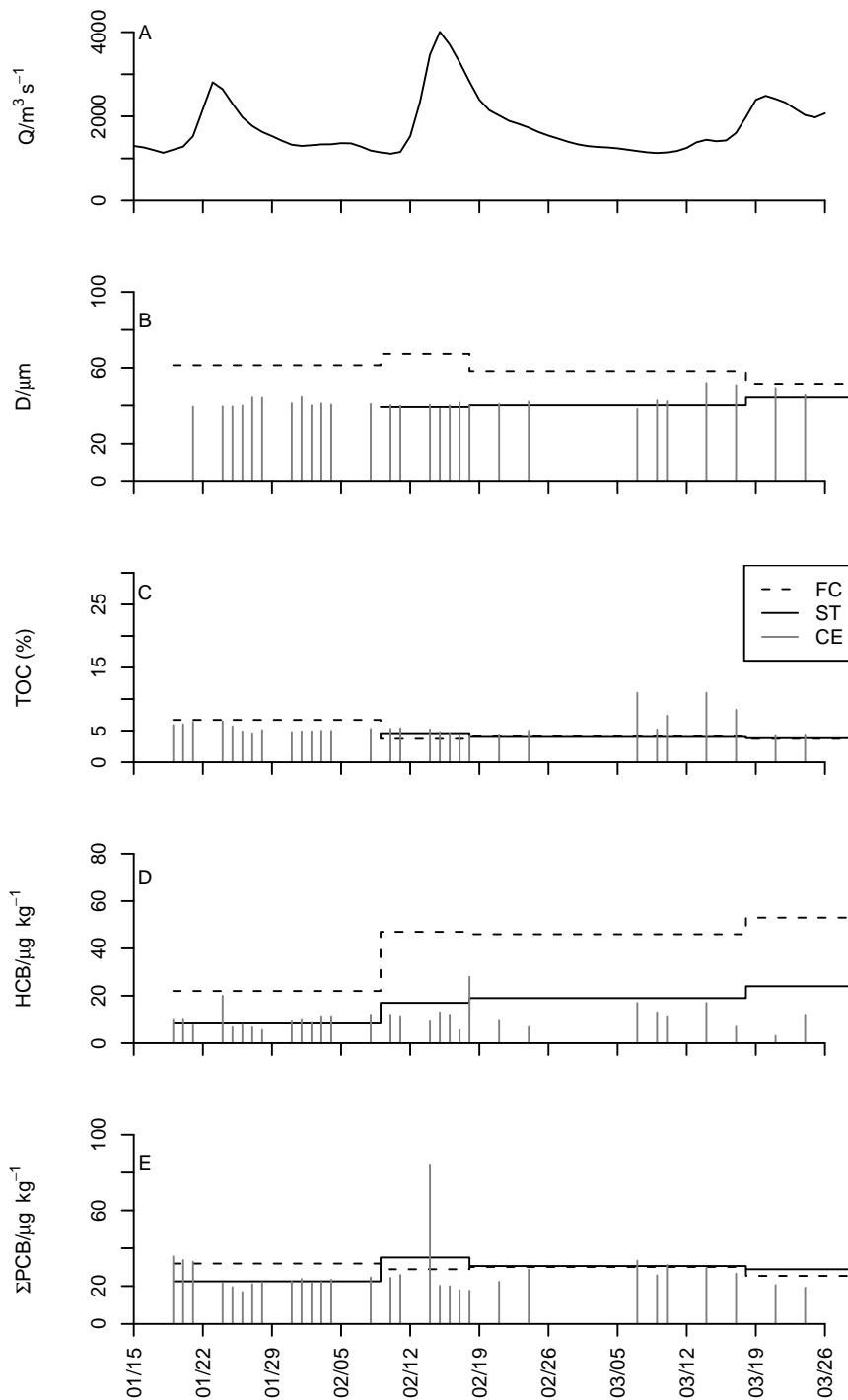


Figure 6: Temporal course of (A) flow , (B) mean particle-size, (C) total organic carbon, (D) hexachlorobenzene in suspended matter and (E) the sum of polychlorinated biphenyls in suspended matter at the monitoring station Koblenz (15. Jan 2005 to 26. Mar 2005). FC, ST, and CE denote floating collector, sedimentation tank and centrifuge.

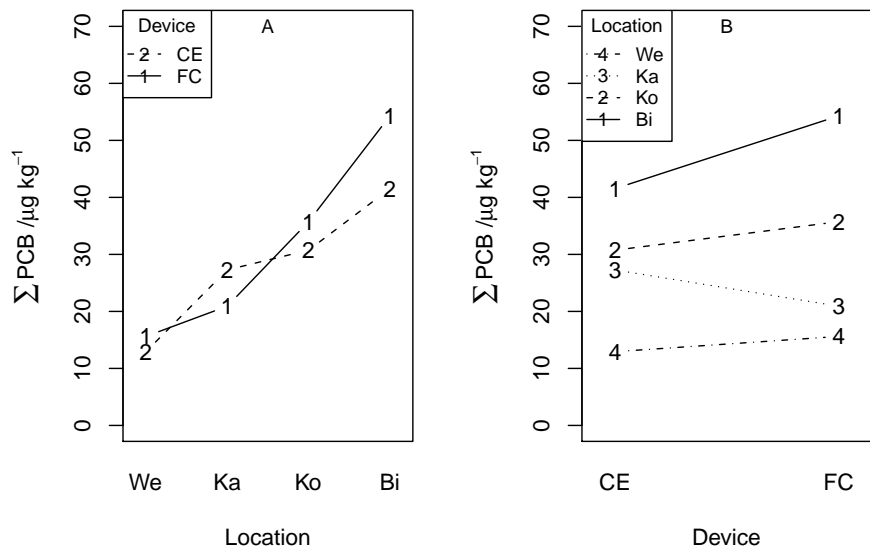


Figure 7: Interaction plot for  $\Sigma\text{PCB}$  in suspended matter. Figure A depicts the mean of  $\Sigma\text{PCB}$  for each location, grouped by the devices. Figure B depicts the reverse. We, Ka, Ko, Bi, CE, and FC denote Weil, Karlsruhe-Lauterbourg, Koblenz, Bimmen, centrifuge and floating collector.

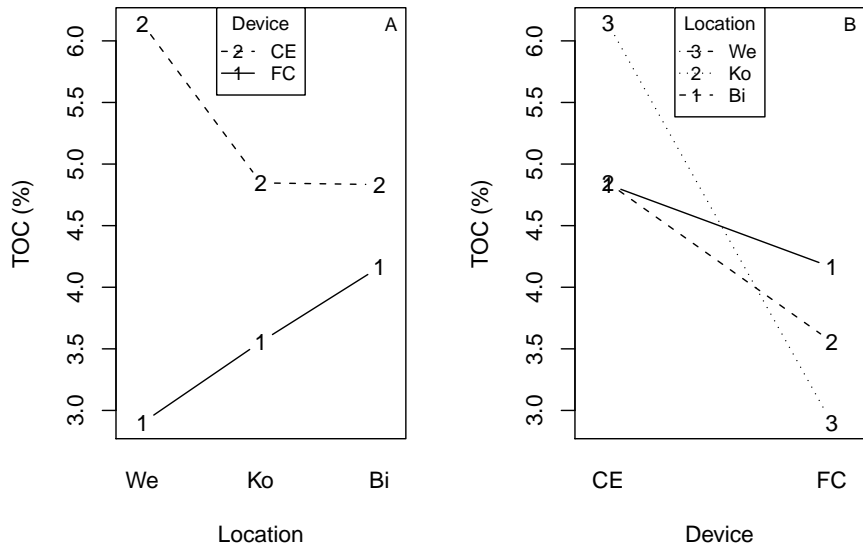


Figure 8: Interaction plot for TOC in suspended matter. Same notation as Fig. 7. Note that Karlsruhe-Lauterbourg was not considered due to incomplete records.

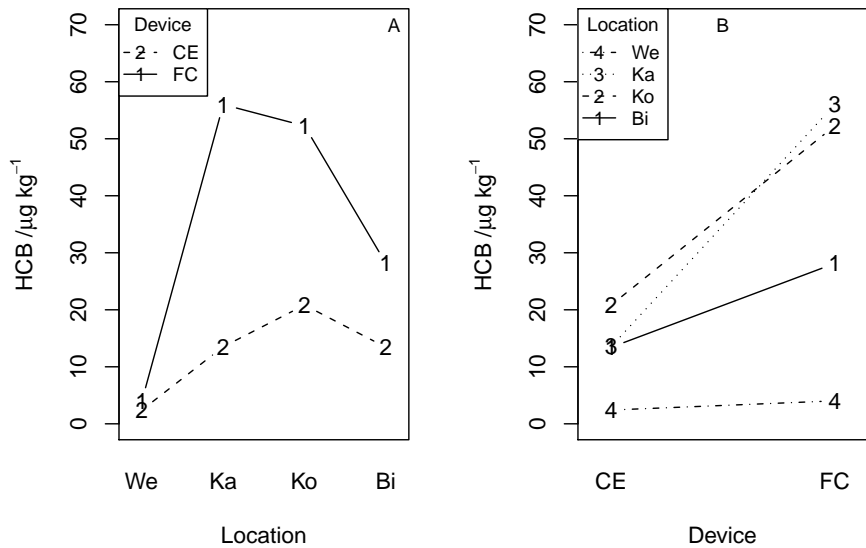


Figure 9: Interaction plot for HCB in suspended matter. Same notation as Fig. 7