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Persistent organic pollutants in stream water – influence of hydrological conditions and landscape type

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Abstract

Concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) in stream water were measured in a remote catchment in northern Sweden and downstream to the Baltic Sea. Sampling took place at seven sites during two years and under different hydrological conditions – during the snow-free, snow-covered, and spring flood seasons. Concentrations varied substantially between seasons, and were up to 20 times higher during spring flood compared to the preceding snow-covered period. The increase in concentrations with runoff was due to higher levels of particle-associated contaminants, while the dissolved concentrations remained stable. Particulate contaminant concentrations were positively correlated primarily to suspended particulate matter (SPM) at sites in areas with a high land-cover fraction of sorted sediment. When comparing upstream sampling locations, a mire-dominated stream had higher concentrations and lower retention of atmospherically deposited contaminants than a forest stream of the same catchment size. Contaminant concentrations (normalized to volume) did not increase consistently downstream despite the presence of several point sources. However, when normalized to the amount of SPM, concentrations were on average >20 times higher at the outlet in the Baltic Sea compared to the outlet from the remote catchment without point sources.

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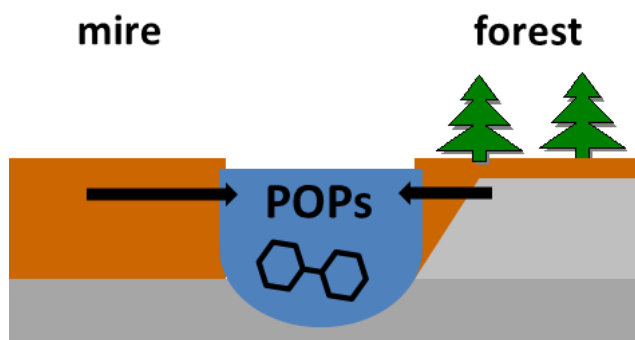
1. Introduction

The environmental fate of legacy persistent organic pollutants (POPs), including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), has been extensively studied. Bans and regulations have been implemented, leading to declining levels of legacy-POPs in the environment[1]. However, in some locations the declines have levelled off and legacy-POP levels are still elevated, for example in fish in the Baltic Sea[2]. Riverine inputs may be an important source of POPs to sea areas (e.g.[3-6]), transporting pollutants from the terrestrial environment to aquatic organisms.

Most legacy-POPs are semivolatile compounds that can undergo long-range atmospheric transport and thus reach areas far from original source areas[7]. Boreal forests cover around 15 million km^2 and constitute almost one third of the world's forests[8]. They receive and store large amounts of atmospherically deposited POPs[9-12], which makes them an important factor in the global fate and transport of contaminants. Snowfall is one of the most important pathways for atmospheric contaminants to reach the terrestrial environment in cold climates[13]. For example, measurements in northern Sweden have shown that ~70% of the yearly deposition of PCDD/Fs occurs during winter (November-March)[12]. During spring snowmelt, contaminants are then remobilized and either revolatilized to the atmosphere or transported with meltwater into soils and streams[14]. Accordingly, relatively high concentrations of organic contaminants have been observed in urban and rural rivers in connection with spring snowmelt[15-19]. There are also landscape-related variations that may impact stream water quality. The boreal landscape is a mixture of forests and mires, which vary fundamentally in both hydrological functioning and biogeochemical dynamics. For example, total organic carbon (TOC) concentration in streams and export from the catchment increases with an increasing proportion of mires[20-22]. It has also been shown that contrasting melt water

69 pathways during spring flood generally result in declining TOC concentrations in streams

70 draining mires and increasing concentrations in streams draining forests[21]. Furthermore, also

71 the quality of TOC is to a large extent controlled by landscape element type, with forests and

72 mires displaying markedly different fluorescence signatures[23]. However, while the controls on

73 riverine fluxes of terrestrially derived TOC is relatively well understood, corresponding

74 controls on POPs are poorly investigated; for example, knowledge is lacking on the influence

75 of different landscape elements and their interplay with hydrological functioning. This

76 knowledge is important to understand how boreal forests function as buffers and reservoirs of

77 atmospherically-derived POPs.

78

79 The aim of this study was therefore *1)* to establish an understanding of the importance of

80 seasonality and land cover type for surface water POP concentrations and exports from boreal

81 environments, and *2)* to assess the contribution of remote boreal catchments compared to

82 downstream point sources for the concentrations of POPs in rivers. To do this, we

83 investigated stream concentrations of PCBs, PCDD/Fs, and hexachlorobenzene (HCB) at

84 seven sites during different seasons – the snow-covered, spring flood and snow-free seasons–

85 for two consecutive years. The main study area is a near-pristine managed forest area in

86 Sweden where long-term monitoring of hydrology as well as soil and stream water chemistry

87 is performed at multiple sites within the Krycklan Catchment Study (KCS)[24]. Levels and

88 environmental dynamics of POPs in air, deposition and soil in this area have been

89 investigated[12, 25].

90

91 **2. Experimental**

92

93 **2.1 Sampling program**

94 Samples were collected from March 2008 to November 2009 in the Krycklan catchment and

95 downstream to the Gulf of Bothnia (Figure 1). Sampling included (*i*) spring flood (SprFl; May

96 2008, April-May 2009), (*ii*) snow-free season (SF; November-December 2008 and November

97 2009), and (*iii*) snow-covered season (SC; March-April 2008 and 2009). Sampling dates and

98 sites are available in Table S1.

99
100 [Please add Figure 1 here]

101

102 Krycklan is a 68 km^2 area located 60 km inland from the Baltic Sea in northern Sweden

103 (64°14´N, 19°46´E). The mean annual precipitation, runoff and temperature of the catchment

104 is 612 mm, 312 mm and +1.8˚C (1981-2010)[24], respectively. Approximately 35% of the

105 annual precipitation falls as snow[26]. Spring flood with the highest annual stream discharge

106 usually occurs in April-May. It is followed by low flow and occasional rain-induced episodes

107 during the snow-free season in summer and autumn (June-October/November), and stable

108 winter low flow during the snow-covered season because of little mid-winter snow melt

109 (November-March/April).

110

111 Four sites in the Krycklan catchment were monitored in this study (Figure 1 and Table 1): a

112 forest sub-catchment (C2); a mire sub-catchment (C4); an intermediate site (C13), and the

113 catchment outlet (C16; sites designated with their usual KCS site number). The three

114 sampling sites downstream of the Krycklan catchment were: Ytterrödå (D1), located in the

115 Vindel River downstream of the Krycklan outlet; Berg (D2), located in the Ume River

116 downstream of the Vindel River outlet; and Norra Bergsboda (D3), located close to the Ume

117 River outlet in the Gulf of Bothnia (Figure 1). The sampling sites D1-D3 represent a gradient

118 from near-pristine (D1) to successively more urbanised areas: D2 is located downstream

119 Vännäs (approximately 5 000 inhabitants) and D3 downstream of the city of Umeå

120   (approximately 80 000 inhabitants). A number of contaminant point sources are present

121   between D2 and D3, including a former saw mill contaminated with PCDD/Fs[27] that was

122   remediated during 2007-2008, and a sewage treatment plant.

123

124   **2.2 Water sampling**

125   Samples were collected by pumping 0.2-0.9 m^3 of stream water on site through filters

126   (Whatman 2.7 μm pre-filter followed by a Whatman GF/F (0.7 μm) filter) and polyurethane

127   foam (PUF) plugs (diameter 60 mm, length 50 mm; 5 plugs in series). The time required to

128   collect a sample varied depending on filter clogging but could be up to 6 hours, and sampling

129   flow rate was 0.5-3 L min^{-1}. All streams were sampled from the shore below relatively mixed

130   river sections. In the smaller streams this resulted in the sampling point being in the middle of

131   the stream section, whereas the sampling in the larger rivers was around 3 m from the shore.

132   Filters and PUFs were wrapped in foil, stored cooled and transported to the freezer the same

133   day. Filters and PUFs were analysed separately, which enabled a differentiation between the

134   particulate (>0.7 μm) and the apparently dissolved (<0.7 μm) phase. The apparently dissolved

135   phase included freely dissolved POPs and POPs associated with colloidal particles or

136   dissolved organic matter[28]. Similar set-ups for high-volume water sampling of POPs have

137   been used previously[29, 30]. Separate samples (250 mL) were collected in polypropylene bottles

138   for analysis of TOC, suspended particulate matter (SPM), and pH. Samples were kept frozen

139   (-18°C) until analysis.

140

141   **2.3 POP analysis**

142   Isotopically labelled (^{13}C) internal standards of all seventeen 2378-substituted PCDD/F

143   congeners ($\Sigma PCDD/F_{17}$), HCB, and nineteen PCB congeners were added to all samples prior

144   to extraction. The PCBs encompassed CBs 28, 52, 101, 118, 138, 153, and 180 (ΣPCB_7), four

145   non-*ortho* congeners (CBs 77, 81, 126, 169), seven mono-*ortho* congeners (CBs 105, 114,

146   123, 156, 157, 167, 189; in addition to CB 118), and one additional poly-*ortho* congener (CB

147   128). CBs 128 and 167 co-elute on the GC column, and are reported as the sum of the two.

148   The analytical method followed a previously published method[29]. In brief, extraction was

149   carried out in Soxhlet-Dean-Stark apparatus by refluxing with 400 mL toluene for at least 15

150   h. Extracts were purified on a multilayer silica column containing acid silica, followed by

151   fractionation on an AX21 carbon/celite column. Prior to analysis, each fraction was purified

152   once more using a miniaturized multilayer silica column and recovery standards (CBs 97 and

153   188 for fraction 1; 1234-TCDD, 12346-PeCDF, 123469-HxCDF and 1234689-HpCDF for

154   fraction 2) were added. Analysis was performed using a GC/HRMS (Agilent 6890N coupled

155   to a Waters Micromass Autospec Ultima) equipped with a 60 m DB-5 column (J & W

156   Scientific, Agilent Technologies, USA; i.d. 0.25 mm; film thickness 0.25 μm), and the

157   quantification was made using the isotope dilution method.

158

2.4 Water flow and POP flux determinations

160   Water flow ($m^3 s^{-1}$) was recalculated into runoff (mm day^{-1}) based on the catchment area:

161

162   Runoff (mm day^{-1}) = 1000 (mm m^{-1}) × flow ($m^3 s^{-1}$) × 86400 (s day^{-1}) / area (m^2)   **Eq. 1**

163

164   Daily water flow data were collected from the continuous measurements at a central

165   catchment in the Krycklan area (site C7), and Krycklan subcatchments were assumed to have

166   equal runoff. Daily water flows for the downstream D1-D3 sites were available from the

167   nearest monitoring station of the Swedish Meteorological and Hydrological Institute (SMHI,

168   www.smhi.se; Granåker in Vindel River and Stornorrfors in Ume River). Fluxes of POPs at

169   sites C2 and C4 were calculated by site-specific regressions between POP concentrations and

170 water runoff in combination with runoff data (for details, see Supporting information). The

171 water flow for site C7, Vindel and Ume Rivers is available in Figure S1.

172

173 **2.5 SPM, TOC, and pH analysis**

174 SPM was determined gravimetrically using a method based on Swedish Standard SS-EN 872;

175 water samples (~200 mL) were filtered through glass fibre filters of the same type as for the

176 POP sampling (Whatman GF/F, 0.7 μm). Before filtering, the filters were rinsed with ultra-

177 pure water, dried at 105°C overnight and cooled in a desiccator before weighing. After

178 filtering the water samples, filters were once again dried at 105°C, cooled in a desiccator, and

179 weighed. Blank filters (filtering using corresponding amounts of ultra-pure water) were used

180 to correct for weight loss. TOC and pH were analyzed using a Shimadzu elemental analyzer

181 and a Mettler Toledo with a DGi117-water electrode, respectively. Samples were not filtered;

182 however, TOC in boreal catchments consists predominantly of dissolved organic carbon

183 (DOC)[31] (e.g. on average 94% DOC in Finnish water-courses[20]) and measurements in streams

184 and riparian soil water in the Krycklan catchment has verified this[32, 33]. TOC, pH and SPM for

185 each sample is available in Table S1 and as average for each season and sampling site in

186 Table S2; TOC and SPM as a function of flow is available in Figure S2.

187

188 **2.6 Quality assurance and calculations**

189 The recoveries ± standard deviation of the internal standards added at the start of the Soxhlet

190 extractions were 86 ± 27 % for PCDD/Fs, 95 ± 37 % for PCBs, and 62 ± 23 % for HCB. For

191 the chromatographic peak detection, the two most intense ions in the molecular cluster of each

192 analyte were monitored, and for a positive identification their ratio had to be within 20% of

193 the theoretical isotope ratio. Furthermore, a signal-to-noise ratio of 3:1 was required for a

194 positive detection, which was also used as the limit of quantification (LOQ). To replace

195   missing values (<LOQ), $0.5 \times$ LOQ was used (635 of 4320 values), primarily PCDDs in PUF

196   samples. Detected values were blank-corrected using average blank values for corresponding

197   sample type (filter or PUF). PCB measurements from the snow cover and spring flood season

198   2008, and the snow free season 2009, were excluded from the results due to high levels from

199   laboratory contamination.

200

201   Due to the long pumping time required for each sample, triplicate samples were only taken

202   over a time period of one day at site D2 on May 21 2008, and the relative standard deviation

203   (RSD) of the bulk (particulate + dissolved) concentrations was 31% for PCDD/F_{17}, 23% for

204   PCB$_7$, and 5% for HCB. Potential breakthrough in the PUF sorbent has been evaluated; the

205   last PUF (L 50 mm) contained on average 10% of the amount of PCDD/Fs, PCBs and HCB in

206   the original PUF configuration (L 200 mm)[29].

207

208   One sample (site D3, sampled during the snow-covered season 2008) had substantially higher

209   PCDD/F_{17} concentrations than remaining samples, and was not included in regressions

210   between POP concentrations and runoff, TOC or SPM, or when comparing between seasons.

211   However, the sample is discussed in the section concerning point sources (3.4). Statistical

212   analyses were performed using JMP 10.0.0 (SAS Institute Inc.).

213

214   3. Results and discussion

215

216   3.1 Seasonal trends in POP concentrations

217   POP bulk concentrations in stream water were highly variable between seasons and sampling

218   locations (Figure 2 a-c). For PCDD/F_{17}, the concentrations varied from 25 to 830 pg m^{-3},

219   excluding one extreme value of 4600 pg m^{-3} caused by a local temporary hotspot (see section

220   3.4). For PCB_7, concentrations varied from 1.8 to 23 ng m^{-3}, and for HCB from 3.0 to 21 ng

221   m^{-3}. These values are in the same range as measured in 2007-2008 in two rivers in an area

222   without major point sources in central Sweden[29]. Measurements of PCBs in the Ume River in

223   1990[4] showed median concentrations of PCBs of 210 ng m^{-3}, on average 15 times higher than

224   the PCB_7 concentrations measured at the Ume River site (D3) in the present study. Data from

225   the 1990 study included 51 congeners, but since the congeners in PCB_7 constitute a large part

226   of the PCBs present in mixtures[34], the measurements indicate that levels have decreased since

227   1990. This corresponds to decreases seen for PCBs in herring and sediment in the Baltic Sea

228   during this time period[35, 36].

229

230   [Please add Figure 2 here]

231

232   There was a general trend of higher POP concentrations during periods of high runoff, such as

233   the spring flood (April-May), while they were lower during the snow-free (June-

234   October/November) and snow-covered seasons (November-March/April; Figure 2a-c). The

235   trend was not consistent for all sites and pollutants. It was mostly apparent for upstream sites

236   (C-sites and D1, except C13), i.e. sites located in a more pristine area, and more evident for

237   the most hydrophobic group of compounds, $PCDD/F_{17}$, although it was observed also for

238   HCB. For PCB_7, data was only available from three samplings, and the concentration during

239   the snow-free season was relatively high (November 2008; Figure 2b). The highest increase

240   during spring flood compared to the preceding snow-covered season was observed for

241   $PCDD/F_{17}$ at forest site C2 in 2008, when concentrations increased by a factor 20 (Figure 2).

242   Several other river studies have demonstrated similar trends during spring flood[15-19], with e.g.

243   up to 100 times higher levels of PAH in an urban stream[18].

244

245 When bulk concentrations increased with runoff, it was caused by an increase in levels of

246 particle-associated POPs, while the concentration of dissolved contaminants remained stable

247 and did not change significantly with runoff (Figures 3 and S3-5, statistically significant

248 regressions listed in Table S3). Similar to our study, elevated levels of PAHs and PCBs in the

249 Susquehanna River were caused by an increase in the particulate fraction (also a particle

250 cutoff size of 0.7 µm) with increased flow[19]. In the St. Lawrence River, the dissolved fraction

251 of PCBs was responsible for the high bulk concentrations[16]; however, the particle cutoff size

252 was not defined, which makes comparisons to our work difficult.

253

254 [Please add Figure 3 here]

255

256 Bulk concentrations of PCBs were generally lower during the snow-covered season compared

257 to the snow-free season (e.g. the SC/SF ratio of PCB_7 stream concentrations were 0.50 ± 0.37,

258 as an average for all sites; Figure 2b, Figure S6). Bearing in mind the positive trend between

259 POP concentrations and discharge, lower concentrations are expected during the snow-

260 covered season due to the low winter base flow, as opposed to episodic rain-driven high-flow

261 events during the snow-free season (Figure 2). For PCDD/Fs and HCB, however, no such

262 differences were observed at any site (Figure 2a and c; Figure S6; ANOVA, $p > 0.05$).

263

264 Studies of the processes of mobilization of contaminants during snowmelt have concluded

265 that more water soluble compounds are likely to be mobilized to the water before more

266 hydrophobic compounds[14, 37, 38]. In the present study, samples were taken with shorter time

267 intervals for site C16 during the spring of 2009, but no hydrophobicity trend in the

268 concentrations over the course of a spring flood could be observed (Figure S7). This shows

269 that a hydrophobicity fractionation in a snowpack during melting will not have an impact on

11

270 higher-order streams that integrates processes occurring in the entire catchment. For example,

271 the speed of snowmelt differs between sunny and less sunny areas of the catchment.

272

273 **3.2 Potential drivers for the observed concentration trends**

274 The positive correlation between POP concentrations and runoff observed at many sites

275 (Figures S4-5) was further investigated for possible relationships to SPM or TOC (Figures

276 S8-11). The particulate POP concentrations generally displayed positive trends to both SPM

277 and TOC at the downstream sites (C16 and D1-3; Table S4). The linear regressions on SPM

278 tended to have higher r^2 values and lower p values than regressions on TOC. For PCDD/F$_{17}$ at

279 C16, the site with the largest range in SPM concentration (22-700 mg L^{-1}), the regression on

280 SPM displayed $r^2 \sim 0.9$ and $p \sim 0.0001$ (TOC: $r^2 \sim 0.5$ and $p \sim 0.02$). This demonstrates that

281 increased mobilization of particles is the likely explanation for higher concentrations of POPs

282 during spring flood.

283

284 On a congener basis, significant positive correlations to SPM were generally displayed by the

285 planar compounds (all 17 PCDD/Fs, 3 of 4 non-*ortho* PCBs, 3 of 8 mono-*ortho* PCBs), but

286 not by the non-planar ones (none of the poly-*ortho* PCBs; Table S5, for site C16). This

287 corresponds well to observations in a previous study on two rivers in central Sweden[29], where

288 a similar structural and hydrophobicity pattern for the SPM-association was found. The

289 observed planarity pattern might be explained by black carbon (BC) being present in the SPM

290 fraction, since sorption to BC is enhanced for planar compounds[39, 40]. Measurements of BC in

291 particles and also in the dissolved fraction in stream water would thus improve our

292 understanding on POP fluxes.

293

294   At upstream sites (C2, C4 and C13), no significant correlations between POP particulate

295   concentrations and SPM or TOC were observed (Table S4). The difference between the

296   upstream and downstream sites was apparent in the regressions on SPM, which tended to be

297   negative for C2 and C4, and slightly positive for C13, in contrast to the more positive

298   regressions further downstream (Figure S8). This demonstrates that the increased bulk

299   concentrations observed during spring flood, e.g. for $PCDD/F_{17}$ at the first-order streams C2

300   and C4 (Figure 2), cannot be explained by increased levels of SPM, or TOC, in the streams.

301   Due to land uplift after the last glaciation, the C2 and C4 catchments are located above the

302   highest postglacial coastline and do not contain fine sorted sediment soils (Table 1). It is

303   therefore likely that the particles at the upstream sites differ in quality from the downstream

304   sites.

305

306   The dissolved POPs concentrations were generally not correlated to SPM and TOC, being

307   significant (and positive) only for HCB at a few sites (Figure S10-11, Table S4). As the DOC

308   constitutes the dominant part of TOC in the stream water of study area (see section 2.5) and

309   the distribution of POPs in water, soil, and sediment generally is explained by partitioning to

310   organic carbon[41, 42], correlations between the dissolved concentrations and TOC were

311   expected.

312

313   **3.3 Influence of landscape type on stream POP concentrations**

314   To investigate the influence of landscape type on POP concentrations, first-order streams of a

315   forest-dominated (C2: 100% forest; Table 1) and a mire-dominated (C4: 56% forest, 44%

316   mire; Table 1) landscape were compared. Bulk concentrations of $PCDD/F_{17}$, PCB_7 and HCB

317   were generally higher in the mire stream (Figure 2; statistically significant for $PCDD/F_{17}$:

318   one-tailed paired *t*-test, *n*=5, *p*=0.03). The higher concentrations in the mire stream was due to

319 higher concentrations in the particle phase, with a C4/C2 ratio for the particulate

320 concentrations of on average 1.2 for $PCDD/F_{17}$ ($n=6$, $p=0.004$), 2.0 for PCB_7 ($n=3$, $p=0.02$),

321 and 2.6 for HCB ($n=6$, $p=0.03$). Dissolved-phase concentrations, on the other hand, were

322 similar between the mire and the forest stream ($p>0.05$). The higher particulate POP

323 concentrations in C4 than in C2 was not linked to higher levels of SPM in the mire stream; on

324 the contrary, SPM was higher in the forest stream during all seasons (Table S2).

325

326 The difference in POP bulk (and particulate) concentrations between C2 and C4 were

327 particularly high during the snow-covered season, followed by the snow-free season, with a

328 smaller difference during spring flood when absolute concentrations were higher in both

329 streams (Figure 2; C4/C2 ratios in Table S6). Forest and mires have different vertical

330 gradients of soil POPs concentrations[25] and markedly different hydrological behavior during

331 snowmelt[21, 43], which may account for the observed seasonal differences. During the snow-

332 covered season, deposition is retained in the snowpack and the groundwater level is low, so

333 stream discharge is primarily from deeper soil levels. In forested catchments (C2), these

334 deeper soils that are hydrologically connected to the stream during low flow periods are poor

335 in organic matter, and also in POPs[25], and hence the leaching is low. At the mire site (C4),

336 there is no vertical gradient of organic matter or POPs in the soil[25], so even during periods

337 with low water table the groundwater passes layers with high TOC and POP concentrations

338 before reaching the stream, which can explain the high C4/C2 bulk POP concentrations ratios

339 during the snow-covered season. During snowmelt in forested catchments, a hydrological

340 activation of more superficial, organic rich, soils occurs. These soils also have higher levels of

341 POPs[25], resulting in increased levels of POPs and TOC in the forested streams during spring

342 flood (Figure 2, Table S2;[21]). In mires, a higher fraction of the melt water reaches the stream

343 through overland flow, since the peat contains more water and thus remains frozen longer

344   than the soil, resulting in a dilution of the TOC levels in mire-dominated streams during

345   spring flood (Table S2;[21]). However, POP bulk concentrations increased also in the mire

346   stream during spring flood (Figure 2). This can be due to the high atmospheric deposition of

347   POPs occurring during winter months[12], accumulating in the snowpack. The POPs are then

348   transported from the melting snowpack in spring by overland flow to the stream, with less

349   interaction with organic rich soil layers than precipitation occurring during the snow-free

350   season.

351

352   The higher POP bulk and particulate concentrations in the mire stream indicates that there is a

353   lower overall POP retention in mires than in forests. The deposition of POPs from the

354   atmosphere has been shown to be higher in forests than at open sites, known as the forest-

355   filter effect[44, 45]. From a previous study, it is known that the Krycklan forest soil has 5-9 times

356   higher levels of $PCDD/F_{17}$ and PCB_7 than the mire peat[25]. If retention is equal in forest and

357   mire, POP concentrations would thus be higher in the forest stream, which is not the case. To

358   evaluate the difference between mires and forests, the stream export of POPs from the C2 and

359   C4 catchments was calculated using site-specific regressions between POP concentrations and

360   runoff (see 2.4 and Supporting information) and compared to the amount of POPs that had

361   been deposited from the atmosphere in the Krycklan area[12] (Table S7; 4 times higher

362   deposition of PCB_7 to forest than open areas). Overall, the export was low from both

363   landscape types, but it was higher from the mire (C4) than from the forest (C2): 0.1-1.6% of

364   the deposited POPs from C4 was exported to the stream compared to 0-0.5% from C2, thus

365   2.8-5.5 times higher values from C4. This shows that there are landscape-specific differences

366   in retaining atmospherically deposited POPs, resulting in higher POP levels leaching out from

367   the mire landscape. The strong retention of atmospherically deposited POPs found for both

368   landscape types corresponds to estimates for the Delaware River catchment using literature

369 deposition values, with around 3% of deposited PCBs found to exit the catchment by

370 streams[46].

371

3.4 POP background levels compared to point sources

373 The seven sampling sites in this study encompassed 4 sites within the Krycklan catchment, of

374 which one was located at the outlet of the catchment (C16), and 3 further downstream: in the

375 Vindel River, downstream the town of Vännäs (~5000 inhabitants), and downstream the town

376 of Umeå (~80 000 inhabitants; Figure 1; D1-3). This enables an evaluation of the contribution

377 from diffuse pollution compared to point sources such as towns and polluted sites.

378

379 On a concentration per water volume basis, POP bulk concentrations did not increase

380 consistently downstream (Figure S12, Figure 2), although levels were slightly higher

381 downstream the town of Umeå (D3) compared to the outlet from the remote Krycklan

382 catchment (C16). Concentrations at D3 were on average 1.4 ± 1.1 times higher for $PCDD/F_{17}$

383 ($n=4$, sample from SC-08 excluded and discussed below), 1.9 ± 0.6 times for PCB_7 ($n=3$) and

384 1.8 ± 1.4 times for HCB ($n=5$). This would indicate that diffuse pollution from atmospheric

385 deposition to the boreal landscape contributes strongly to overall riverine POP concentration,

386 and thus also to the flux to the sea. However, due to the association between the POPs and

387 SPM that is apparent at C16 and further downstream and the high SPM levels at site C16 (see

388 section 3.2), an alternative way to evaluate the influence of point sources as compared to

389 background/diffuse sources is to normalize the POP concentrations to the concentration of

390 SPM. At the smaller streams, the sampled volume is more representative for the entire water

391 volume than at the larger streams, where there can be large differences in levels of particulate

392 matter between the surface water and the water closer to the stream bed. After normalizing

393 POP bulk concentrations to the levels of SPM, there was a clear increasing downstream trend

394 for all compounds (Figure 4). Concentrations of PCDD/F$_{17}$ (pg g^{-1} $_{SPM}$) were on average

395 25±10 ($n=4$) times higher at D3 compared to C16, and the corresponding increase for PCB$_7$

396 and HCB (ng g^{-1} $_{SPM}$) were 29±10 ($n=3$) and 20±9 ($n=5$), respectively. Further studies are

397 needed to see if downstream increases in SPM-normalized POP concentrations are occurring

398 also in other river systems.

399

400 [Please add Figure 4 here]

401

402 Another way to evaluate the influence of point sources is to study the contaminant congener

403 pattern, assuming that the pattern from background sources (atmospheric deposition) differs

404 from point source patterns, which has been shown to be the case for e.g. PCDD/Fs in

405 sediment[47, 48]. An evaluation of the congener pattern of PCB$_7$ displayed no trend related to the

406 location of the sampling sites, although the fraction of more hydrophobic compounds

407 increases during spring flood (Figure S13b), likely connected to the increased mobilization of

408 particles in many higher-order streams during this hydrological event (Table S2). The

409 congener pattern of PCDD/F$_{17}$ also displays a larger fraction of hydrophobic compounds

410 during spring flood (primarily HpCDD and OCDD; Figure S13a, Table S8). Overall, OCDD

411 and HpCDD are characteristic congeners in atmospheric deposition, and can thus be expected

412 to dominate in background areas such as the Krycklan catchment. Interestingly, the

413 percentage that HpCDD and OCDD constituted of total PCDD/F$_{17}$ bulk concentrations

414 increased consistently downstream, from 34±5% at site C2 to 71±5% at D3 (excluding spring

415 flood samples; Table S8). Since these congeners are also characteristic for PCDD/F

416 contamination in technical pentachlorophenol products for wood preservation[47, 49], used at e.g.

417 sawmill sites, it could be related to increased influence of pentachlorophenol related point

418 sources along the river.

419

420   The sample from D3 at the snow-covered season in 2008 (SC08) clearly deviated in both

421   PCDD/F$_{17}$ concentration and congener pattern (Figure 4, Figure S12a, Figure S13a). The

422   PCDD/F$_{17}$ bulk concentration (4600 pg m^{-3} or 350 pg g$^{-1}_{SPM}$) was almost ten times higher than

423   for the other samples at D3 (180-490 pg m^{-3}). The congener pattern is dominated by furans

424   (PCDFs), primarily OCDF and 1234678-HpCDF, with dioxins (PCDDs) constituting less than

425   20%. This congener pattern is characteristic for contamination in technical tetrachlorophenol

426   products for wood preservation[47, 49]. A former sawmill site in central Umeå (Öbacka) located

427   approximately 7 km upstream the sampling site was being remediated at the time of this

428   sampling, which is a likely explanation for the extremely high levels of PCDD/F$_{17}$ in this

429   sample.

430

431   The high PCDD/F$_{17}$ levels measured at D3 during the snow-covered season 2008 demonstrate

432   that point sources are crucial for stream levels and the riverine flux from land to sea, but also

433   that the influence of point sources compared to the contribution from diffuse sources is

434   difficult to assess due to the often more intermittent character of point source releases. The

435   boreal landscape clearly functions as a filter for atmospherically deposited POPs; both forest

436   and mires have a high capacity for retaining hydrophobic POPs. However, the current study

437   has also shown that particles in the stream water are of great importance for the fluxes of

438   POPs, especially during the high flow events of the spring flood. More knowledge on the

439   characteristics of particles, and in particular the organic fraction of these particles, is needed

440   as it is vital for understanding the fluxes of POPs from the terrestrial to the aquatic

441   environment, and from rivers into surrounding sea areas.

442

443

450 **Supporting information available**

451 Supporting information as tables and figures: on sampling; determined concentrations of

452 POPs and geochemical parameters; regressions of bulk, particulate and dissolved POPs on

453 runoff, SPM and TOC; calculations and comparisons of retention in forest and mires; and

454 congener patterns of POPs at the various sampling sites.

455

456

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Supporting information

Persistent organic pollutants in stream water –

influence of hydrological conditions and landscape type

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CONTENT

Table S1. Sampling seasons (SC=snow-covered, SprFl=spring flood, SF=snow-free) and dates, as well as determined bulk concentrations of PCDD/F$_{17}$, PCB$_7$, HCB, total organic carbon (TOC), suspended particulate matter (SPM), and pH; na = not available. Triplicate samples were taken for site D2 during the spring flood 2008; these values are given as average ± standard deviations.

Season	Site	Date	PCDD/F$_{17}$ (pg m^{-3})	PCB$_7$ (ng m^{-3})	HCB (ng m^{-3})	TOC (mg L^{-1})	SPM (mg L^{-1})	pH
SC	C2	2008.03.10	35	na	3.3	11.0	14.7	5.4
SC	C13	2008.03.11	107	na	4.6	20.8	51.4	5.9
SC	C4	2008.03.12	118	na	6.0	36.0	7.7	4.3
SC	C16	2008.03.28	52	na	4.2	7.1	22.4	6.7
SC	D1	2008.03.29	45	na	6.8	5.4	8.8	7.0
SC	D2	2008.03.30	60	na	8.2	2.9	2.7	6.9
SC	D3	2008.04.03	4649	na	17	4.4	13.4	6.8
SprFl	C4	2008.05.02	807	na	9.7	18.1	7.8	4.3
SprFl	C2	2008.05.03	739	na	7.4	26.1	14.2	4.5
SprFl	C13	2008.05.06	261	na	7.9	17.7	63.2	5.0
SprFl	C16	2008.05.07	475	na	21	15.4	430.8	5.7
SprFl	D1	2008.05.15	396	na	14	7.6	37.8	6.8
SprFl	D2	2008.05.16	160	na	9.7	7.8	9.3	6.9
SprFl	D3	2008.05.20	180	na	9.4	6.7	7.4	6.8
SprFl	D2	2008.05.21	92		8.5	7.9	7.6	6.8
SprFl	D2	2008.05.21	±	na	±	±	±	±
SprFl	D2	2008.05.21	44		0.5	0.2	1.0	0.1
SF	C2	2008.11.04	*	*	*	18.6	18.5	na
SF	C13	2008.11.06	405	13	5.4	19.7	27.2	na
SF	C4	2008.11.07	172	9.7	3.3	37.9	10.6	na
SF	C16	2008.11.14	136	13	6.4	11.8	33.1	na
SF	D3	2008.11.24	395	16	8.3	4.4	2.5	na
SF	D2	2008.12.03	109	8.4	7.1	3.2	1.5	na
SF	D1	2008.12.04	68	3.4	5.7	5.1	5.6	na
SC	C2	2009.03.17	123	2.2	3.0	10.5	21.3	5.6
SC	C4	2009.03.18	136	3.8	3.1	27.8	18.6	4.6
SC	C13	2009.03.18	164	3.4	4.6	12.5	41.0	5.9
SC	C16	2009.03.19	151	3.9	3.3	4.2	30.0	6.8
SC	D3	2009.03.30	253	9.8	8.2	3.0	2.9	6.7
SC	D1	2009.03.31	111	4.0	5.9	4.2	5.2	6.9
SC	D2	2009.04.01	85	1.8	6.7	2.4	0.9	7.0
SC	C16	2009.04.15	204	4.3	5.1	11.2	62.8	6.6
SprFl	C16	2009.04.27	707	13	9.3	21.0	325.7	6.0
SprFl	C2	2009.05.02	300	3.3	4.4	25.8	10.7	4.6
SprFl	C4	2009.05.03	361	4.2	5.0	15.6	5.3	4.4
SprFl	C16	2009.05.03	834	13	14	15.8	696.0	5.9
SprFl	C13	2009.05.04	152	3.1	4.1	21.9	13.8	5.1
SprFl	C16	2009.05.08	471	11	9.7	15.6	344.0	6.0
SprFl	D2	2009.05.11	185	6.9	8.2	8.0	12.7	6.9
SprFl	D1	2009.05.12	177	3.9	7.2	9.9	25.9	6.7
SprFl	C16	2009.05.13	233	5.7	6.1	12.8	129.3	6.4
SprFl	D3	2009.05.14	492	23	10	8.9	19.1	6.9
SF	C2	2009.11.09	25	na	4.5	16.3	19.8	5.2
SF	C4	2009.11.10	44	na	4.0	39.7	11.4	4.4
SF	C13	2009.11.10	50	na	9.4	18.0	25.5	5.8
SF	C16	2009.11.19	148	na	10	17.0	42.4	6.4

*PUF sample, i.e. dissolved concentrations, missing due to spilled sample.

POP flux calculations for sites C2 and C4

Daily POP fluxes were calculated for sites C2 and C4 as the product of estimated dissolved and particulate contaminant concentrations and daily water flow. First, water runoff was calculated by multiplying flows (m^3 s^{-1}) by 86 400 s d^{-1} to obtain daily flows, and dividing by catchment area (470 000 m^2 for subcatchment C7 for which daily flow was measured; runoff was assumed equal for all Krycklan subcatchments) to obtain runoff in m d^{-1}. This was multiplied by 1000 mm m^{-1} to produce runoff in mm d^{-1}.

Site-specific linear regressions predicting contaminant concentration as a function of runoff were produced for sites C2 and C4. Separate regressions were created for dissolved and particulate contaminant fractions at each site. Daily POP concentrations (e.g. in ng m^{-3}) for sites C2 and C4 were then estimated based on daily runoff and the site-specific regression parameters. The daily POP concentrations were transformed into daily POP fluxes by multiplying with daily water flow. Daily flux estimates were then summed to derive monthly and annual values.

Table S2. Average and standard deviation of TOC, SPM and pH for the seven sampling sites during the three different hydrological seasons.

	Snow-covered							Spring flood							Snow-free					n^1
	TOC		SPM		pH		n	TOC		SPM		pH		n	TOC		SPM		pH	
	Ave.	STD	Ave.	STD	Ave.	STD		Ave.	STD	Ave.	STD	Ave.	STD		Ave.	STD	Ave.	STD	Ave.	
C2	10.7	0.4	18.0	4.7	5.5	0.13	2	25.9	0.3	12.4	2.5	4.6	0.10	2	17.4	1.6	19.1	0.9	5.2	2 (1)
C4	31.9	5.8	13.2	7.7	4.5	0.19	2	16.8	1.7	6.6	1.7	4.3	0.06	2	38.8	1.3	11.0	0.6	4.4	2 (1)
C13	24.2	5.9	46.2	7.4	5.9	0.04	2	19.8	3.0	39	35	5.1	0.07	2	18.8	1.2	26.4	1.2	5.8	2 (1)
C16[2]	5.7	2.1	26.2	5.4	6.8	0.08	2	16.1	3.0	385	206	6.0	0.25	5	14.4	3.6	37.7	6.5	6.4	2 (1)
D1	4.8	0.9	7.0	1.3	6.9	0.07	2	8.7	1.6	31.9	8.4	6.7	0.02	2	5.1		5.6			1 (0)
D2	2.7	0.3	1.8	1.2	6.9	0.07	2	7.9	0.1	8.9	2.4	6.8	0.07	5	3.2		1.5			1 (0)
D3	3.7	1.0	8.2	7.4	6.8	0.03	2	7.8	1.6	13.2	8.3	6.9	0.03	2	4.4		2.5			1 (0)

[1] n within parenthesis denotes the number of samples for pH when different from TOC and SPM.

[2] Sample from 2009.04.15 not included in snow-covered average due to being influenced by spring flood.
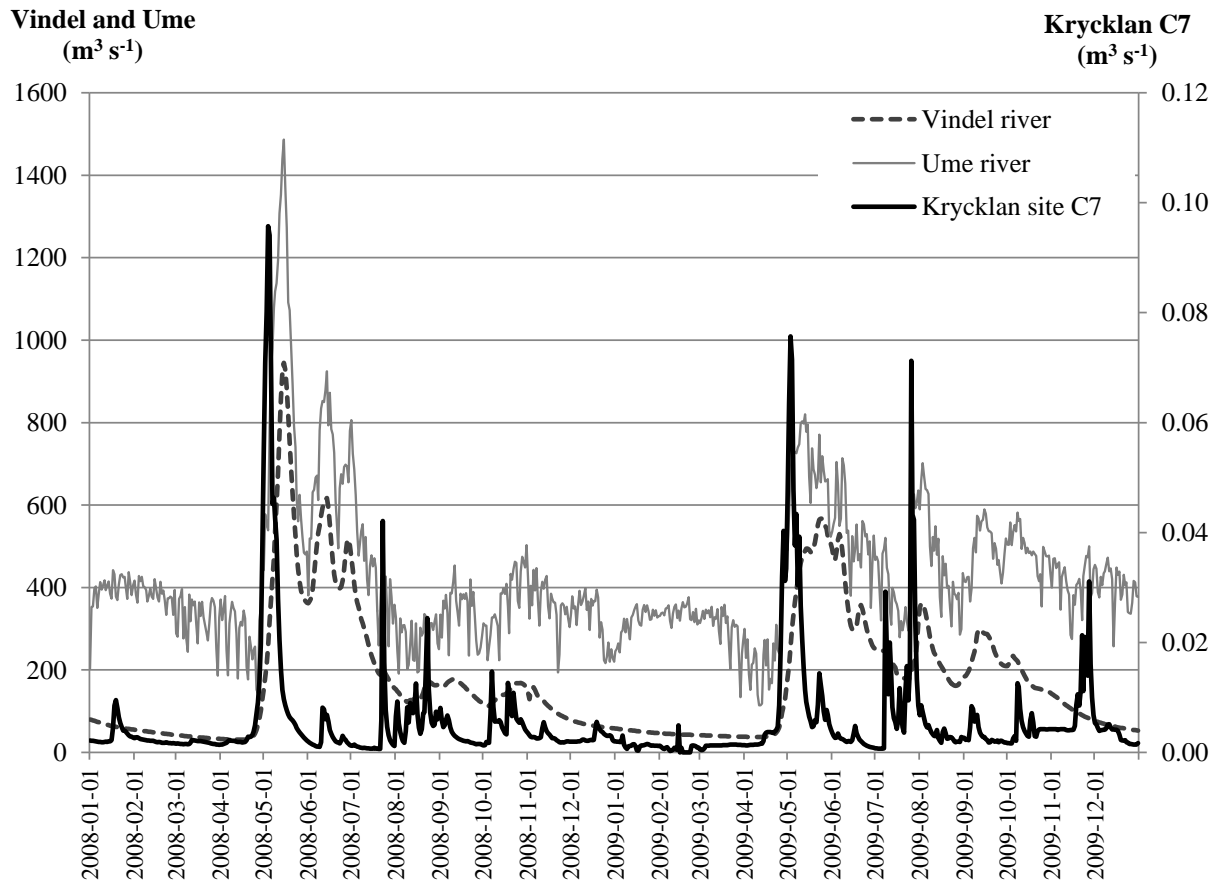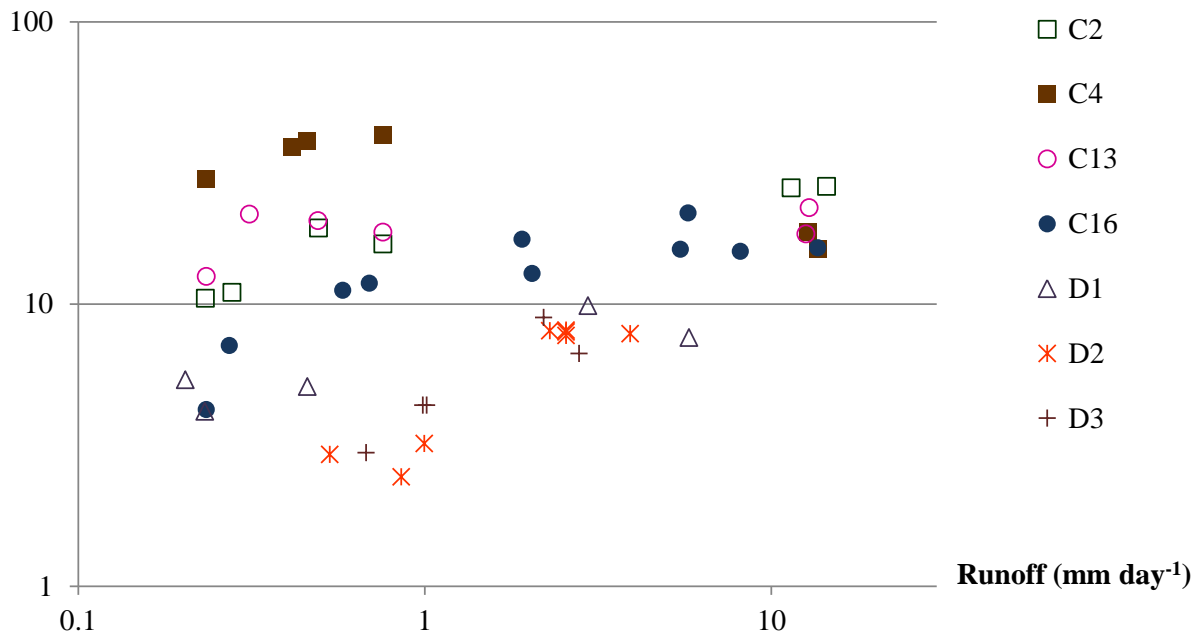
Figure S1. Water flow for Krycklan (Site C7), Ume River (Stornorrfors) and Vindel River (Granåker) during 2008-2009.
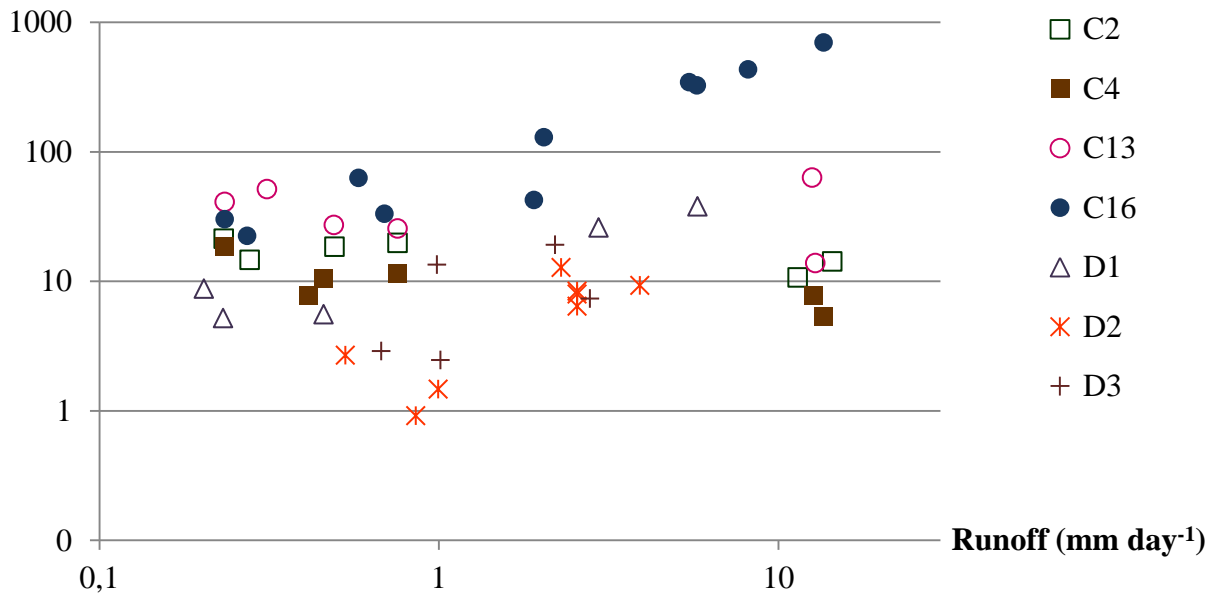
a)

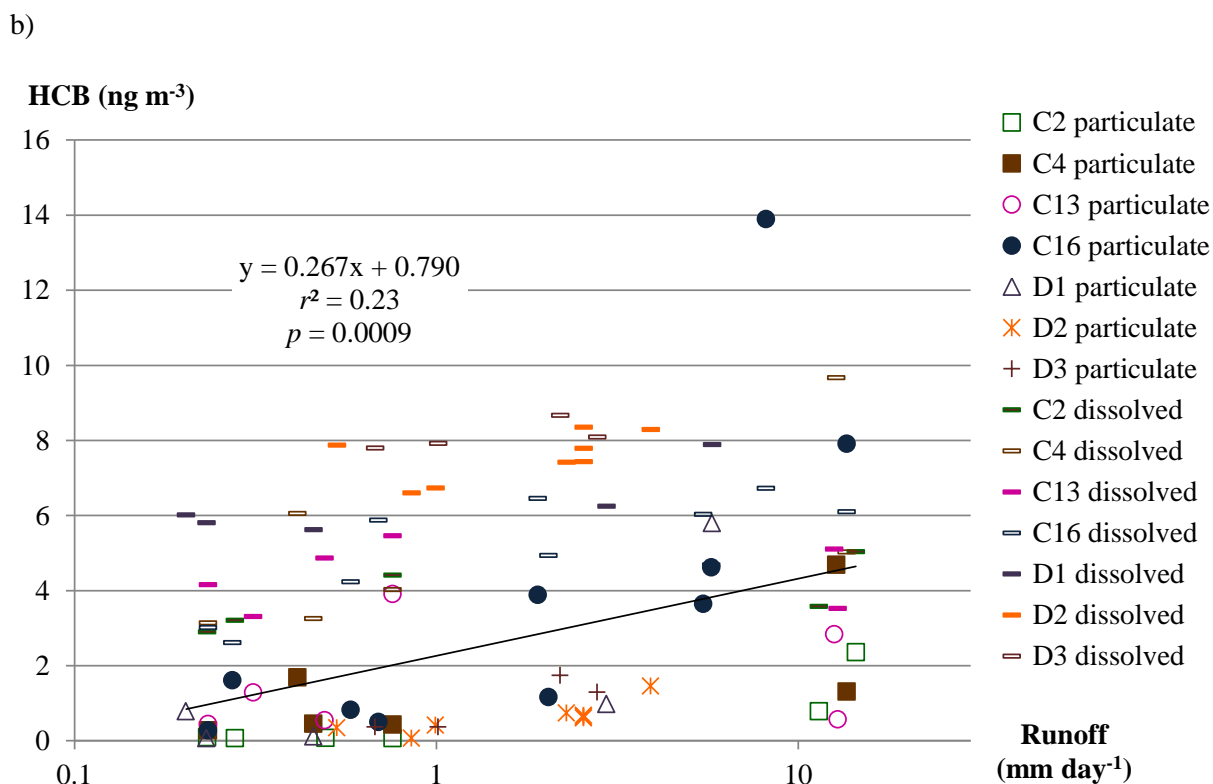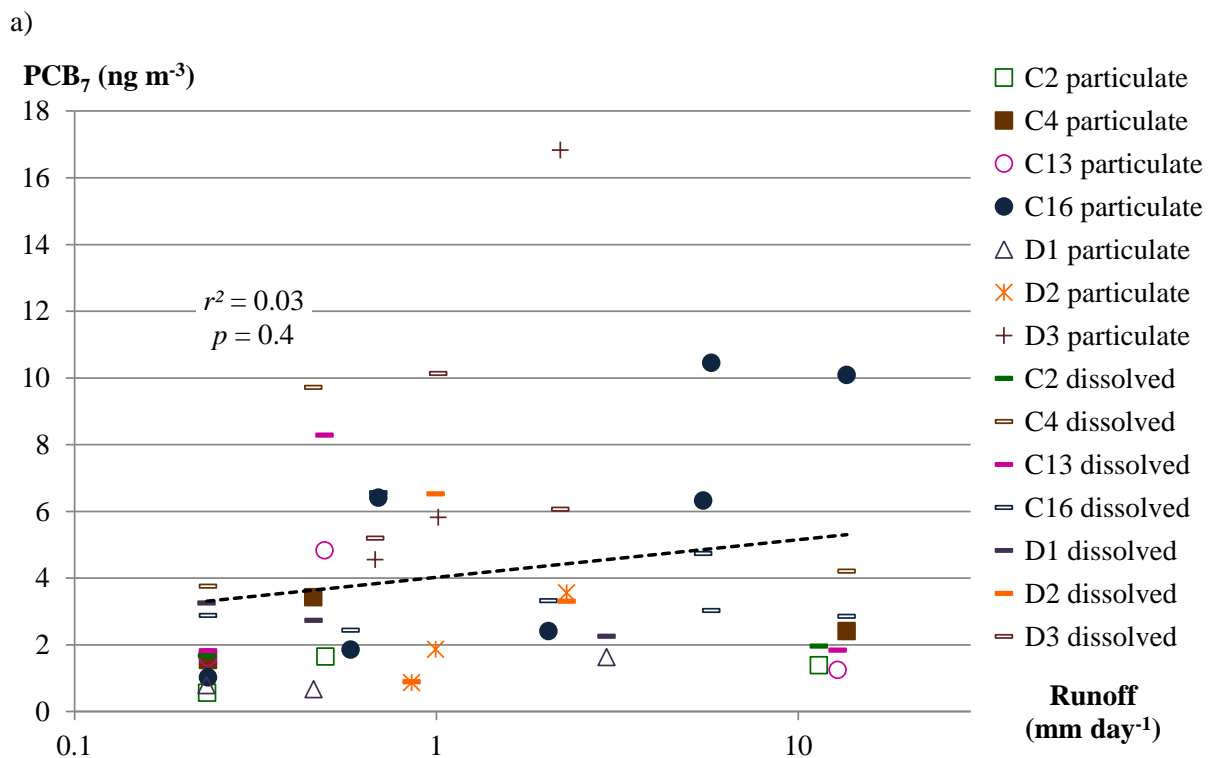**TOC (mg L⁻¹)**

b)

SPM (mg L⁻¹)

Figure S2. Concentrations of *a)* TOC and *b)* SPM for the seven sampling sites as a function of runoff.

a)

PCB$_7$ (ng m^{-3})

$r^2 = 0.03$
$p = 0.4$

□ C2 particulate
■ C4 particulate
○ C13 particulate
● C16 particulate
△ D1 particulate
✳ D2 particulate
+ D3 particulate
▬ C2 dissolved
═ C4 dissolved
▬ C13 dissolved
═ C16 dissolved
▬ D1 dissolved
▬ D2 dissolved
═ D3 dissolved

Runoff (mm day^{-1})

b)

HCB (ng m^{-3})

y = 0.267x + 0.790
$r^2 = 0.23$
$p = 0.0009$

□ C2 particulate
■ C4 particulate
○ C13 particulate
● C16 particulate
△ D1 particulate
✳ D2 particulate
+ D3 particulate
▬ C2 dissolved
═ C4 dissolved
▬ C13 dissolved
═ C16 dissolved
▬ D1 dissolved
▬ D2 dissolved
═ D3 dissolved

Runoff (mm day^{-1})

Figure S3. Concentrations of particulate and dissolved *a)* PCB$_7$ and *b)* HCB at the seven sampling sites as a function of runoff, and the linear regression for the particulate fraction (not significant for PCB$_7$ or for the dissolved fraction for PCB$_7$ or HCB).
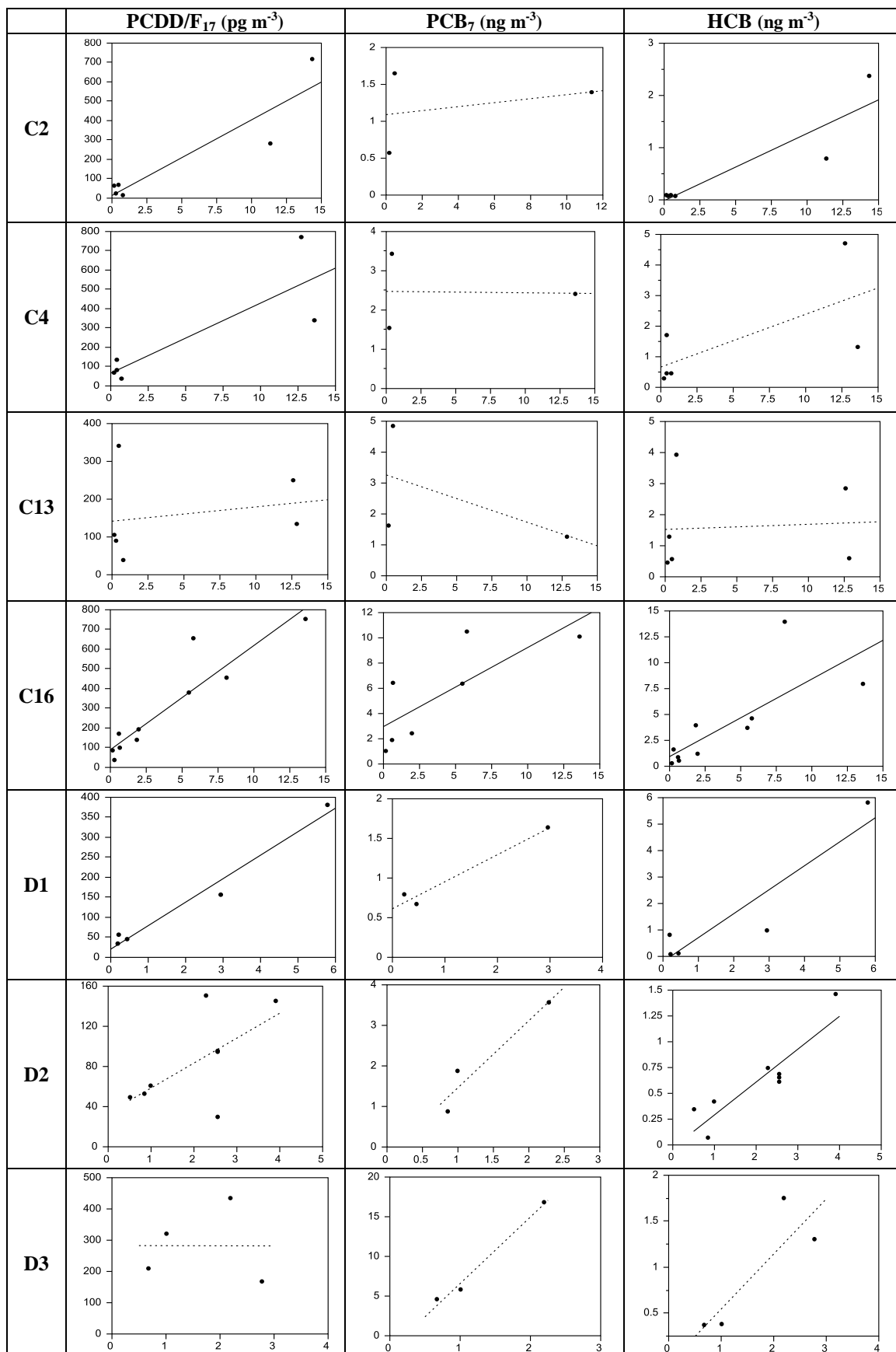
Figure S4. Particulate POP concentrations versus runoff (mm day^{-1}) for the seven sampling sites. Parameters for significant regressions are available in Table S3; not significant regressions (p>0.05) marked with dashed lines.
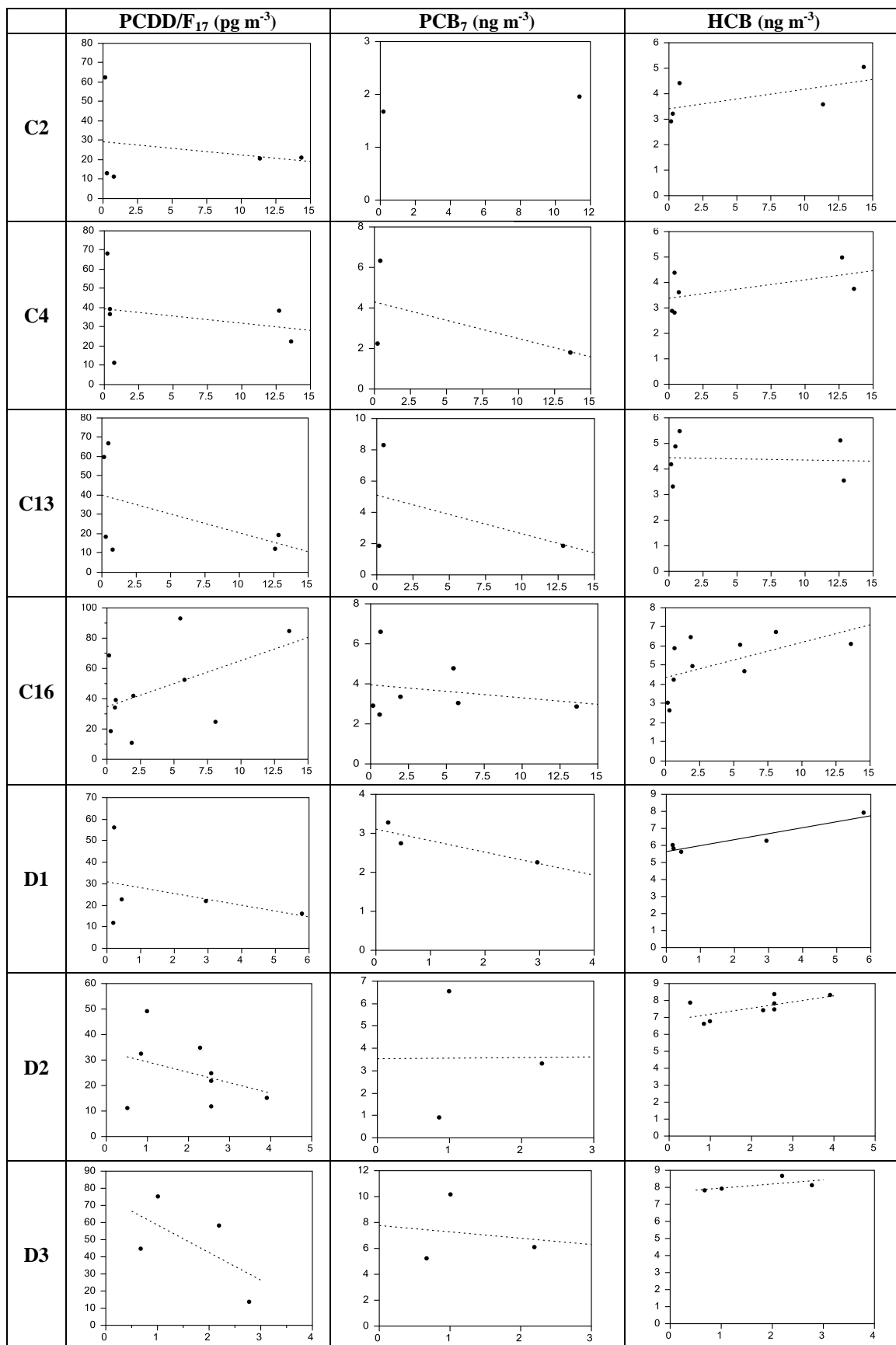
Figure S5. Dissolved POP concentrations versus runoff (mm day^{-1}) for the seven sampling sites. Parameters for significant regressions are available in Table S3; not significant regressions ($p>0.05$) marked with dashed lines.

Table S3. Parameters for significant linear regressions (y=a+bx) of different POPs on runoff (from Figures S4-S5).

Site	y	Fraction	a	b	p	r^2	n
C2	PCDD/F$_{17}$	Part	13.8	39.0	0.009	0.85	6
C2	HCB	Part	-0.02	0.13	0.012	0.83	6
C4	PCDD/F$_{17}$	Part	66.3	36.3	0.034	0.72	6
C16	PCDD/F$_{17}$	Part	89.8	52.9	0.000	0.85	10
C16	PCB$_7$	Part	3.0	0.63	0.040	0.60	7
C16	HCB	Part	0.94	0.75	0.009	0.59	10
D1	PCDD/F$_{17}$	Part	20.5	58.7	0.002	0.97	5
D1	HCB	Part	-0.20	0.91	0.026	0.85	5
D2	HCB	Part	-0.03	0.32	0.002	0.82	8
D1	HCB	Diss	5.64	0.35	0.016	0.89	5

a)
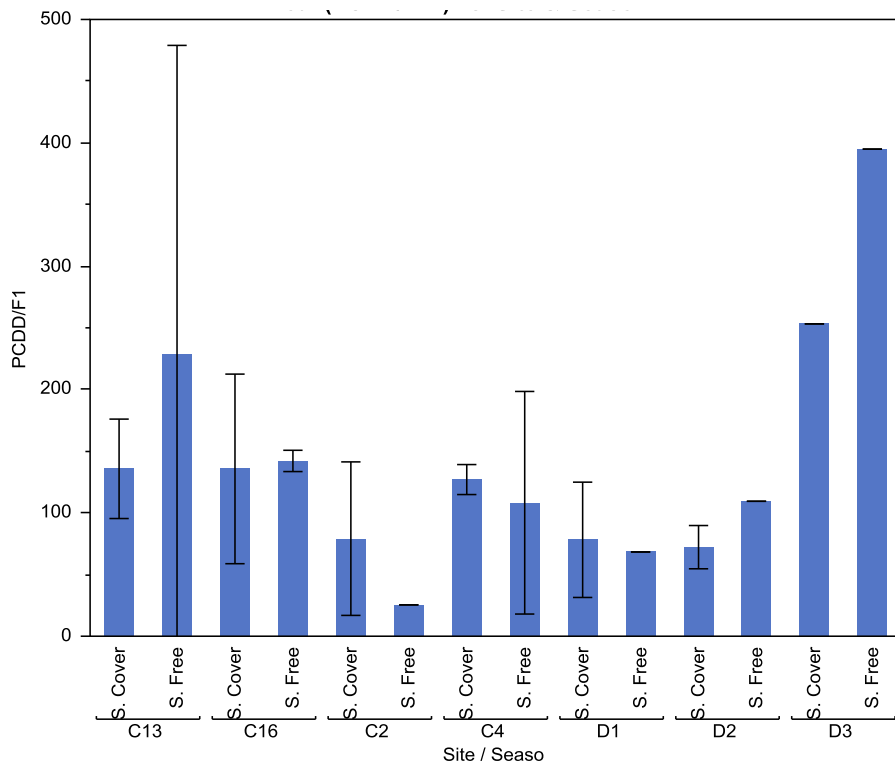
b)
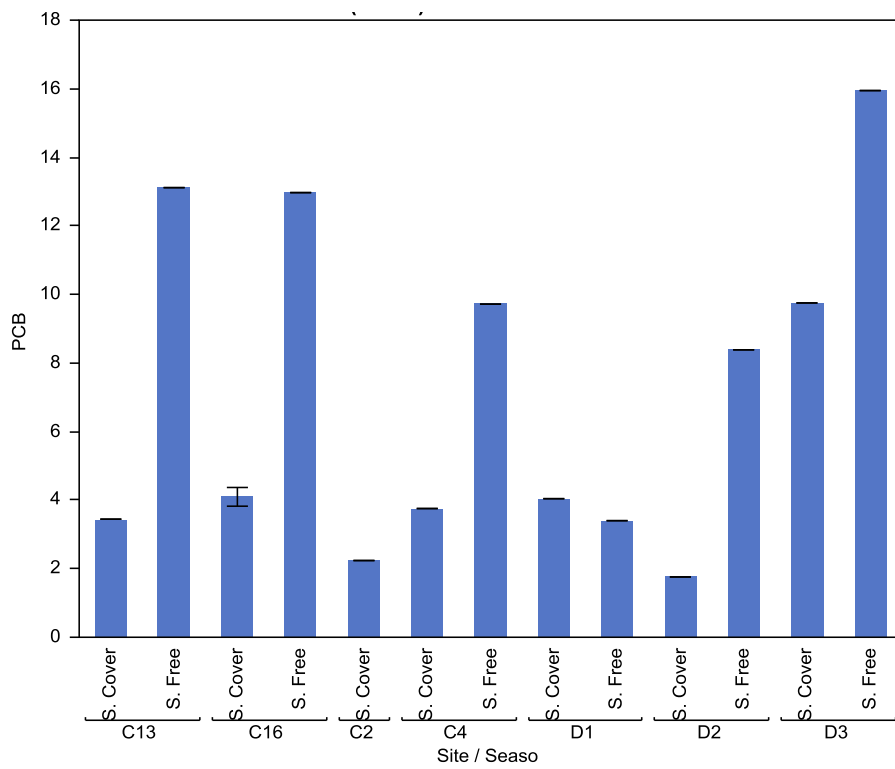
c)
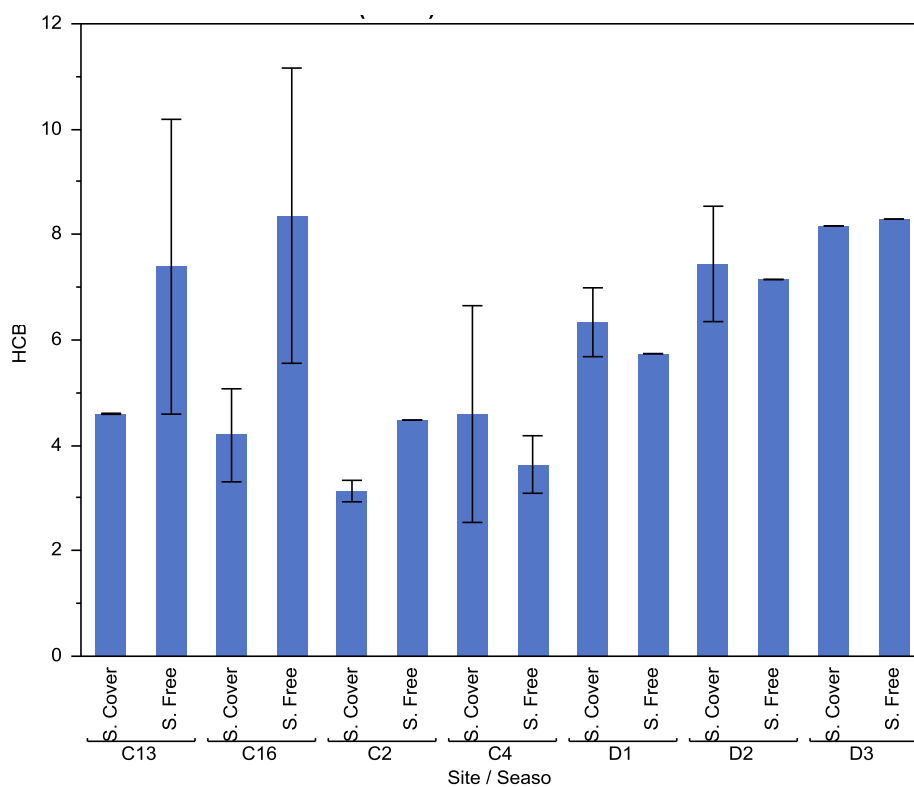
Figure S6. Comparisons of *a)* PCDD/F$_{17}$ (pg m^{-3}) *b)* PCB$_7$ (ng m^{-3}) and *c)* HCB (ng m^{-3}) bulk concentrations between the snow-covered and the snow-free season at the seven sampling sites. Error bars denote 1 standard deviation (*n*=2 or 3; if error bars are not present, *n*=1).
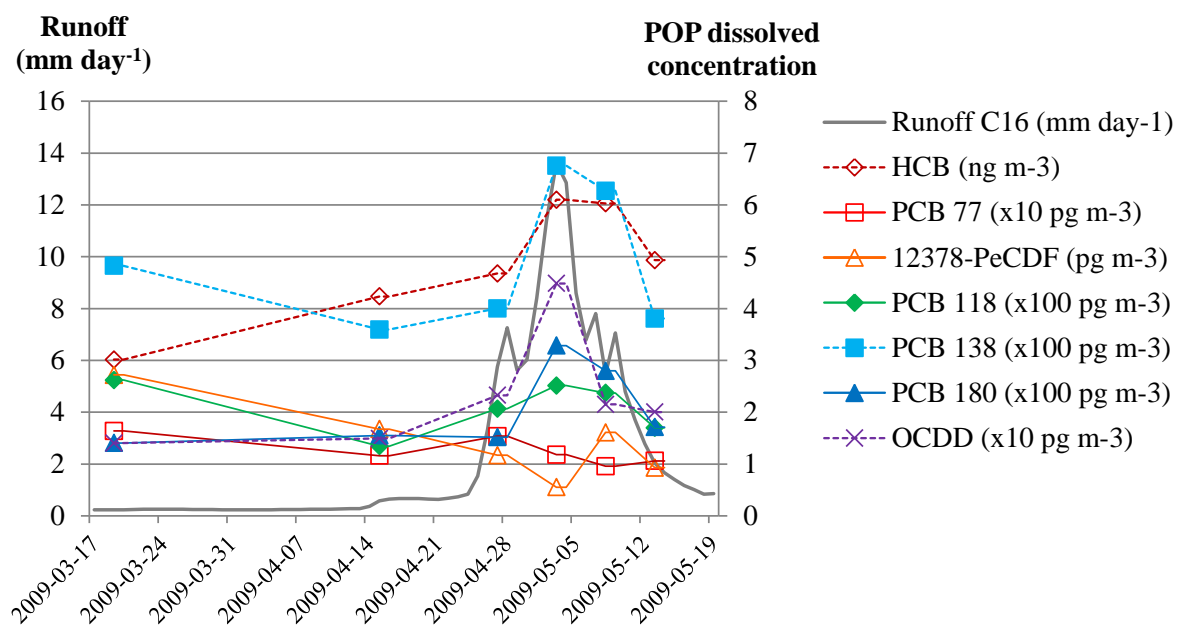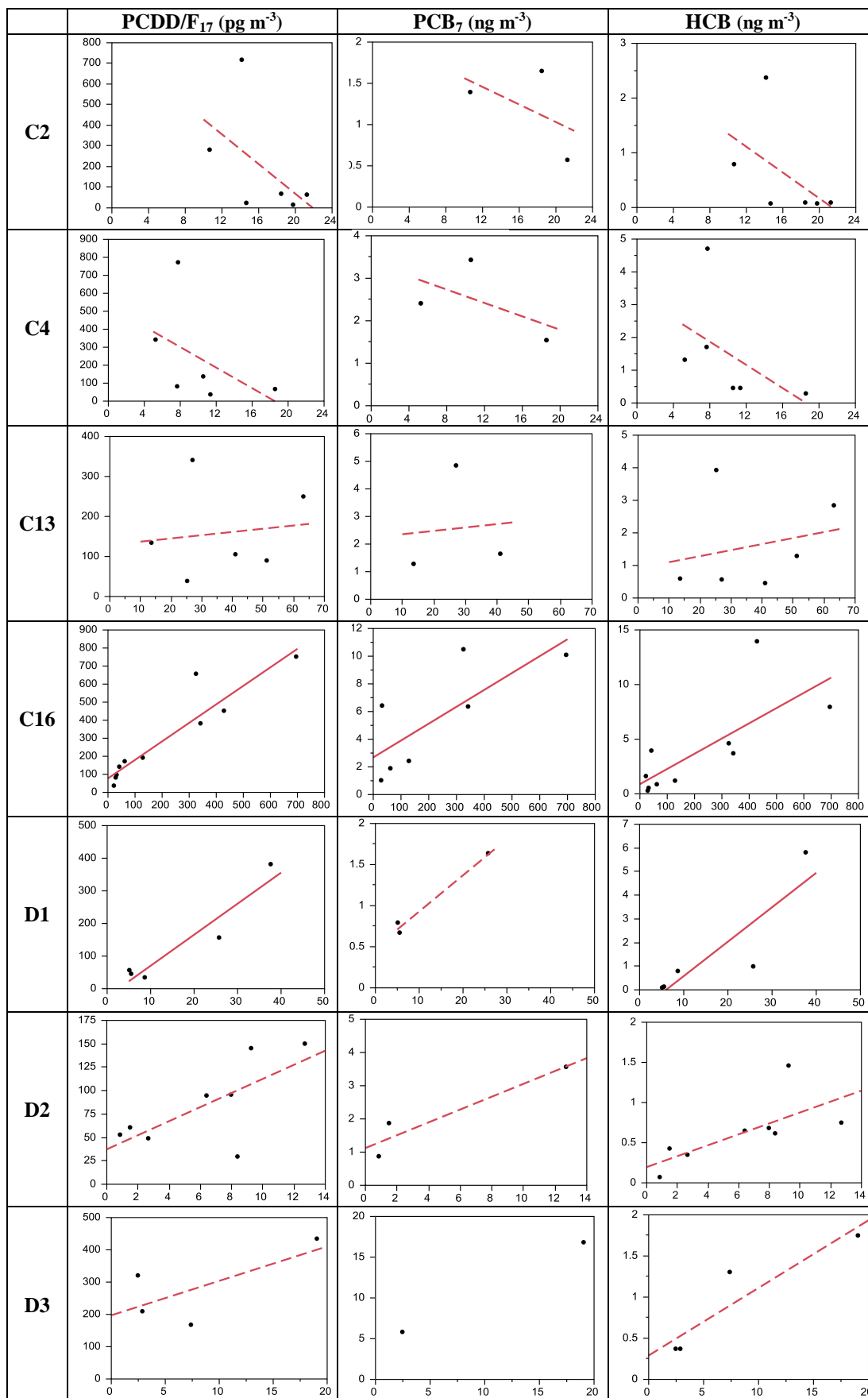
a)

b)

S14
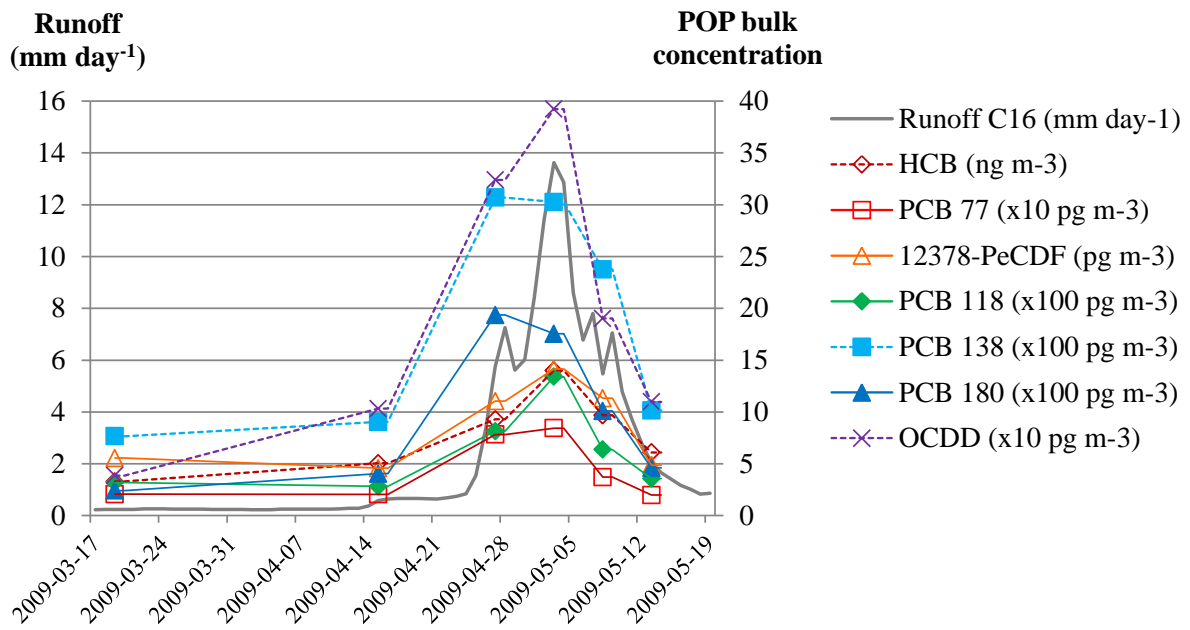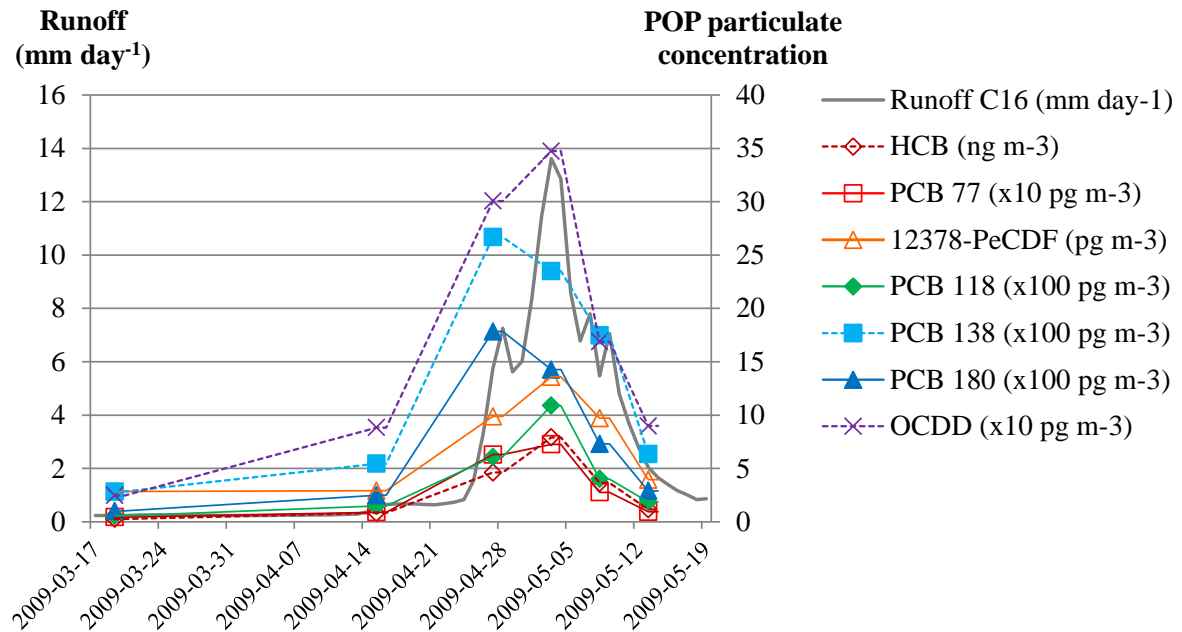
c)

Figure S7. The concentration of different POPs in the *a)* bulk (particulate+dissolved) phase, *b)* particulate phase and *c)* dissolved phase in water at site C16 during spring flood 2009. The plotted POPs had no or a few non-detects and were selected to cover a wide range of K_{OW} values (log K_{OW} 5.5-8.3).

Figure S8. Regressions of particulate POP concentration vs. SPM. Parameters for significant regressions are available in Table S4; not significant regressions ($p > 0.05$) marked with dashed lines.
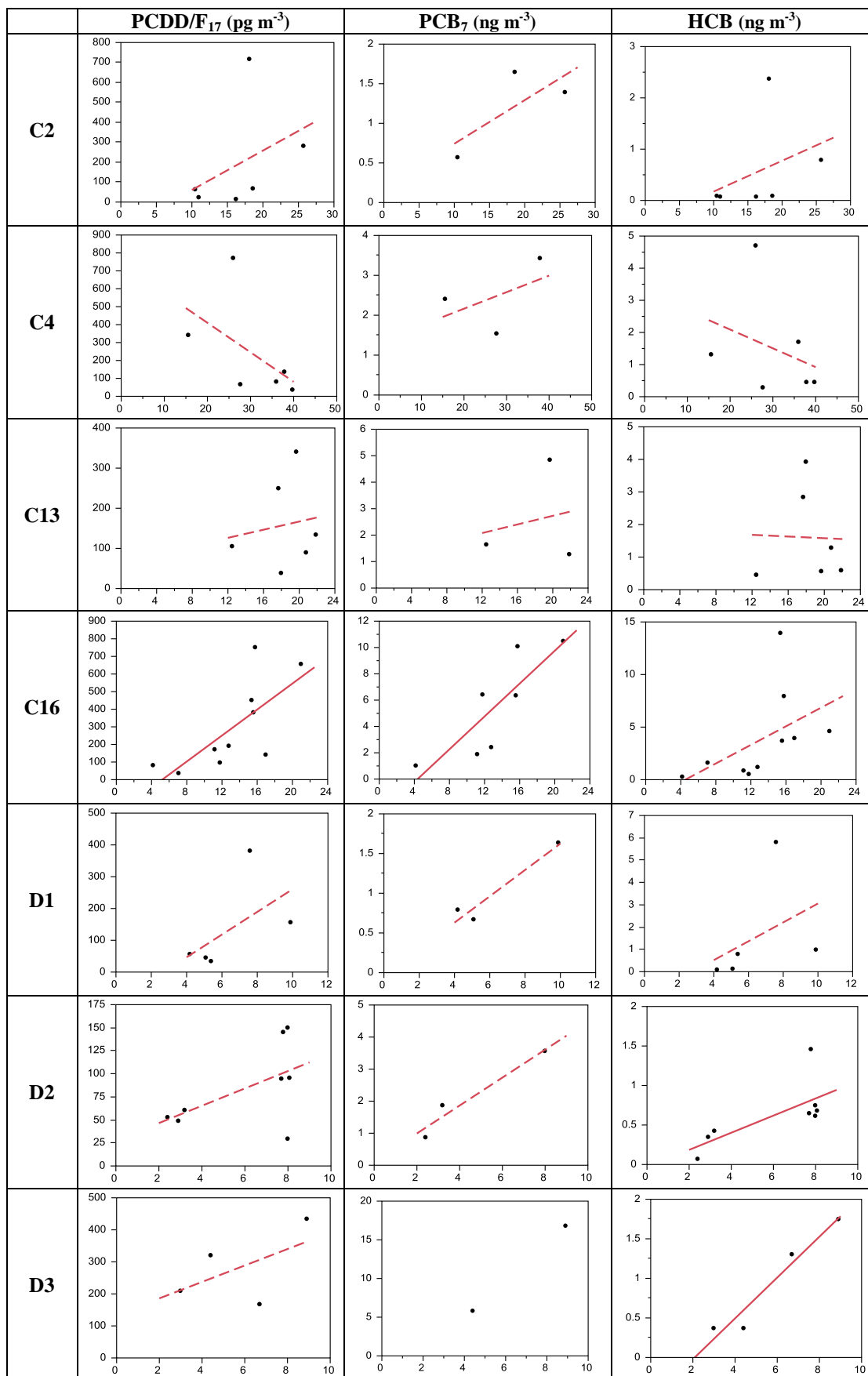
Figure S9. Regressions of particulate POP concentration vs. TOC. Parameters for significant regressions are available in Table S4; not significant regressions ($p>0.05$) marked with dashed lines.
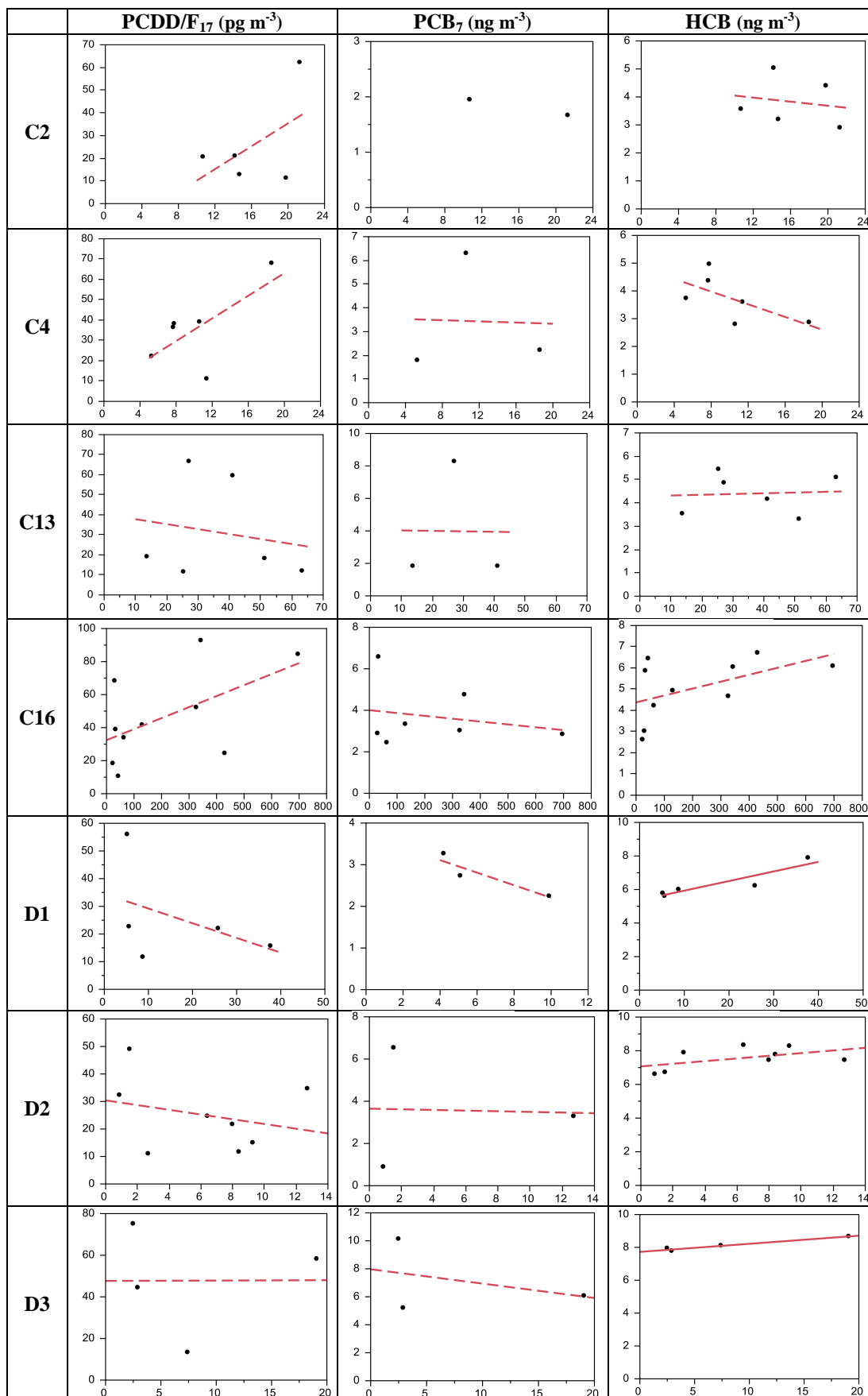
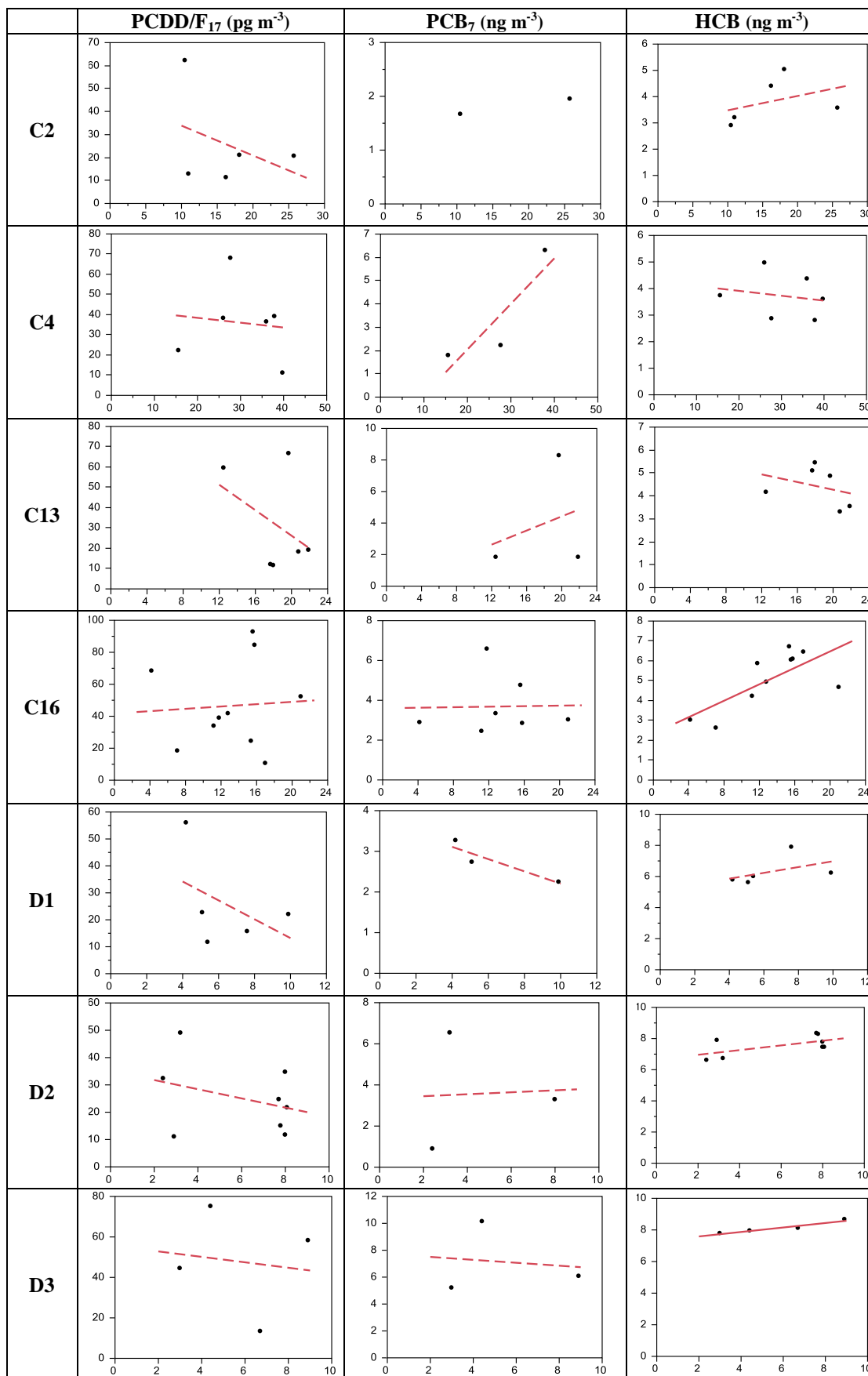**Figure S10.** Regressions of dissolved POP concentration vs. SPM. Parameters for significant regressions are available in Table S4; not significant regressions (*p*>0.05) marked with dashed lines.

Figure S11. Regressions of dissolved POP concentration vs. TOC. Parameters for significant regressions are available in Table S4; not significant regressions (*p*>0.05) marked with dashed lines.

Table S4. Parameters for significant linear regressions (y=a+bx) of different POPs on SPM and TOC (from Figures S8-S11).

	Site	y	Fraction	a	b	p	r^2	n
SPM	C16	PCDD/F$_{17}$	Bulk	110	1.1	0.0001	0.88	10
	D1	PCDD/F$_{17}$	Bulk	9.7	9.0	0.024	0.86	5
	C16	PCDD/F$_{17}$	Particulate	77	1.0	0.0001	0.87	10
	D1	PCDD/F$_{17}$	Particulate	-25	9.5	0.014	0.90	5
	C16	PCB$_7$	Particulate	2.7	0.012	0.044	0.69	7
	C16	HCB	Bulk	5.3	0.017	0.013	0.56	10
	D1	HCB	Bulk	4.5	0.20	0.043	0.79	5
	D3	HCB	Bulk	8.0	0.13	0.035	0.93	4
	C16	HCB	Particulate	0.89	0.014	0.013	0.56	10
	D1	HCB	Particulate	-0.87	0.15	0.049	0.77	5
	D1	HCB	Dissolved	5.4	0.057	0.029	0.84	4
	D3	HCB	Dissolved	7.7	0.049	0.012	0.98	4
TOC	C16	PCDD/F$_{17}$	Bulk	-151	37.3	0.029	0.47	10
	C16	PCDD/F$_{17}$	Particulate	-192	36.9	0.019	0.52	10
	C16	PCB7	Particulate	-2.7	0.62	0.020	0.59	7
	D2	HCB	Bulk	6.6	0.26	0.049	0.50	8
	D3	HCB	Bulk	6.8	0.40	0.016	0.97	4
	D2	HCB	Particulate	-0.032	0.11	0.048	0.50	8
	D3	HCB	Particulate	-0.54	0.26	0.028	0.94	4
	C16	HCB	Dissolved	2.3	0.21	0.021	0.50	10
	D3	HCB	Dissolved	7.3	0.14	0.049	0.90	4

Table S5. *p*-values of linear regressions of particulate concentration of different compounds on SPM and TOC at C16; n=10; $p < 0.05$ indicates significant (positive) regressions, marked in bold. For the dissolved concentrations, only OCDD and PCB 169 had significant (positive) regressions, both with SPM (*p*=0.011 and 0.008, respectively).

		SPM	TOC
PCDD/F$_{17}$	2378-TeCDD	**0.011**	*0.775*
	12378-PeCDD	**0.001**	*0.059*
	123478-HxCDD	**0.002**	*0.111*
	123678-HxCDD	**0.000**	**0.049**
	123789-HxCDD	**0.000**	**0.017**
	1234678-HpCDD	**0.000**	**0.012**
	OCDD	**0.000**	**0.018**
	2378-TeCDF	**0.011**	*0.066*
	12378-PeCDF	**0.001**	*0.057*
	23478-PeCDF	**0.004**	**0.016**
	123478-HxCDF	**0.001**	**0.032**
	123678-HxCDF	**0.000**	**0.021**
	234678-HxCDF	**0.003**	**0.015**
	123789-HxCDF	**0.033**	*0.185*
	1234678-HpCDF	**0.000**	**0.014**
	1234789-HpCDF	**0.001**	**0.016**
	OCDF	**0.000**	**0.036**
non-*ortho* PCBs	PCB77	**0.008**	**0.034**
	PCB81	*0.076*	*0.092*
	PCB126	**0.000**	**0.042**
	PCB169	**0.000**	*0.114*
mono-*ortho* PCBs	PCB105	**0.011**	**0.028**
	PCB114	**0.039**	*0.107*
	PCB118	**0.026**	*0.091*
	PCB123	*0.221*	*0.134*
	PCB156	*0.647*	*0.091*
	PCB157	*0.148*	**0.036**
	PCB128/167	*0.987*	*0.520*
	PCB189	*0.599*	*0.398*
PCBs with ≥2 Cl in *ortho* positions	PCB28	*0.374*	*0.311*
	PCB52	*0.812*	*0.628*
	PCB101	*0.716*	*0.542*
	PCB138	*0.174*	**0.021**
	PCB153	*0.072*	**0.027**
	PCB180	*0.899*	*0.088*

Table S6. Average ratios between bulk concentrations of POPs in C4 and C2 during different hydrological seasons. The number is always >1, demonstrating that concentrations were higher in C4.

	PCDD/F$_{17}$	PCB$_7$	HCB
Snow-covered	2.4	2.7	13.1
Spring flood	2.2	2.1	6.2
Snow-free	1.1	1.8	1.8
n **(per season)**	*2*	*1*	*2*

Table S7. Calculations for site-specific retention of POPs in forest and mires.

Site characteristics:

	C2	C4
Area (m^2)	129900	190000
Forest	100%	55.9%
Mire	0%	44.1%
Forest (m^2)	129870	106210
Mire (m^2)	0	83790

Deposition to open areas = mires (Bergknut et al. 2011):

PCDD/F$_{17}$ using glass fibre thimble (GFT) sampler:	10	pg m^{-2} day^{-2}
PCDD/F$_{17}$ using amberlite (AMB) sampler:	39	pg m^{-2} day^{-2}
PCB$_7$ using AMB sampler:	3.9	ng m^{-2} day^{-2}

Deposition to forested areas, assumed to be 4 times higher (Bergknut et al. 2011):

PCDD/F$_{17}$ using glass fibre thimble (GFT) sampler:	41	pg m^{-2} day^{-2}
PCDD/F$_{17}$ using amberlite (AMB) sampler:	156	pg m^{-2} day^{-2}
PCB$_7$ using AMB sampler:	16	ng m^{-2} day^{-2}

Yearly deposition (µg year^{-1}):

	C2			C4		
	Total	*Forest*	*Mire*	*Total*	*Forest*	*Mire*
PCDD/F$_{17}$ using GFT sampler:	1958	1958	0	1917	1601	316
PCDD/F$_{17}$ using AMB sampler:	7395	7395	0	7240	6048	1193
PCB$_7$ using AMB sampler:	735056	735056	0	719703	601142	118561

Yearly export by streams (µg year^{-1}):

	C2	C4
PCDD/F$_{17}$:	11	19
PCB$_7$:	147	423

Retention = (deposition - export)/deposition (%):

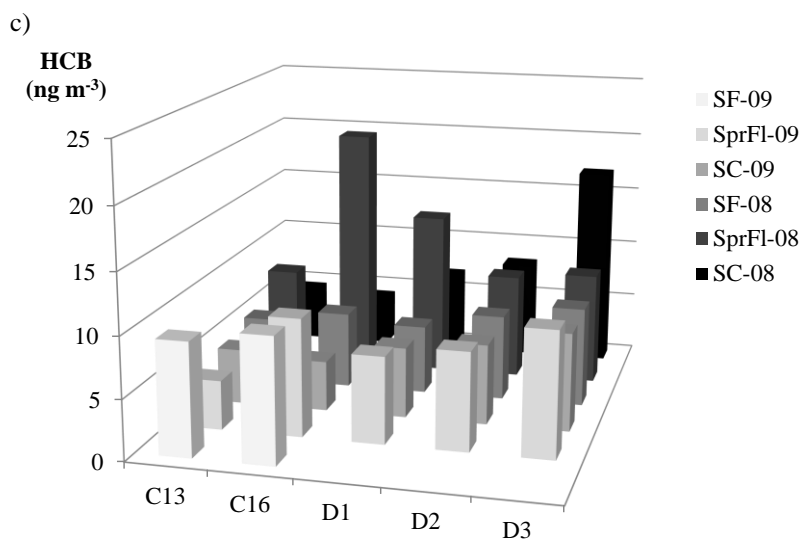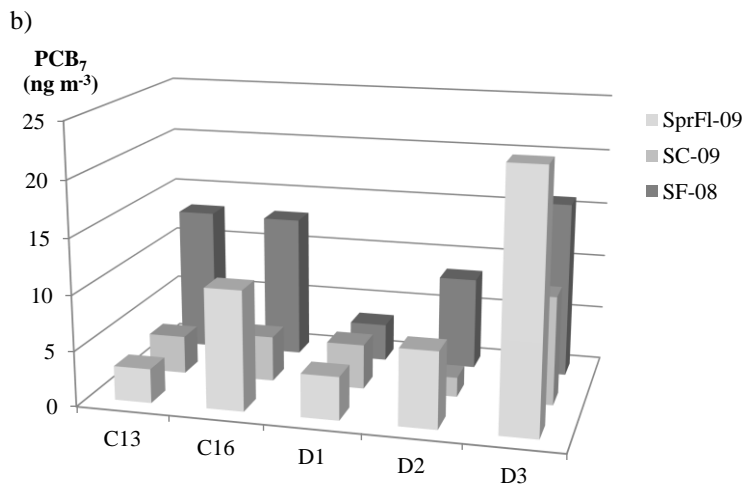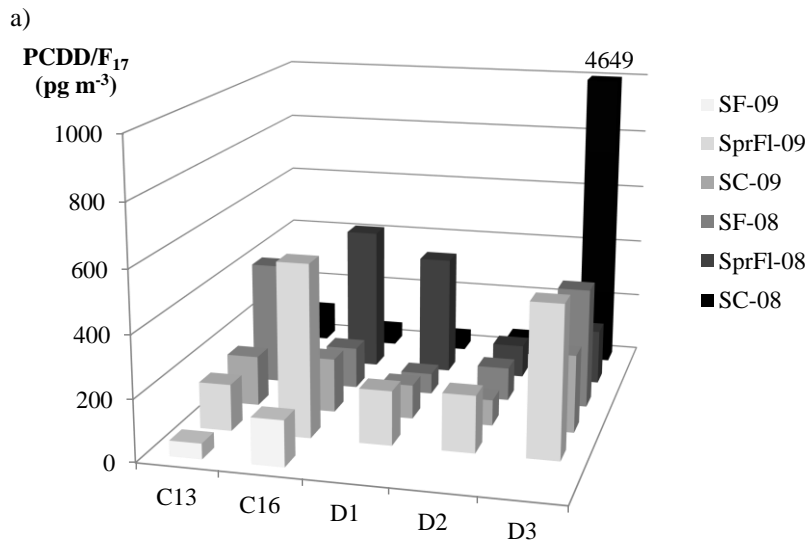|	C2	C4
PCDD/F$_{17}$ using GFT sampler:	99.5	99.0
PCDD/F$_{17}$ using AMB sampler:	99.9	99.7
PCB$_7$ using AMB sampler:	100.0	99.9

Retention in mire, assuming retention in C2 corresponds to retention in forest:
Retention$_{Mire}$ = (Retention$_{C4}$ - Retention$_{C2}$ × Percentage$_{Forest, C4}$)/Percentage$_{Mire, C4}$ (%)

PCDD/F$_{17}$ using GFT sampler:	98.4
PCDD/F$_{17}$ using AMB sampler:	99.6
PCB$_7$ using AMB sampler:	99.9

Export = 100 - retention (%):

	Mire	**Forest (=C2)**	**Ratio mire/forest**
PCDD/F$_{17}$ using GFT sampler:	1.6	0.5	2.9
PCDD/F$_{17}$ using AMB sampler:	0.4	0.2	2.8
PCB$_7$ using AMB sampler:	0.1	0.0	5.5

a)

PCDD/F$_{17}$
(pg m^{-3})

4649

1000

800

600

400

200

0

C13   C16   D1   D2   D3

- SF-09
- SprFl-09
- SC-09
- SF-08
- SprFl-08
- SC-08

b)

PCB$_7$
(ng m^{-3})

25

20

15

10

5

0

C13   C16   D1   D2   D3

- SprFl-09
- SC-09
- SF-08

c)

HCB
(ng m^{-3})

25

20

15

10

5

0

C13   C16   D1   D2   D3

- SF-09
- SprFl-09
- SC-09
- SF-08
- SprFl-08
- SC-08

Figure S12. Bulk concentrations of *a)* PCDD/F$_{17}$ (pg m^{-3}), *b)* PCB$_7$ (ng m^{-3}) and *c)* HCB (ng m^{-3}) at the seven sampling sites during different hydrological seasons (SF: snow-free; SprFl: spring flood; SC: snow-covered; -08: year 2008; -09: year 2009).

a)

b)
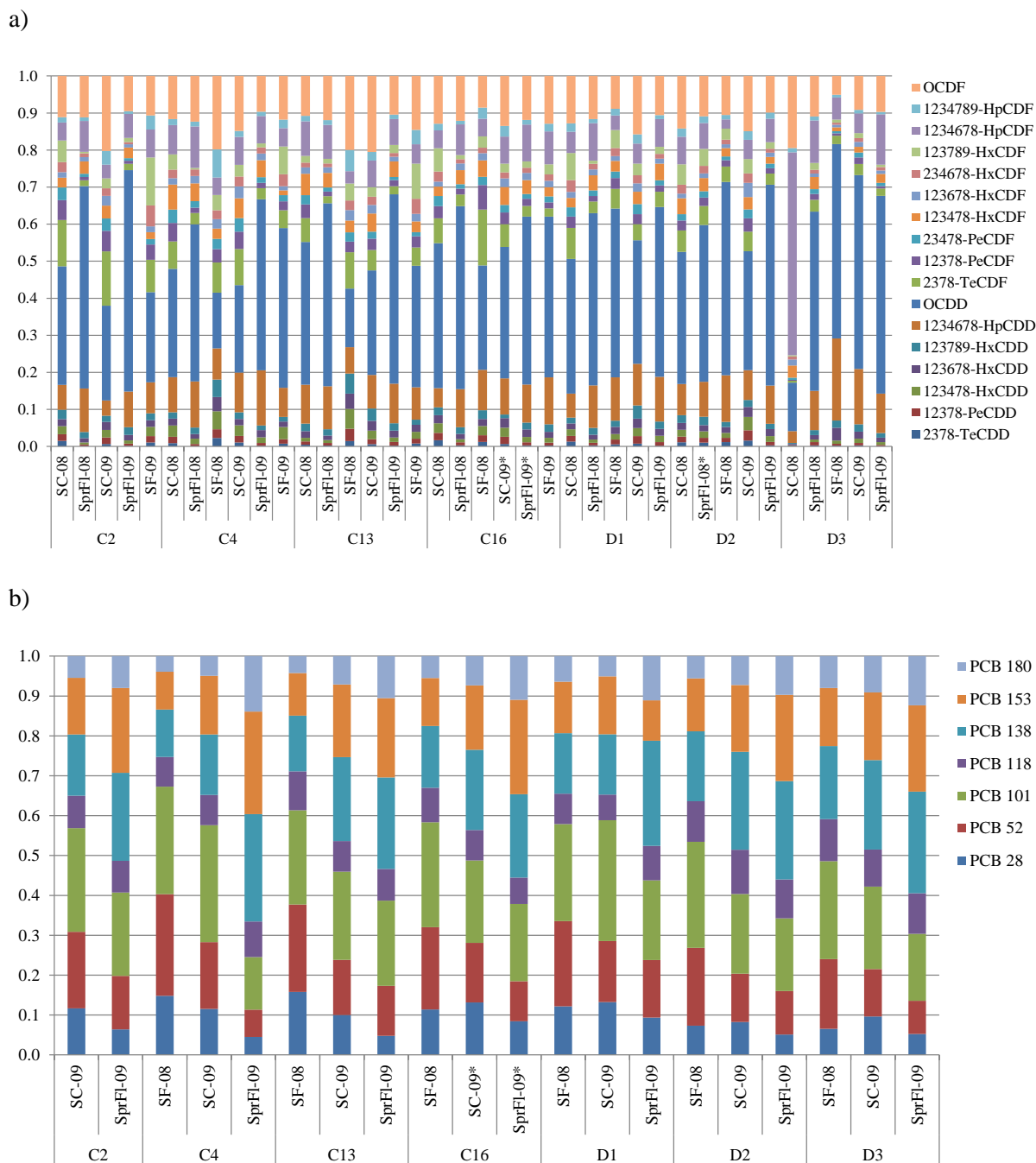
Figure S13. Congener patterns of *a)* PCDD/F$_{17}$ and *b)* PCB$_7$ at the seven different sampling sites during different hydrological seasons (SF: snow-free; SprFl: spring flood; SC: snow-covered; -08: year 2008; -09: year 2009). * denotes an average value when several samplings were performed at a site during one season.

Table S8. The percentage of HpCDD and OCDD of total PCDD/F$_{17}$ concentrations at the different sites. Numbers are average and standard deviation (SD) of samples in snow-covered + snow-free (SC + SF) seasons, or spring flood (SprFl) season. The deviating high-level SC-08 sample from D3 is not included; its fraction of HpCDD+OCDD was 16%.

Site	SC + SF		SprFl	
	Average ± SD	*n*	Average ± SD	*n*
C2	34 ± 5%	3	68 ± 2%	2
C4	37 ± 11%	4	58 ± 4%	2
C13	38 ± 11%	4	61 ± 0.5%	2
C16	46 ± 7%	4	58 ± 3 %	2
D1	48 ± 8%	3	58 ± 0.1%	2
D2	50 ± 13%	3	58 ± 9%	2
D3	71 ± 5%	2	61 ± 4%	2