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1 **The organic pollutant status of rivers in Bosnia and Herzegovina as determined by a**  
2 **combination of active and passive sampling methods**

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20

21 **Keywords**

22 High Volume Water Sampling; Persistent Organic Pollutants; Balkans; Monitoring; LDPE;

23 Passive Sampling

24

## 25 **ABSTRACT**

26 There is an overall lack of data concerning the pollution status of Bosnia Herzegovina, which  
27 is confounded by fragmented national environmental management. The present study  
28 aimed to provide some initial data for concentrations of priority substances in two major  
29 Bosnian Rivers, using two types of passive sampler (PS) as well as by using high volume  
30 water sampling (HVWS). Overall, concentrations of most persistent organic pollutants  
31 (POPs), including polychlorinated biphenyls (PCBs) and legacy pesticides were shown to be  
32 low. However, around the town of Doboje on the Bosna River, concentrations of polycyclic  
33 aromatic hydrocarbons (PAH) breached European standards for several compounds and  
34 reached  $67 \text{ ng L}^{-1}$  for freely dissolved concentrations, and  $250 \text{ ng L}^{-1}$  for total concentrations.  
35 In general contamination was lower in the Neretva River compared to the Bosna, although  
36 for brominated diphenyl ethers (PBDEs) results suggested an active source of PBDEs at one  
37 location based on the ratio of congeners 47 and 99. Direct comparisons between the  
38 different sampling techniques used are not straightforward, but similar patterns of PAH  
39 contamination were shown by HVWS and PS in the Bosna River. There are both scientific and  
40 practical considerations when choosing which type of sampling technique to apply and this  
41 should be decided based on the goals of each individual study.

42

## 43 **INTRODUCTION**

44 The complex socio-political situation in Bosnia and Herzegovina (BiH) means that realising  
45 the monitoring goals obliged after ratifying the Stockholm convention in 2009 and those  
46 required by EU membership aspirations remain challenging. Whilst these issues may be true  
47 of some Balkan states in general (Skoulidakis et al., 2009), the lack of a functioning single  
48 state in BiH means environmental management and regulation are fragmented. In addition,

49 there is an overall need to build capacity regarding environmental monitoring and analyses  
50 in BiH. Thus in contrast to most European countries there are few data concerning  
51 concentrations of POPs and other organic pollutants in BiH waters including the 21  
52 compounds of the Stockholm Convention or the 45 priority pollutants of the EU's Water  
53 Framework Directive (EU, 2013).

54 From the available data from Eastern Europe in general, the trend is for elevated  
55 concentrations compared to Western Europe (Parlar et al., 2004; Ruzickova et al., 2008), for  
56 example for PCBs (Adamov et al., 2003; Vojinovic Miloradov et al., 1996; Franciskovic-Bilinski  
57 et al., 2005). This includes studies which consider contamination from military operations,  
58 following the dissolution of Yugoslavia (Turk et al., 2007; Dalmacija et al., 2003; Klanova et  
59 al., 2007). Our previous studies in BiH have found varying levels of contamination depending  
60 on the geographical location and the target compounds. For example, relatively low  
61 concentrations of organic and inorganic compounds were shown in the Neretva River  
62 (Djedjibegovic et al., 2010; 2011), whereas in the Bosna River there were examples of  
63 sediments highly contaminated with both PAH and legacy pesticides (Harman et al., 2013).  
64 Low concentrations of pesticides have also been reported in wastewaters from the capital  
65 Sarajevo (Terzic et al., 2008), although this may not be the case in more agricultural areas.  
66 Therefore, there is an overall need for cheap and simple techniques in order to achieve  
67 widespread and broad chemical screening of Bosnian aquatic ecosystems. One approach  
68 which can help to address this need is the use of passive samplers (PS). These cost effective  
69 devices are exposed in the environment where they accumulate chemicals in a totally  
70 passive manner, without external energy requirements. These techniques are now widely  
71 applied to many different monitoring environments and measurement scenarios (Mills et al.,  
72 2014). The three most widely stated advantages of using PS are; detection of fluctuating

73 concentrations over time; detection of very low concentrations, as larger water samplers are  
74 taken; and only sampling the freely dissolved, biologically relevant fraction, through similar  
75 diffusive cut-off limits in the polymers used and in biological membranes. Thus correlations  
76 between uptake in biota and PS have been shown to be good where the water phase is the  
77 dominating exposure pathway (Harman et al., 2009). However, some biota may also  
78 accumulate contaminants through particulates and regulatory instruments such as the  
79 European Water Framework Directive (WFD) often require total concentrations to be  
80 measured. Thus an approach using two types of PS; SPMDs (Huckins et al., 1993) and LDPEs  
81 (Booij et al., 2002), together with large volume spot samples using a high volume water  
82 sampler (HVWS) was applied in this study. The HVWS filters particles from water before  
83 water soluble compounds are extracted using polyurethane foam (PUF). The technique  
84 therefore gives an indication of the level of contaminants in both suspended material  
85 present in the rivers, as well as in the dissolved phase, if they are analysed separately. The  
86 overall objective of this study was to provide data for a suite of relevant organic  
87 contaminants from two major rivers in BiH, and to compare to concentrations found in  
88 water samples taken by both passive and high volume sampling methods.

89

## 90 **METHODS AND MATERIALS**

### 91 **Sampling**

92 Two major BiH rivers were sampled which have catchment areas covering a large area of the  
93 country, and represent a transect from the Croatian border in the North to the Adriatic Sea  
94 in the South (see Figure 1). The Bosna River has its source near Sarajevo and flows  
95 northwards for 270 km and into the Sava River. It passes through several heavily  
96 industrialised areas and was previously sampled in 2008 and 2009 (Harman et al., 2013).

97 The Neretva River Flows Southwards for over 200km, with its mouth in Croatia. It is an  
98 important watercourse for irrigation and drinking water and flows through several important  
99 conservation areas including a wetland listed as of international importance under the  
100 Ramsar International Convention on Wetlands. It is under increasing anthropogenic  
101 pressure, including some industry, although contaminant concentrations were low, when  
102 previously sampled in 2007 (Djedjibegovic et al., 2010).

103 A total of 11 sites were strategically chosen for deployment of passive samplers ( $n = 6$  and 5,  
104 Bosna and Neretva, respectively) based on previous results and the locations of potential  
105 major point sources of contamination. In order to more easily compare to earlier results  
106 Semipermeable membrane devices (SPMDs) were the primary PS chosen. Additionally, low-  
107 density polyethylene (LDPE) samplers were co-deployed for comparison. Both sampler types  
108 were held in commercially available stainless steel holders (EST labs, St. Joseph, USA),  
109 fastened to ropes, and deployed using weights and floats, according to the local conditions.  
110 Field controls (FC) were exposed to air during deployment and retrieval procedures to  
111 correct for any air contamination during these operations, and trip controls (TC) which  
112 follow the transport and storage of exposed samplers but are never opened. In addition  
113 laboratory controls (LC) were used to examine both any initial contamination and also  
114 starting concentrations of so-called performance reference compounds (PRCs), which are  
115 used to determine sampling rates ( $R_s$  L d<sup>-1</sup>) and subsequently water concentrations (Booij et  
116 al., 1998; Huckins et al., 2002). High volume water samples were taken at each of the passive  
117 sampler sampling sites, as close to the sampler rig as possible. More than one filter was used  
118 at most sites due to clogging reducing the water flow through the HVWS significantly. The  
119 amount of water extracted was determined manually using a graduated container. On arrival  
120 at the laboratory all types of samples were kept frozen at -20°C until analysis.

121

122 **Chemicals and equipment preparations**

123 Solvents were from Rathburn (Walkerburn, Scotland) except for cyclohexane (J.T. Baker,  
124 Deventer, Holland) and were of HPLC grade or better. Extra pure 98% sulphuric and nitric  
125 acids were from Merck (Darmstadt, Germany). Internal standards for analysis were from LGC  
126 (Wessel, Germany). Glassware was baked in a muffle furnace at 560 °C, and all other  
127 sampling equipment was cleaned thoroughly and solvent rinsed before use.  
128 SPMDs (91.4 × 2.5 cm LDPE tubing, containing 1 mL triolein), were obtained from  
129 ExposMeter (Tavelsjo, Sweden) and were spiked with five deuterated PAH (acenaphthene-  
130 d10, fluorene-d10, phenanthrene-d10, chrysene-d12 and benzo[e]pyrene-d10) as PRCs.  
131 LDPE was obtained from the same supplier as is used in commercial SPMDs (Brentwood  
132 Plastics, St Louis, USA). LDPE was cut open from its lay-flat tube form, and made to similar  
133 dimensions given above for SPMDs after mounting loops were created at either end using a  
134 heat sealer. The similar dimensions allow for straightforward deployment using standard  
135 equipment. LDPE was washed with water and further cleaned in methanol using Soxhlet  
136 extraction, before spiking with PRCs using a co-solvent method based on that of Booij et al.  
137 (2002). A suite of mono-fluorinated PAH (F-PAH) were tested for their suitability as PRCs in  
138 LDPE (F-Naphthalene, F-Biphenyl, F-Phenanthrene, F-Pyrene, F-Chrysene, F-  
139 Benzo[k]fluoranthrene), and were obtained from Chiron (Trondheim, Norway). PRC spiking  
140 procedures in LDPE are described elsewhere in more detail (Allan et al., 2010).

141 The HVWS was constructed in house and consisted of a pump which draws water  
142 through two filters, the first of glass fibre (GF) and the second of PUF, where the retained  
143 fractions were defined as particulate and dissolved, respectively. GF filters without binders  
144 and 0.7 µm pore size were from Pall (Ann Arbor, US) and PUF plugs were obtained from

145 Sigma-Aldrich (Munich, Germany), and both were solvent cleaned before use. GF Filters  
146 were held in a 293 mm disc filter holder (Millipore, Billerica, USA) and PUF plugs in a 47 mm  
147 pressure filtration tube (Pall, Ann Arbor, USA). All other components were stainless steel or  
148 PTFE.

149

#### 150 **Extraction of passive samplers**

151 Solvent extraction methods for both LDPE and SPMDs are described in detail elsewhere  
152 (Allan et al., 2010). Briefly samplers were cleaned thoroughly with water and paper tissues,  
153 before mounting loops were cut off. Cleaned samplers were then dialysed in hexane (ca. 150  
154 mL) for 2 × 24 h, in the dark at room temperature, with surrogate internal standards added.  
155 Extracts were combined, and reduced with a stream of nitrogen, dried over sodium sulphate,  
156 and adjusted to 3 mL. Clean up to remove analytical interferences such as co-extracted  
157 oligomers, was carried out on 2 mL of extract by gel permeation chromatography (GPC), as  
158 described previously (Harman et al., 2008). Following GPC, extracts were split into two  
159 fractions; one for PAH analysis, and one for combined PCB and OCP (organo-chlorine  
160 pesticides) analysis. The remaining (non-GPC) 1 mL fraction was analysed for PBDEs.

161

#### 162 **Extraction of High Volume Water Sampler (HVWS)**

163 PUF plugs and combined filter papers from the HVWS were extracted using accelerated  
164 solvent extraction. As the PUF represents the dissolved fraction and the filter papers a  
165 fraction associated with particles, they were extracted separately. The extraction consisted  
166 of 5 min static extraction of 3 cycles using a 1:1 ratio of dichloromethane/cyclohexane. The  
167 temperature was 100 °C and the pressure was 2000 psi. Resulting extracts were dried and  
168 reduced in volume using nitrogen before analysis. Contamination of PUF blanks, resulted in



169 higher than normal detection limits, and prevented quantification of PCBs, OCP and PBDEs.  
170 Thus only results of PAH (which were quantifiable) are considered in any detail.

171

## 172 **Analysis of PAHs**

173 The PAH fractions from all samplers (SPMDs, LDPE and HVWS) were analysed by gas  
174 chromatography-mass spectrometry (GC-MS). An 6890GC coupled to a 5973 mass selective  
175 detector (Santa Clara, USA) was used with the inlet in splitless mode. The GC was equipped  
176 with a 30 m column with a stationary phase of 5% phenyl methylpolysiloxane (0.25 mm  
177 internal diameter and 0.25  $\mu\text{m}$  film thickness (Agilent, Santa Clara, USA). Quantification of  
178 individual components was conducted by the relative response of internal standards.

179 Analytical limits of detection (LOD) were set as the average value of triplicate solvent blanks,  
180 plus three times the standard deviation of that average. Concentrations of target  
181 compounds in sampler blanks are considered separately. Where the sum of PAH is referred  
182 to in the text, this is the sum of the 16 priority PAH as defined by the US Environmental  
183 Protection Agency (EPA PAH16).

184

## 185 **Analysis of PCBs and OCPs**

186 The PCB fractions from all sample types (SPMDs, LDPE and HVWS) received further clean up  
187 by partitioning twice with concentrated sulphuric acid (Harman et al., 2008). The PCB  
188 congeners analysed for were; 28; 52; 101; 105; 118; 138; 153; 156; 180; 209 (hereafter  
189 referred to as  $\Sigma\text{PCB}$ ), and the OCP analysis included the following compounds;  
190 pentachlorobenzene (QCB);  $\alpha$ -hexachlorocyclohexane (HCH-A);  $\gamma$ -hexachlorocyclohexane  
191 (HCH-G); hexachlorobenzene (HCB); octachlorostyrene (OCS); 4,4'-  
192 dichlorodiphenyldichloroethane (4,4-DDD); 4,4-dichlorodiphenyltrichloroethane (DDT) and

193 4,4'-dichlorodiphenyldichloroethylene (4,4-DDE). The same instrumentation as described for  
194 PAH was used, except a 60 m version of the same column was installed instead. This analysis  
195 also included the F-PAH, used as PRCs in the LDPE.

196

### 197 **Analysis of PBDEs**

198 Samples that were analysed for PBDEs were acid treated similarly to PCBs before receiving  
199 an additional step of partitioning with acetonitrile (no GPC performed, due to high losses).

200 The same GC-MS system as outlined above was used but with a Rtx-1614 60 m column with  
201 a 0.1 µm film (Restek, Bellefonte, USA) fitted, and the ion source switched to chemical  
202 ionisation. Instrumental parameters are given in detail previously (Allan et al., 2013).

203

### 204 **Calculation of water concentrations from passive sampler accumulations**

205 A non-linear least squares (NLS) method was applied to calculate water concentrations from  
206 contaminant concentrations in passive samplers as described in detail by Booij et al., (2010).

207 The statistical package *R*, version 2.15.2 (R core team, 2012) was used to model the data  
208 using code supplied by Booij et al (2010). Briefly;  $R_s$  were estimated from the PRC data using  
209 NLS methods by considering  $f$  as a continuous function of the sampler-water partition  
210 coefficient ( $K_{sw}$ ) with  $R_s$  as an adjustable parameter

$$211 \quad f = \exp\left(-\frac{R_s t}{K_{sw} V_s}\right)$$

212 Where  $V_s$  is the volume of the sampler,  $t$  is the deployment time.  $K_{sw}$  values were modelled  
213 from  $K_{ow}$  according to Lohmann et al. (2010) and Booij et al. (2010), for SPMDs and LDPE  
214 respectively

$$215 \quad \text{Log } K_{sw} = 1.05 \text{ Log } K_{ow} - 0.59 \text{ (LDPE)}$$

216 
$$\text{Log } K_{sw} = 0.988 \text{ Log } K_{ow} + 0.03 \text{ (SPMD)}$$

217 Sampling rate ( $R_s$ ) values were modelled by

218 
$$\frac{1}{R_s} = \left( \frac{1}{AB_m K_{ow}^{0.682}} \right) + \left( \frac{1}{AB_w K_{ow}^{-0.044}} \right)$$

219 Where  $A$  is the sampler surface area and  $B_m$  and  $B_w$  are empirical parameters of transfer  
220 coefficients through the membrane and diffusive boundary layer respectively, obtained from  
221 modelling experimental sampling rates as a function of  $K_{ow}$ . An estimated value of  $34 \text{ nm s}^{-1}$   
222 was used for  $B_m$  (giving  $0.135 \text{ L d}^{-1} AB_m$  for  $460 \text{ cm}^2$  samplers) with  $B_w$  being then the only  
223 parameter to be gained from the PRC results (Booij et al., 2010). Using the same  $B_m$  value for  
224 LDPE as for SPMDs is somewhat erroneous as the single layer LDPE samplers are thinner, but  
225 this had little effect on the  $R_s$  values of the largely water boundary layer controlled, target  
226 compounds in the present study (see results and discussion). Once  $R_s$  values were calculated  
227 then water concentrations  $C_w$  could then be derived from analyte concentrations in the  
228 sampler  $C_s$  using the following equation (Huckins et al., 1993)

229 
$$C_w = \frac{C_s}{V_s K_{sw} \left( 1 - \exp \left( -\frac{R_s t}{V_s K_{sw}} \right) \right)}$$

230

## 231 **RESULTS AND DISCUSSION**

### 232 **SPMDs and LDPEs**

#### 233 *Blanks*

234 A total of 30 SPMDs controls were analysed, all from the same batches as exposed samplers.

235 Overall there was little difference between the various control types (LCs, TCs, and FCs)

236 indicating that any contamination occurred during manufacture or laboratory treatment of

237 samplers, rather than in during field operations. Exceptions were fluoranthene and pyrene

238 which were present in SPMD FC used in the Bosna River, at 8.8 and 9.6 ng/sampler (average  
239 concentrations respectively,  $n = 4$ ), but were not found in LC or TC. Overall LDPE controls  
240 were free from contamination, apart from naphthalene (10-20 ng/sampler) which tends to  
241 be ubiquitous in sampler controls, and benzo[k]fluoranthrene (8.5 ng/sampler). Similar to  
242 previous results, several other PAH were also present in all SPMD controls, acenaphthene,  
243 fluorene and phenanthrene (6.5, 12 and 35 ng/sampler, respectively). As deuterated  
244 versions of these compounds were used as PRCs then this is the likely source of this  
245 contamination.

246

#### 247 *PRCs and sampling rates*

248 Estimated sampling rates ranged from 14 L d<sup>-1</sup> for phenanthrene (Station L1, Bosna River), to  
249 2.4 d<sup>-1</sup> for PBDE 209 (Station L3, Neretva River), which equates to equivalent water volumes  
250 sampled of up to approximately 200 L, during the 21 day deployment. As mentioned  
251 previously, using the same  $B_m$  value for SPMDs and LDPE is not strictly correct. Changing the  
252 value of  $B_m$  for LDPE to half that of SPMDs in order to better represent the thickness,  
253 affected estimated sampling rates by less than 1% for most compounds. More significant  
254 effects were observed for the least hydrophobic compounds such as naphthalene (14%  
255 lower  $R_s$ ). As the PRC results show that these compounds reached equilibrium, this is of little  
256 consequence for the  $C_w$  calculations. Estimated  $R_s$  were similar between SPMDs and LDPE as  
257 shown in Figure 2, although LDPE values were on average ca. 25% lower. It should be noted  
258 however that Log  $K_{ow}$  (and Log  $K_{sw}$ ) values are not available for the F-PAH, and for simplicity  
259 the value for the non-fluorinated PAH was used. Assuming the F-PAH are slightly more  
260 hydrophobic (+ 0.2 Log units using fragment methods) then recalculating using higher values  
261 increased the  $R_s$  values for LDPE by roughly one third. A thorough consideration of the

262 factors influencing the applicability of F-PAH as PRCs is not the purpose of the current study.  
263 Despite any uncertainties they appear to be suitable for use as PRCs, and generally gave  
264 small residuals from the NLS fit (Figure 2).

265

#### 266 *Contaminant concentrations*

267 A summary of results is shown below in Figure 3 and data for individual compounds is  
268 provided in Table S1 (Supporting Information). A few analytes very close to the LOD in LDPE  
269 extracts were >LOD in SPMD extracts. This was probably because the LDPE extracts were  
270 slightly cleaner, due to the absence of triolein, which allowed a slightly lower LOD. Overall  
271 both types of sampler gave comparable results (Figure 3) which is similar to previous  
272 comparisons (Allan et al., 2010). Slight differences between them were apparent, but largely  
273 for compounds that were close to the LOD.

274

275 There were clear differences between the two rivers, with overall higher concentrations in  
276 the Bosna, compared to the Neretva (Figure 3). The pattern was also different between the  
277 two study rivers with concentrations decreasing downstream in general in the Bosna, and  
278 the lowest concentrations being found in the uppermost stretch of the Neretva. This is not  
279 particularly surprising seeing as the city of Sarajevo, is near the source of the Bosna River. An  
280 exception to this overall decrease in concentrations downstream was for PAH, where a  
281 significant input (ca. 70 ng L<sup>-1</sup>) was shown from the tributary Sprecca, at Doboj (Figure 1),  
282 which drains an area including some heavy industry. However, compared to previous studies  
283 this represents a substantial improvement from the nearly 500 ng L<sup>-1</sup> and 200 ng L<sup>-1</sup>  
284 measured in 2008 at stations L9 and L8, respectively (Harman et al., 2013). Although care  
285 must be taken in drawing conclusions concerning trends based on a few years of sampling, it

286 appears that concentrations were now more comparable to other large cities in the region  
287 e.g. Brno in the Czech Republic (Grabic et al., 2010). Revised environmental quality standards  
288 for PAH in the WFD include, for example, a value for benzo[a]pyrene of 0.17 ng L<sup>-1</sup>, and 8.2  
289 ng L<sup>-1</sup> for fluoranthene, which are lower than the concentrations measured at station L9  
290 (0.29 and 28.56 ng L<sup>-1</sup> respectively). As the EQS relates to total concentrations and we have  
291 measured freely dissolved concentrations it is clear that total concentrations were higher  
292 and that the EQS values are likely periodically exceeded.

293 Concentrations of both PCBs, and OCPs were low in both rivers, with slightly higher results in  
294 the Bosna (e.g. range  $\sum$ PCB in LDPE ca. 0.3-0.06 ng L<sup>-1</sup> vs. 0.1-0.01 ng L<sup>-1</sup>, Bosna and Neretva,  
295 respectively). These concentrations, were relatively similar to previous results, for example  
296  $\sum$ PCB at Sarajevo of 0.17 ng L<sup>-1</sup> in 2009 (Djedjibegovic et al., 2010; Harman et al., 2013), and  
297 0.29 ng L<sup>-1</sup> in this study. As mentioned previously, there was an overall trend of decreasing  
298 concentrations after an initial input at Sarajevo in the Bosna River for both PCBs and OCPs,  
299 and a minor input of PCBs at station A1 in Neretva (Figure 3). The pattern was similar  
300 between the two different types of passive samplers. Concentrations of PBDEs were low in  
301 both rivers, with generally only PBDE 47 and 99 being >LOD. In the Neretva River  
302 concentrations of PBDEs at station A1 were highest, 10 pg L<sup>-1</sup> for PBDE 47 and 6 and 8 pg L<sup>-1</sup>  
303 for congener 99 (SPMD and LDPE, respectively). Higher concentrations were observed in the  
304 Bosna River, highest at Sarajevo (L13) 67 pg L<sup>-1</sup> and decreasing downstream to 8 pg L<sup>-1</sup>. At  
305 these most upstream stations, congeners 66 and 71 were also detected. Due to the  
306 extremely low EU EQS values for PBDEs of  $4.9 \times 10^{-8} \mu\text{g L}^{-1}$  ( $\sum$  28,47, 99, 100, 153, 154), then  
307 any measurement is automatically higher than the EQS values, even when using the low pg L<sup>-1</sup>  
308 LOD described in this study. This highlights a fundamental issue associated with these EQS,

309 that even by using very sensitive passive sampling methodologies, it will be extremely  
310 difficult to achieve measurement at these concentrations.

311

### 312 **HVWS results**

313 The volume of water sampled using the HVWS was between 147-200 L with slightly smaller  
314 samples taken in the Bosna River compared to the Neretva due to higher amounts of  
315 particulate matter, which caused clogging of the filters. Procedural error in the handling of  
316 the PUF blanks during extraction resulted in high LOD for all halogenated compounds (PCBs,  
317 OCPs and PBDEs) and these results are therefore not considered further. For PAH the LODs  
318 were in general low  $\text{pg L}^{-1}$ . Total concentrations of PAH (both PUF fraction and filter fraction)  
319 in the Neretva were unremarkable, and can be considered as background, i.e. without  
320 significant point sources, never exceeding  $5 \text{ ng L}^{-1}$ . Samples taken near an aluminium plant  
321 (site A1), where there was an assumption of elevated PAH concentrations, also showed  
322 background concentrations of  $4.9 \text{ ng L}^{-1}$ . This corresponds well with both previous  
323 measurements of PAH using SPMDs by Djedjibegovic et al. (2010), who found concentrations  
324  $< 4 \text{ ng L}^{-1}$  and with those of this study, which were between  $3.6\text{-}7.0 \text{ ng L}^{-1}$  at site A1. In the  
325 Bosnia River however, the HVWS revealed much higher concentrations of PAH between 15-  
326  $250 \text{ ng L}^{-1}$  (sum of both fractions), with the highest concentrations around Doboj. Earlier  
327 measurements in the same location revealed freely dissolved (using SPMD) concentrations  
328 of  $\Sigma\text{PAH}$  to be roughly  $500 \text{ ng L}^{-1}$  in 2008 and  $100 \text{ ng L}^{-1}$  in 2009, and levels in river sediments  
329 exceeding international criteria (Harman et al., 2013). Despite this apparent improvement,  
330 the HVWS revealed that EQS values were exceeded at 3 locations in the Bosna River for  
331 fluoranthene (L2; L4 and L8), with concentrations as high as  $53 \text{ ng L}^{-1}$  at Doboj.  
332 Concentrations of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene,

333 indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene were also exceeded at this station (13, 6, 9,  
334 5, and 6 ng L<sup>-1</sup>, respectively). All raw data from the HVWS are provided in Table S2 in  
335 supporting information.

336 In this study the HVWS was only used to supplement the PS deployments in order to provide  
337 some preliminary data concerning concentrations in the particulate fraction and to our  
338 knowledge this is only one of a few studies to use HVWS in this way. Although these are just  
339 spot samples, compared with the time integrated measurements of the PS, the large  
340 volumes achieved allow for low LOD and facilitate the comparison. Results were not  
341 corrected for the amount of particulates retained on the filters, or the amount of organic  
342 carbon present. In addition the actual fraction which is retained by the filter and PUF is  
343 relatively poorly defined, as are the water-PUF partitioning coefficients and overall PUF  
344 capacity. These issues require further attention before this method can contribute to  
345 monitoring studies in a more quantitative way. However this technique allows a rudimentary  
346 examination of the fate of compounds based on their hydrophobicity. Figure 4 shows the  
347 ratio of individual compounds operationally defined as the “freely dissolved fraction” (PUF)  
348 and the “particulate fraction” (filter). This suggests that compounds up to about pyrene, are  
349 mainly present in the water phase, which is higher than might be expected, based on their  
350 Log  $K_{ow}$  values. As mentioned above the cut off point between the two fractions is poorly  
351 studied, and it is likely that a particulate fraction smaller than the filter size of 0.7  $\mu\text{m}$  may be  
352 partly retained by the PUF, co-extracted and therefore contribute to the freely dissolved  
353 fraction fraction.

354

355 **Comparison between different sampling techniques**



356 Direct comparisons between the different techniques are not straightforward, as they  
357 extract different fractions of contaminants from the water phase. Whilst the LDPE used in  
358 both types of PS and the PUF may have a similar cut off for diffusion into the polymer, the  
359 PUF is porous and particulates which pass through the filter may accumulate and be co-  
360 extracted, as mentioned above. This may result in bias in concentrations measured in the  
361 HVWS freely dissolved fraction, but together with the filtered fraction should still provide a  
362 reasonable estimate of total concentrations. Such total concentrations remain the standard  
363 in many national and international regulatory monitoring programs, where PS is often not  
364 applied. Accumulation of hydrophobic contaminants in PS has been shown to be similar to  
365 accumulation in a range of aquatic organisms, where the main exposure pathway is from the  
366 water phase. Such studies are not available for HVWS, but it might potentially over-estimate  
367 risk to biota. Both methods offer low LOD, due to their ability to concentrate contaminants  
368 from a large sample volumes, but only PS offers time integrated exposures, as the HVWS is  
369 essentially a large spot sample. The only compound group adequately measured in all three  
370 sampler types was PAH and despite the differences discussed above all show higher  
371 concentrations of PAH in the Bosna River compared to the Neretva and increased  
372 concentrations around or downstream of the town of Doboj. The pattern of PAH  
373 contamination was also similar downstream in the Bosna River between the techniques  
374 (Figure 3). Additionally, there are often other practical issues which can dictate the final  
375 sampling protocol and again there are differences between the techniques in this regard as  
376 well. For example, PS may be tampered with or lost due to flooding, whereas this is not the  
377 case for the HVWS. Thus the types of samples to be collected should be decided according to  
378 the aims of each individual study.

379

380 **CONCLUSIONS**

- 381 - Total concentrations of several PAH, measured using HVWS, exceed EU EQS.
- 382 - Despite apparent reductions over time at these locations these discharges require  
383 further attention and site remediation
- 384 - SPMDs and LDPE suggest an active PBDE source into the Neretva River
- 385 - Concentrations of OCPs and PCBs found in SPMDs, were unremarkable, similar to  
386 previous surveys
- 387 - Results between LDPE and SPMDs were highly comparable
- 388 - Overall results between PS and the HVWS were comparable, for example showing  
389 higher concentrations of contamination in the Bosna River compared to the Neretva
- 390 - Both HWVS and PS are suitable for initial screening contaminant purposes, with the  
391 former offering total concentrations and the latter time integrated measurements
- 392 - Sampling methods should be chosen according to the aims of the study and care  
393 must be taken when drawing conclusions concerning overall contamination levels

394

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513

514 **Figure Captions**

515 Figure 1. Sampling sites in both rivers, for SPMDs and HVWS (round circles). Source: ESRI.

516

517 Figure 2. Comparison of PRC results for SPMDs and LDPE. Fraction of initial concentrations of

518 PRCs ( $t_0$ ) retained after exposure shown against hydrophobicity (average of all samplers at

519 all stations in the Bosna River). Curves fitted to these average values, using the NLS method,

520 solid line SPMDs, dotted line LDPE.

521

522 Figure 3. Freely dissolved concentrations of PAH, PCB, OCP and PBDE ( $\text{ng L}^{-1}$ ) measured in

523 SPMDs and LDPE.

524

525 Figure 4. Ratio of accumulated PAH on PUF and filter fractions, versus hydrophobicity.

526 Average values for all sites ( $n=11$ ), both rivers, non-detects disregard