

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

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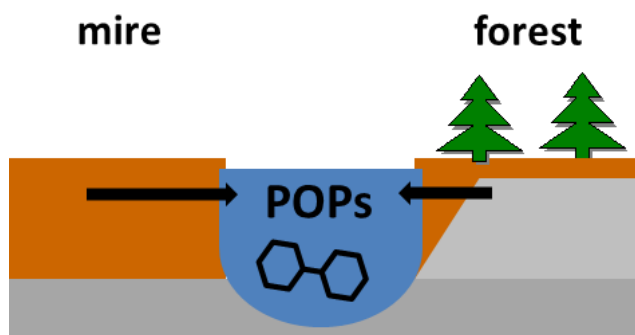
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23 **Abstract**

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

41

42 **TOC Art**



43

44 **1. Introduction**

45 The environmental fate of legacy persistent organic pollutants (POPs), including
46 polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated
47 biphenyls (PCBs), has been extensively studied. Bans and regulations have been
48 implemented, leading to declining levels of legacy-POPs in the environment¹. However, in
49 some locations the declines have levelled off and legacy-POP levels are still elevated, for
50 example in fish in the Baltic Sea². Riverine inputs may be an important source of POPs to sea
51 areas (e.g.³⁻⁶), transporting pollutants from the terrestrial environment to aquatic organisms.

52

53 Most legacy-POPs are semivolatile compounds that can undergo long-range atmospheric
54 transport and thus reach areas far from original source areas⁷. Boreal forests cover around 15
55 million km² and constitute almost one third of the world's forests⁸. They receive and store
56 large amounts of atmospherically deposited POPs⁹⁻¹², which makes them an important factor
57 in the global fate and transport of contaminants. Snowfall is one of the most important
58 pathways for atmospheric contaminants to reach the terrestrial environment in cold climates¹³.
59 For example, measurements in northern Sweden have shown that ~70% of the yearly
60 deposition of PCDD/Fs occurs during winter (November-March)¹². During spring snowmelt,
61 contaminants are then remobilized and either revolatilized to the atmosphere or transported
62 with meltwater into soils and streams¹⁴. Accordingly, relatively high concentrations of organic
63 contaminants have been observed in urban and rural rivers in connection with spring
64 snowmelt¹⁵⁻¹⁹. There are also landscape-related variations that may impact stream water
65 quality. The boreal landscape is a mixture of forests and mires, which vary fundamentally in
66 both hydrological functioning and biogeochemical dynamics. For example, total organic
67 carbon (TOC) concentration in streams and export from the catchment increases with an
68 increasing proportion of mires²⁰⁻²². 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 forests²¹. 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 signatures²³. 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 km² 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 snow²⁶. 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/Fs²⁷ 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 m³ 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 matter²⁸. 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 (¹³C) internal standards of all seventeen 2378-substituted PCDD/F
143 congeners (ΣPCDD/F₁₇), 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 (ΣPCB₇), 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 method²⁹. 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

159 **2.4 Water flow and POP flux determinations**

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

161

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

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-courses²⁰) 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 \pm 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), $0.5 \times \text{LOQ}$ 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/F₁₇, 23% for
204 PCB₇, 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/F₁₇ 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/F₁₇, 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 PCB₇, 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 Sweden²⁹. Measurements of PCBs in the Ume River in
223 1990⁴ showed median concentrations of PCBs of 210 ng m⁻³, on average 15 times higher than
224 the PCB₇ 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 PCB₇ constitute a large part
226 of the PCBs present in mixtures³⁴, 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/F₁₇, although it was observed also for
238 HCB. For PCB₇, 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/F₁₇ 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 flood¹⁵⁻¹⁹, with e.g.
243 up to 100 times higher levels of PAH in an urban stream¹⁸.

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 flow¹⁹. In the St. Lawrence River, the dissolved fraction
251 of PCBs was responsible for the high bulk concentrations¹⁶; 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 PCB₇ 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

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/F₁₇ 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 Sweden²⁹, 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/F₁₇ 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/F₁₇, PCB₇ and HCB
317 were generally higher in the mire stream (Figure 2; statistically significant for PCDD/F₁₇:
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/F₁₇ ($n=6$, $p=0.004$), 2.0 for PCB₇ ($n=3$, $p=0.02$),
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 concentrations²⁵ 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 POPs²⁵, and hence the leaching is low. At the mire site (C4),
336 there is no vertical gradient of organic matter or POPs in the soil²⁵, 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 POPs²⁵, 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 months¹², 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/F₁₇ and PCB₇ than the mire peat²⁵. 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 area¹² (Table S7; 4 times higher
362 deposition of PCB₇ 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 streams⁴⁶.

371

372 **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/F₁₇
383 ($n=4$, sample from SC-08 excluded and discussed below), 1.9 ± 0.6 times for PCB₇ ($n=3$) 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/F₁₇ (pg g⁻¹ SPM) were on average
395 25±10 (n=4) times higher at D3 compared to C16, and the corresponding increase for PCB₇
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 PCB₇ 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/F₁₇ 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/F₁₇ 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/F₁₇ concentration and congener pattern (Figure 4, Figure S12a, Figure S13a). The
422 PCDD/F₁₇ 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/F₁₇ in this
429 sample.

430

431 The high PCDD/F₁₇ 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

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449

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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