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1 **Screening for Stockholm convention persistent organic pollutants in the Bosna River**
2 **(Bosnia and Herzegovina).**

3

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22

23 **ABSTRACT**

24 The Stockholm Convention which aspires to manage persistent organic pollutants (POPs) at
25 the international level was recently ratified in Bosnia and Herzegovina (BiH). Despite this
26 fact, there is in general a paucity of data regarding the levels of POPs in the environment in
27 BiH. In the present study screening for POPs was conducted in one of the country's major
28 rivers, the Bosna. A two pronged approach was applied using passive samplers to detect the
29 freely dissolved and bioavailable concentrations in the water phase, and sediment analysis
30 to provide an integrated measure of historical contamination. At several places along the
31 river, concentrations of polycyclic aromatic hydrocarbons (PAH) were high, and exhibited
32 potential for both chronic and acute effects to biota. River water also showed elevated

33 concentrations of PAH, up to 480 ng L⁻¹ near the city of Doboj, and diagnostic ratios
34 suggested combustion sources for the contamination present in both types of sample. Levels
35 of the other contaminants measured; polychlorinated biphenyls (PCBs), organo-chlorine
36 pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs), were generally low in the
37 water phase. However PCBs and some OCPs were present in river sediments at levels which
38 breach international criteria and thus suggest potential for ecological damage. Additionally
39 levels of heptachlor breached these criteria at many of the sites investigated. This study
40 presents the first screening data for some of these Stockholm Convention relevant
41 compounds in BiH and reveals both low concentrations of some chemical groups, but
42 significant point sources and historic contamination for others.

43

44 **KEYWORDS**

45 Contaminated Sediments, SPMDs, Passive Sampling, River Monitoring, Balkans

46

47 **INTRODUCTION**

48 Persistent organic pollutants (POPs) can be defined as organic chemical substances which
49 possess a particular combination of properties which once released into the environment
50 they; remain intact for exceptionally long periods of time, become widely distributed,
51 accumulate in the fatty tissue of organisms, are found at higher concentrations at higher
52 levels in the food chain and are toxic to both humans and wildlife (UNEP, 2001). As they can
53 often be found at elevated levels in regions where they have not been in used, their
54 management and control requires a global approach. One such international instrument in
55 this regard is the Stockholm Convention. Measures proposed by this treaty to reduce or
56 eliminate POPs include; eliminating production and use, restriction and control, reduce or
57 eliminate releases from unintentional production and to develop strategies that identify and
58 manage stockpiles and wastes containing POPs (UNEP, 2001). Initially the list comprised of
59 12 compounds, but a further 9 have been recently added.

60 In Bosnia and Herzegovina (BiH) the convention was recently ratified (March 2010)
61 and the formulation of a national implementation plan is underway. It is therefore necessary
62 to assess the environmental status of POPs in the country. Additionally BiH is a potential
63 candidate country for EU accession, requiring (eventually) adherence to for example, the
64 water framework directive (WFD) and its list of 33 priority pollutants (EU, 2006). There are

65 several challenges in this respect, not least of which is the complex socio-political situation in
66 the country. Some of these issues are inherent for many rivers in the Balkans in general. In a
67 recent review of the environmental state of rivers in the region, Skoulikidis (2009) states that
68 wars, political instability, economical crises, administrative and infrastructure constraints,
69 poor environmental planning and inspection, and a lack of environmental awareness in
70 general, results in significant environmental pressure on rivers. Thus in contrast to most EU
71 states there is almost no existing information concerning levels of POPs and other organic
72 pollutants in BiH waters. Additionally some of the compounds listed in the Stockholm
73 Convention or the WFD have never been measured in BiH at all. Limited data from the
74 Western Balkans region are available however, including neighbouring states that were
75 formerly part of Yugoslavia. For example, elevated levels of polychlorinated biphenyls (PCBs)
76 have been shown in aquatic biota from Serbia (Adamov et al., 2003; VojinovicMiloradov et
77 al., 1996) and in sediment samples from Croatia (Franciskovic-Bilinski et al., 2005) which is in
78 agreement with the general trend for Eastern Europe (Parlar et al., 2004; Ruzickova et al.,
79 2008). Several studies have considered human exposure to PCB concentrations, largely
80 utilising air monitoring (Turk et al., 2007) and including sites within BiH (Klanova et al., 2007).
81 Reasonably high concentrations of polycyclic aromatic hydrocarbons (PAH) have also been
82 reported, in air at urban locations within BiH (Skarek et al., 2007), and in water and
83 sediments following military operations in Serbia (Dalmacija et al., 2003). Despite what
84 appears therefore, to be a significant potential for elevated levels of POPs in BiH aquatic
85 systems the only relevant study available, in the Neretva River in the South of BiH, generally
86 showed low (pg/L) concentrations of those POPs which were detected (Djedjibegovic et al.,
87 2010). However, elevated concentrations of heavy metals in certain fish species in the
88 Neretva River have been reported (Djedjibegovic et al. 2011) and organo-chlorine pesticides
89 (OCPs) have also been detected in wastewater treatment effluents in BiH (Terzic et al.,
90 2008). In the present study concentrations of contaminants in the more industrial and more
91 polluted Bosna River which drains to the North of BiH were evaluated. Due to the assumed
92 low concentrations of many of the target compounds, passive sampling devices (PSDs) were
93 chosen as appropriate tools for measurement of the freely dissolved and bioavailable
94 fraction. Such devices accumulate chemicals by diffusive and partitioning processes and
95 provide integrative (time-averaged) measurements, and typically lower detection limits than
96 those achievable with traditional bottle sampling methods. Additionally they may offer

97 significant advantages over biomonitoring organisms (Harman et al., 2011). One such PSD is
98 the semipermeable membrane device (SPMD) (Huckins et al., 1990) which as been shown to
99 accumulate a wide range of relevant hydrophobic contaminants and has therefore been
100 applied to many different monitoring situations (Esteve-Turrillas et al., 2008). Sediment
101 samples were also taken in order to examine longer term contamination, as sediments
102 function as sinks for hydrophobic contaminants. Sediment analysis included therefore
103 certain pesticides which are now banned under the Stockholm Convention, in order to
104 ascertain their historical use in the region. Thus SPMDs and sediment samples may provide
105 complimentary information, one a measure of dissolved concentrations during the sampling
106 period, the other a measure of bound concentrations over a longer time period (Vrana et al.,
107 2001).

108 The objective of this study is to provide the first water and sediment concentration
109 data for a suite of organic contaminants relevant to the Stockholm convention and the WFD
110 in the Bosna River and to examine the patterns and the potential for biological effects, from
111 those concentrations.

112

113 **METHODS AND MATERIALS**

114 ***Sampling rationale and deployment***

115 The Bosna River is one of the major rivers in Bosnia and Herzegovina, flowing northwards for
116 271 km from its source just outside the capital Sarajevo. The Bosna River Valley is the
117 country's industrial centre with considerable metallurgical industry, coke plants, a thermal
118 power plant, an oil refinery and paper production. It is therefore considered to be the most
119 heavily polluted river in BiH today. The catchment has a population close to a million people,
120 and the river thus passes through several other large cities before eventually joining the Sava
121 River (a tributary of the Danube) at the border with Croatia. A total of eight sites were
122 strategically chosen along the river for sampling in 2008 (Fig. 1), from the source just outside
123 Sarajevo to the confluence with the Sava. At the industrial town of Doboj (STN 6), three
124 sediments and two SPMD sites were sampled, including a tributary (River Spreca, STN 6c)
125 with assumed high concentrations. This station (STN 6c) was sampled again in 2009, as was
126 the site assumed to be the most urban influenced, just after Sarajevo (STN 3, co-ordinates
127 for all stations provided in supporting information, S1: Sampling locations). This included the
128 deployment of extra SPMDs for extended analysis to include polybrominated diphenyl

129 ethers (PBDEs) and the use of small scale bioassays to ascertain in situ toxicity (results not
130 presented). Passive samplers were deployed using simple rigs consisting of an anchored line
131 with float (where appropriate) or tied to overhanging trees etc. Rigs were placed in order to
132 minimise the chances of tampering as much as possible, which has been a problem in both
133 previous and subsequent studies in the area. SPMDs were placed in commercially available
134 stainless steel holders (EST labs, St Joseph, USA) which were attached to the ropes of rigs.
135 Deployment lasted for 36 days in 2008 and in 22 days in 2009. The longer deployment time
136 in 2008 was due to exceptional river flow which prevented the planned sampler collection.
137 On retrieval samplers were kept frozen at -20°C until analysis at the Norwegian Institute for
138 Water Research laboratory in Oslo, Norway.

139

140 ***Sediment sampling***

141 Sediment samples were taken at 10 locations (Fig. 1), including at or near to the 7 sites
142 where passive samplers were deployed, one extra at Doboij (making three in total at STN 6)
143 and two extra ones near the source of the river. Samples were taken as close to where
144 SPMDs were deployed as possible, assuming suitable substrate was available. In some cases
145 this resulted in a difference of several hundred metres. The upper most layers (0.5-1 cm) of
146 organic containing sediment were sampled using a stainless steel scraper and collected in a
147 baked glass jar, which was then frozen. Sediments were taken from river banks or flooded
148 river banks, depending on the local conditions. Sediments were analysed for the same suite
149 of compounds as were SPMDs with the addition of some extra pesticides listed in the
150 Stockholm Convention such as Aldrin and Dieldrin, which may have been used historically in
151 the region.

152

153 ***Evaluation of ecotoxicological significance of sediment contamination levels***

154 In Norway, the Climate and Pollution Agency has guidelines for classifying the environmental
155 quality of aquatic sediments (Bakke et al., 2010). The classification system has five quality
156 classes that are based on the toxicity of individual prioritised contaminants and on the
157 European Union system for defining environmental quality standards and performing risk
158 assessment. Within the classification system, class I is considered to represent background
159 conditions. The upper limits for class II and III are based on the PNEC (predicted no effect
160 concentrations), for chronic and acute exposures to that compound. The upper limit of class

161 IV is defined as concentrations between 2 and 5 times the PNEC (depending on the
162 compound) with class V representing concentrations above this level. The upper limit of
163 class II represents the concentration of a contaminant which over time may have a negative
164 effect on certain organisms in the aquatic environment. The upper limit of class III is the
165 concentration at which acute effects to aquatic organisms may occur over a short time. The
166 concentration in the upper limit of class IV will give rise to further effects, both in the degree
167 of harm and the number of organisms affected. These classes are used as a tool for the
168 management of the aquatic environment in Norway. However, since they are based on
169 ecotoxicity, they may also be applied to other areas, including Bosnia. As some of the study
170 pesticides were never used in Norway, guidelines for them do not exist. Thus Canadian
171 environmental guidelines which are similar (CCME, 2002) were used for effects evaluation, in
172 those cases. The Canadian guidelines operate with two levels; the threshold effect level (TEL,
173 the concentration below which adverse biological effects are never or almost never
174 observed) and probable effect level (PEL, above which adverse biological effects are usually
175 or always observed).

176

177 ***Chemicals and equipment***

178 Solvents were from Rathburn (Walkerburn, Scotland) except for cyclohexane (J.T. Baker,
179 Deventer, Holland) and were of HPLC grade or better. Extra pure 98% sulphuric acid was
180 from Merck (Darmstadt, Germany). SPMDs (91.4 × 2.5 cm LDPE tubing, containing 1 mL
181 triolein), were spiked with five deuterated PAH (acenaphthene-d10, fluorene-d10,
182 phenanthrene-d10, chrysene-d12 and benzo[e]pyrene-d10) as performance reference
183 compounds (PRCs) for exposure adjustment (Booij et al., 1998; Huckins et al., 2002) and
184 were obtained from ExposMeter (Tavelsjo, Sweden). Several other PRCs were present in
185 SPMDs including C13 labelled PCBs, which were not included in analysis due to financial
186 constraints. All glassware was baked in a muffle furnace at 560 °C before use.

187

188 ***Extraction of SPMDs and organic chemical analysis***

189 Extraction, clean up and chemical analysis is given in detail elsewhere (Harman et al., 2008).
190 Briefly, the surface of SPMDs were wiped clean using paper towels and pure water, before
191 dialysis with 2 × 150 mL hexane (Huckins et al., 1990). Extracts were combined and reduced
192 using nitrogen before clean-up using gel permeation chromatography (GPC) as described

193 previously (Harman et al., 2008). The resulting extracts were sent to *either* PAH (including
194 the PRCs) or PCB/OCP analysis. The PCB fraction received further clean up by partitioning
195 with concentrated sulphuric acid. The PAH fraction was analyzed by gas chromatography-
196 mass spectrometry (GC-MS) and the PCB fraction by GC with electron capture detection
197 (ECD). An Agilent Technologies 6890GC (Santa Clara, USA) was used in both cases with the
198 inlet in splitless mode. The GC was equipped with either a 30 or 60 m column (PAH and PCB,
199 respectively) with a stationary phase of 5% phenyl methylpolysiloxane (0.25 mm internal
200 diameter and 0.25 μm film thickness, Agilent Technologies). Samples from 2009 that were
201 also analysed for PBDEs were acid treated similarly to PCBs and also received an additional
202 step of partitioning with acetonitrile (no GPC performed). The same GC-MS system as
203 outlined above was used but with a Rtx-1614 30 m x 0,25 mm column with a 0.1 μm film
204 (Restek, Bellefonte, USA) fitted, and used in negative chemical ionisation (NCI) mode.
205 Quantification of individual components was conducted by the relative response of internal
206 standards. Analytical detection limits were set as the average value of triplicate procedural
207 solvent blanks, plus 3 times the standard deviation of that average. Levels of target
208 compounds in SPMD field controls (FCs) and laboratory controls (LCs) are considered
209 separately.

210

211 ***Extraction and analysis of sediments***

212 Sediments were dried at 40 °C before soxhlet extraction using hexane/diethyl-ether. Sample
213 clean up and analysis proceeded largely as for SPMDs with the following changes; additional
214 clean up was carried out using silica and aluminium oxide columns, high resolution MS was
215 applied for analysis of PCBs, Hexachlorobenzene (HCB), Hexachlorohexanes (HCHs), and
216 Dichlorodiphenyltrichloroethane (DDT), and NCI mode was used for Chlordanes. More
217 detailed descriptions of these methods, extraction procedures, instrumental parameters,
218 uncertainties etc. are provided elsewhere (Evenset et al. 2003; Halse et al. 2011). Analytical
219 detection limits were typically 0.01 ng g⁻¹ (dry wt.) for PCBs and OCPs. Extraction and
220 analyses of sediments was carried out at the Norwegian Institute for Air Research (NILU),
221 laboratory in Norway.

222

223 ***Calculation of water concentrations from SPMDs***

224 Accumulation of hydrophobic organic contaminants by SPMDs can be explained by an initial
225 linear and integrative uptake phase followed by curve linear and equilibrium partitioning
226 stages. A model describing uptake at any stage was used to calculate freely dissolved water
227 concentrations (C_w) from SPMD data (Huckins et al., 1993).

$$228 \quad C_w = \frac{N}{V_s K_{sw} \left(1 - \exp \left(- \frac{R_s t}{V_s K_{sw}} \right) \right)} \quad (1)$$

229 Where N is the absorbed amount (ng), V_s is the volume of the sampler (cm^3), K_{sw} is the SPMD
230 water partitioning coefficient ($\text{cm}^3 \text{ cm}^{-3}$) and R_s is the apparent water sampling rate (L d^{-1}).
231 Log K_{sw} was estimated from log K_{ow} of PRCs and target compounds using the quadratic
232 equation from Huckins et al., (2006),

$$233 \quad \log K_{sw} = a_0 + 2.321 \log K_{ow} - 0.1618 (\log K_{ow})^2 \quad (2)$$

234 (where the intercept $a_0 = -2.61$ for most hydrophobic compounds). Sampling rates (R_s) were
235 determined *in situ*, by the use of PRCs and an empirical model (Huckins et al., 2006). PRCs
236 where the amount remaining after deployment was between 10 and 90% of that analysed in
237 LCs were used in calculations. Other approaches have also been recently suggested (Booij
238 and Smedes, 2010). See Harman et al. (2009) for more detailed descriptions of how these
239 PRC values are used in the empirical model. Water concentration data was estimated for
240 each individual SPMD from its PRC data as small differences in the deployment conditions
241 may change sampling rates even between co-deployed samplers. Concentrations were then
242 averaged, where more than one replicate was available.

243

244 **RESULTS AND DISCUSSIONS**

245 ***SPMD controls***

246 SPMDs are highly sensitive to contamination from air exposure during deployment and
247 retrieval operations, and in subsequent laboratory procedures. Therefore each site had a
248 dedicated field control (FC) which was exposed to air whilst deployment and retrieval took
249 place. Additionally, laboratory controls (LCs) followed exposure from solvents, glass
250 equipment, laboratory procedures, and were also used to determine initial concentrations of
251 PRCs. Several target compounds were found in low concentrations in both types of control
252 ($n = 12$); naphthalene, (81 ng SPMD $^{-1}$, RSD 13%), phenanthrene, (15 ng SPMD $^{-1}$, RSD 35%)
253 and gamma-hexachlorocyclohexane (γ HCH, 2 ng SPMD $^{-1}$, RSD 22%). As both naphthalene

254 and γ HCH are likely to be at equilibrium after the 33 d deployment period then
255 concentrations in exposed samplers are valid in theory. This assumption has however, not
256 been tested and both compounds have been reported in blanks elsewhere (Boehm et al.,
257 2005; Djedjibegovic et al., 2010; Harman et al., 2009; Short et al., 2008). For phenanthrene,
258 control concentrations were typically <1% of accumulated amounts in exposed samplers and
259 thus of little consequence. Contamination by phenanthrene may be due to impurities in the
260 deuterated phenanthrene spiked at 3 $\mu\text{g SMPD}^{-1}$ as a PRC. Additionally PBDE-47 and 99 were
261 found at low levels (<1 ng SPMD^{-1}) in controls from 2009 ($n = 3$). As these two compounds
262 will be in the linear stage of uptake at the end of the deployment period, then such
263 concentrations may be subtracted from results, assuming that blank values are consistent.

264 ***SPMD derived concentrations of POPs***

265 With the exception of some of the high molecular weight compounds such as; Perylene,
266 Indeno[1,2,3-*cd*]pyrene and Dibenzo[*ac/ah*]anthracene, all 19 PAH were detected in all
267 SPMD samples. For chlorinated compounds four out of the ten PCB congeners targeted,
268 were present in all samples (28, 52, 118 and 138) and PCB 153 and 180 were also detected in
269 some samples. Additionally both HCB and metabolites of DDT were also present in all
270 samples. In order to increase the chances of detection of single compounds, a single SPMD
271 was sent to each group analysis ($\times 3$) in 2008, thus the variation is not known. However, in
272 previous studies we have shown relative standard deviations (RSD) to be <20% between
273 replicate SPMDs and usually much lower (Harman et al., 2011). This assumption is supported
274 from samplers from 2009 (duplicates) which showed percent differences of typically <10%,
275 except for a few compounds present at concentrations close to the D.L.

276 Starting concentrations of PRCs showed little variation (RSD 2-5%, $n = 9$). The fraction
277 retained after deployment obviously varied depending on the exposure conditions at each
278 site, for example 4% of acenaphthene-d10 at L8, versus 40% at L9. This difference translated
279 to sampling rates of 2.4 and 7.8 L d^{-1} for acenaphthene at those locations respectively. In
280 general however, differences in sampling rates between stations were small (Fig. 2) and the
281 average remaining fraction of both acenaphthalene-d10 and fluorene-d10 (15 and 18%,
282 respectively) means target compounds with a $\text{Log } K_{ow} < 4.4$ were approaching equilibrium at
283 the end of the deployment period. Photo-degradation of has been shown to cause an
284 underestimation of PAH concentrations in SPMDs by a factor of up to 5 (Komarova et al.,

285 2009). As the retained percentage of Benzo[*a*]pyrene-d12, which is sufficiently hydrophobic
286 as not to be expected to be dissipated from SPMDs during typical deployment conditions,
287 averaged 102% (RSD 18%, *n* = 9, Fig. 2), then we conclude that this has not been significant.
288 PRC data was used to determine *in situ* sampling rates and then to calculate water
289 concentrations as outlined in the methods section.

290 SPMD derived concentrations of PAH ranged from 22 ng L⁻¹ at Sarajevo (STN 3) to 75
291 ng L⁻¹, upstream of Doboj city centre (STN 6). This is similar to levels seen in moderately
292 contaminated systems such as; industrial areas of Germany (~20-30 ng L⁻¹) (Vrana et al.,
293 2001); large European cities like Paris and Brno in the Czech Republic, (~20-90 ng L⁻¹)
294 (Gourlay-France et al., 2008; Grabic et al., 2010), and the Yangtze River in China (~20-100 ng
295 L⁻¹) (Wang et al., 2009). At the River Spreca (Doboj) and downstream (STN 8) levels were
296 higher, 480 and 200 ng L⁻¹, respectively, which is more typical of those measured by SPMDs
297 (~100-2000 ng L⁻¹) at the inlets to wastewater treatment systems (Augulyte and Bergqvist,
298 2007; Gourlay-France et al., 2008; Grabic et al., 2010). Elevated levels of PAH were not
299 surprising at this station. The River Spreca drains a valley containing a large amount of coal
300 (lignite) with extensive mining activities, associated industries such as coke production, the
301 country's largest power station and the third largest city (Tuzla). However, comparison of
302 PAH accumulations in SPMDs between 2008- 09 revealed practically identical concentrations
303 at station 3 (Sarajevo, 20 vs. 22 ng L⁻¹ ΣEPA16) but lower in the Spreca tributary at Doboj
304 (480 vs. 99 ng L⁻¹ ΣEPA16). This may suggest that these high levels were related to some
305 specific event and this is supported by the unusual dominance (> 50% ΣPAH, Table 1) of
306 acenaphthene in this sample. For PCBs, and OCPs, levels were low, typically tens to hundreds
307 of pg L⁻¹ for totals of those compounds which were detected (Table 1). Levels were similar
308 but slightly higher in 2009, 0.13 vs. 0.14 and 0.14 vs. 0.18 (ng L⁻¹ Σ seven Dutch), stations 3
309 and 6 respectively). Levels of organo-chlorine pesticides were also higher in 2009 and at
310 station 3, compared to station 6 (Table 1).

311 Additionally in 2009, SPMDs were analysed for PBDEs at these two stations. Only
312 PBDEs 47, 99 and 100 were detected, at 0.3-3 ng SPMD⁻¹, with the higher values coming
313 from Station 3 (Sarajevo), the calculated water concentrations of these congeners was 2-19
314 pg L⁻¹. For PBDE 100, accumulated amounts were only just above the detection limit of 0.2
315 SPMD⁻¹ and thus must be treated cautiously. Due to the highly hydrophobic nature of these
316 compounds reports of dissolved concentrations of PBDEs in natural waters are not

317 abundant. For comparison during a previous study in BiH, 0.7-7.3 and 0.4-6.8 ng L⁻¹ (PBDEs
318 47 and 99, respectively) were shown using SPMDs (Djedjibegovic et al., 2010), and Bogdal et
319 al. (2010) found concentrations of 17-78 pg L⁻¹ using high volume water sampling equipment
320 in lake Thun, Switzerland.

321 ***Target chemical analysis in sediments***

322 The target chemical results of PAHs, PCBs and PBDEs in sediments are presented in
323 Table 2. The sum of PAH 16 ranged from 198 to almost 50 000 ng g⁻¹ (dry wt.). The
324 concentrations are assessed according to the the Norwegian environmental guidelines with
325 different colours representing the corresponding environmental classification. The
326 ecotoxicological assessment range from Class I or II upstream the river to Class III-V
327 downstream. The highest PAH concentrations are found at STN6b near Dobož. The
328 concentrations of PCBs and PBDEs were much lower, and ranged from 0.8-79 and 0.4-40 ng
329 g⁻¹ respectively. All PCB and PBDE results were in Class I or II except for PCBs in STN6b
330 which was in Class III.

331 The sediments were also analysed for a range of OCPs, including groups of HCH,
332 DDT and its metabolites, and cyclodiene pesticides (aldrin, dieldrin, isodrin and endrin;
333 heptachlor and chlordane and some metabolites of the two last). The results are presented in
334 Table 3. The concentrations of HCHs were very low, and with few exceptions, only the γ -
335 isomer (lindane) was detected. The highest level observed was STN7 where 0.10 ng g⁻¹ was
336 detected. The levels of DDT ranged from 0.7-4.6 ng g⁻¹, and the highest levels were observed
337 at STNs 4, 6b and 7. The relative concentrations of the metabolites DDD and DDE and the
338 parent DDT can be used for information regarding source and input history to the
339 environment as well as the degradation pathways involved. A ratio of (DDE+DDD)/ Σ DDT >
340 0.5 indicates that the DDT has been subject to long time weathering (Hites and Day, 1992;
341 Wang et al., 2007). This ratio was above 0.5 (0.64-0.90) for all sites investigated except
342 STN6b where the ratio was 0.45, indicating a less weathered DDT in these sediments and
343 thus a more recent source. DDE is the aerobic degradation product of DDT, while DDD is the
344 anaerobic degradation product. The ratio DDD/DDE were less than 1 in all the sites,
345 indicating that the major part of DDT broke down under aerobic conditions before
346 deposition into Bosna.

347 With regards to the “drin” cyclodiene pesticides (aldrin, dieldrin, isodrin and endrin),
348 the levels ranged from < 0.01 to 3.3 ng g^{-1} , the highest level was observed for endrin at
349 STN6b. Of the other cyclodiene pesticides, heptachlor was detected in all the sediment
350 samples investigated with levels ranging from 0.48 to 9.2 ng g^{-1} . Also the endo-epoxidic
351 metabolite was detected in all the samples investigated. The highest level of the epoxidic
352 metabolite of heptachlor was observed in STN6b, exceeding the parent pesticide five times.
353 This might indicate weathered heptachlor in this area (Wurl and Obbard, 2005). For the
354 other stations, the ratio of metabolite to the sum of metabolite and parent compound was
355 very low, possibly indicating a more recent release of heptachlor. Clordane and its
356 metabolites were only detected in some stations at very low levels. These pesticides were
357 not analysed for in SPMD samples due to financial constraints.

358

359 ***Patterns of PAH contamination along the Bosna River***

360 Ratios of parent PAH were determined in order to elucidate whether the observed
361 concentrations could be attributed to pyrogenic or petrogenic sources. The ratio of the less
362 thermodynamically stable PAH isomer relative to the more stable isomers was applied for
363 the following compounds; Anthracene/ Anthracene + Phenanthrene (An/178);
364 Fluoranthrene/ Fluoranthrene + Pyrene (Fl/Fl + Pyr); Benzo[*a*]anthracene/
365 Benzo[*a*]anthracene + Chrysene (BaA/228) and indeno[1,2,3-*cd*]pyrene/ indeno[1,2,3-
366 *cd*]pyrene + benzo[*ghi*]perylene(IP/IP + Bghi) (Yunker et al., 2002). The sediment samples
367 appear to be separated into two groups, most pronounced in Fig. 3(a), but also apparent in
368 the other two ratio plots, with stations 1-4 (upstream) grouped lower and to the left than
369 the other stations (5-8, further downstream), in all cases. This suggests (slightly) more
370 influence from petroleum sources at these upstream sites and or increasing influence from
371 combustion sources downstream, possibly the coal industry. The normal scenario is that the
372 signal from combustion towards petroleum follows a gradient of increasing urbanisation
373 (Yunker et al., 2002). However, in the present study this is hampered somewhat by the
374 source of the Bosna, being located close to the capital city of Sarajevo. In either case the
375 difference between these two ‘groups’ is small, and all of the four ratios used clearly suggest
376 that combustion sources overall are dominating PAH accumulations in sediments throughout
377 the course of the River.

378 Parent PAH ratios between SPMDs and sediment samples may be expected to be
379 different as one measures an historical particle bound fraction and the other measures an
380 exposure specific dissolved fraction. It is also important to note in the present study that we
381 present ten sediment samples, with eight SPMD samples two of which are from a different
382 year and that there was some distance between the two sampling points at some stations.
383 Generally however, the ratios of Fl/Fl + Pyr and BaA/228 were similar between SPMDs and
384 sediment samples (Fig. 3), again suggesting primarily combustion sources. For the ratio of
385 IP/IP + Bghi the comparison is likely hampered by some non-detects in SPMDs and analytical
386 variability associated with those concentrations reported which were just above the D.L.
387 Results for SPMDs are influenced by specific events which may happen during the exposure
388 period, such as accidents and spills, precipitation, etc. This is perhaps illustrated by the
389 difference in the ratios at the same locations between subsequent years, for example 0.05
390 and 0.1 for An/178 at station 3 (2008 and 2009, respectively). Interestingly this difference is
391 large for station 6c, where the highest concentrations of PAH were observed in 2008, with
392 that sample being isolated from the others in Fig. 3 (a), whereas the 2009 sample is more
393 closely grouped to the others to the far right of Fig. 3 (a). This may be further evidence that
394 the concentrations in 2008 are not typical, but represent some significant contamination
395 event. Conversely such differences are small when considering the spread in such ratios
396 reported in the literature generally (Yunker et al., 2002).

397

398 ***Ecotoxicological interpretation of findings***

399 For the dissolved fraction of PAH as measured by SPMDs, concentrations were below
400 guideline values where these exist. For example even at the most polluted site in the River
401 Spreca, levels of anthracene and fluoranthrene were 10 and 5-fold lower than the WFD EQS
402 for these compounds (100 ng L^{-1}). It must be noted however that these guidelines are for
403 total concentrations whereas we have measured only the freely dissolved fraction, which
404 will be smaller due to binding with particulates and DOC (Gourlay-France et al., 2008). What
405 proportion of the total is represented by the freely dissolved fraction will be dependent on
406 both the amount of DOC and on the hydrophobicity of individual target compounds. Thus a
407 two fold reduction in the freely dissolved fraction may be expected somewhere in the range
408 of $\log K_{ow}$ 6-8.6, at DOC concentrations of 1 mg L^{-1} (Huckins et al., 2006). As the sampling
409 point was just before the confluence with the River Bosna, it is likely that concentrations are

410 higher upstream, nearer to the point sources in the Tuzla valley. Such concentrations are
411 feasibly above WFD EQS values with associated potential for biological effects. The freely
412 dissolved concentrations of individual congeners of PCBs, PBDEs and pesticides were low,
413 typically tens of pg L^{-1} and thus assumed not to be of environmental significance. For
414 example, for PBDEs it was well below the 500 pg L^{-1} environmental quality standard (EQS,
415 Σ penta-brominated) defined for inland surface waters in the WFD (EU, 2006). Again it must
416 be remembered that (especially) for highly hydrophobic compounds total concentrations
417 (referred to in the EQS) will have been higher.

418 With regards to POPs in sediments, the the most striking result was that the PAHs
419 were high in parts of the Bosna river. Near Dobož (STN6b), most of the PAH levels were in
420 class V, which means that the levels were more than 5 times the PNEC (Bakke et al., 2010). In
421 the tributary river Spreca near Dobož (STN6c), the level of PAHs were also quite high, and
422 above the PNEC for acute toxicity. At STN6b, the total PCB-level was classified in class III,
423 which means that chronic effects can be observed after long time exposure. This is the same
424 level of pollution which was noted in the highest measured levels in the Kupa river drainage
425 basin in Croatia (Franciskovic-Bilinski et al., 2005).

426 Since HCH compounds are not assessed in the Norwegian environmental guidelines,
427 we turned to other authorities' guidelines, e.g. as established by Canada (CCME, 2002). The
428 TEL and PEL levels for for freshwater sediment for HCH are 0.94 and 1.38 ng/g respectively.
429 The levels observed in Bosna are very low compared to the PEL, and are therefore assumed
430 to be of little environmental concern. The highest level of Σ DDT was observed near Dobož at
431 stations STN6b and STN7, and also at STN 3, further upstream. According to the Norwegian
432 guidelines, this level of DDT is in class II, which means little concern for ecotoxicological
433 effects. The TEL and PEL for heptachlor are 0.6 and 2.74 ng g^{-1} respectively (CCME, 2002).
434 With the exception of STN1 and STN6b, all the other stations had concentrations exceeding
435 the TEL, and most of them also exceeding the PEL. This means that heptachlor is of
436 environmental concern in many parts of the Bosna River, and adverse biological effects can
437 be expected. The levels of cyclodiene "drins" were quite low in all stations except STN6b
438 where endrin was exceeding the TEL, but not the PEL level (Table 3).

439

440 **CONCLUSIONS**

- 441 • The use of SPMDs and sediment analysis is complementary and provides a powerful
442 screening approach for areas where little data is currently available.
- 443 • Freely dissolved concentrations of PAH were elevated in the Bosna River, with
444 significant point source(s) around Doboj.
- 445 • Concentrations of PAH in sediments showed the potential for chronic and acute
446 effects at several places along the watercourse, with the highest levels around Doboj.
- 447 • Diagnostic ratios in PAH concentrations suggest that contamination is largely from
448 combustion sources.
- 449 • Freely dissolved concentrations of PCBs, OCPs and PBDEs in the Bosna River were
450 generally low.
- 451 • Several pesticides and PCBs at one site were present in sediments at levels which
452 breach international criteria.
- 453 • The level of heptachlor breaches international criteria at many of the sites
454 investigated in this study.
- 455 • Future work should focus on pinpointing the sources of contamination in the Doboj
456 area, especially the contributions from the Tuzla valley.

457

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461 technical assistance.

462

463

464 **TABLES**

465 **Table 1** Water concentrations (ng L⁻¹) of POPs in the Bosna River, derived from SPMDs. All
 466 PAH data shown, but totals only for PCBs, OCPs and PBDEs due to infrequent detections.
 467 Where target compounds were not detected then the detection limit was used in
 468 calculations in order to provide a theoretical maximum average concentration (< ng L⁻¹).
 469 Complete data tables are provided in supporting information (S2: SPMD derived water
 470 concentrations)
 471

	2008						2009	
	<i>ST 3</i>	<i>ST 4</i>	<i>ST 5</i>	<i>ST 6a</i>	<i>ST 6c</i>	<i>ST 8</i>	<i>ST 6c</i>	<i>ST 3</i>
Naphthalene*	<0.763	<7.650	10.288	<7.665	<7.639	16.487	<10.033	<10.037
Acenaphthylene*	0.655	0.775	1.232	0.930	5.962	1.751	1.121	0.181
Acenaphthene*	1.076	0.851	19.334	17.402	256.572	80.539	13.746	1.150
Fluorene*	2.587	1.854	15.507	18.776	144.804	51.851	11.993	1.732
Dibenzothiophene	1.047	0.695	2.171	2.273	4.264	3.169	1.333	1.094
Phenanthrene*	11.885	9.178	21.637	24.180	26.964	25.427	9.945	9.417
Anthracene*	0.691	0.547	1.643	1.886	10.127	4.764	2.053	1.078
Fluoranthene*	2.155	1.911	4.667	5.485	18.099	9.475	35.035	3.111
Pyrene*	1.912	1.580	3.306	4.246	14.681	6.661	21.140	2.202
Benzo[<i>a</i>]anthracene*	0.180	0.132	0.412	0.485	1.166	0.850	1.095	0.154
Chrysene*	0.326	0.282	0.512	0.743	0.801	0.921	1.052	0.290
Benzo[<i>b,j</i>]fluoranthene*	0.124	0.096	0.182	0.239	0.293	0.519	0.567	0.132
Benzo[<i>k</i>]fluoranthene*	<0.041	0.031	0.067	0.079	0.130	0.190	0.183	0.034
Benzo[<i>e</i>]pyrene	0.118	0.093	0.138	0.180	0.562	0.417	0.795	0.107
Benzo[<i>a</i>]pyrene*	<0.044	<0.029	0.054	0.048	0.200	0.156	0.249	0.035
Perylene	<0.044	<0.029	0.044	<0.130	0.063	0.167	0.086	0.028
Indeno[1,2,3- <i>cd</i>]pyrene*	0.078	0.098	0.122	<0.160	0.153	0.444	0.079	<0.034
Dibenz[<i>ac/ah</i>]anthracene*	<0.048	<0.031	<0.038	<0.141	0.084	0.079	0.033	<0.030
Benzo[<i>ghi</i>]perylene*	0.215	0.123	0.153	<0.175	0.408	0.454	0.236	0.055
ΣPAH (EPA16*)	21.885	17.456	79.114	74.499	480.444	200.567	98.525	19.571
ΣPCBs (seven dutch)	0.123	0.147	0.148	0.221	0.133	0.242	0.169	0.134
ΣOCPs (eight compounds)	0.069	0.070	0.171	0.105	0.028	0.073	0.059	0.195
ΣPBDEs (17 congeners)							0.002	0.041

472

473 **Table 2** POPs in sediments from river Bosna. Toxicity classification from Bakke et al. (2010)

474

(ng g ⁻¹)	Compound	STN1	STN2	STN3	STN4	STN5	STN6a	STN6b	STN6c	STN7	STN8
PAHs	Naphthalene	4.83	1.9	11.4	6.35	32	17.2	150	67.3	27.1	44.5
	Acenaphthalene	4.42	0.59	1.41	1.34	21.1	12.8	622	162	85.9	49.4
	Acenaphthene	1.65	4.11	6.58	3.22	36	8.69	2 444	471	354	94.1
	Fluorene	6.01	4.8	11.6	5.97	152	28.2	5 399	670	703	162
	Phenanthrene	46.8	13.9	63.3	25.5	280	196	5 303	1 067	643	428
	Anthracene	11.7	2.47	13.2	4.65	99.1	60.2	2 060	438	202	143
	Fluoranthene	156	34.3	113	50.7	490	270	7 797	2 500	838	853
	Pyrene	127	27.7	95.5	40.4	363	195	5 127	1 739	594	636
	Benzo[<i>a</i>]anthracene	61.4	14.5	40	18.6	217	99.3	3 345	1 154	358	361
	Benzo[<i>k</i>]fluoranthene	112	31.2	90.9	39.1	369	151	6 257	2 315	723	679
	Benzo[<i>a</i>]pyrene	55.7	17	1.41	15.2	194	64.7	3 691	1 260	417	371
	Indeno(1,2,3- <i>cd</i>)pyrene	65.7	15.4	36.1	14.1	163	67.3	2 275	877	268	281
	Dibenzo[<i>ac/ah</i>]anthracene	11.8	2.38	7.87	3.32	30.3	15.5	546	201	65.2	53.8
	Benzo[<i>ghi</i>]perylene	47.2	12.5	35	13.5	120	55.3	1 499	598	183	216
	Sum PAH 16	773	198	578	266	2 778	1 330	48 973	14 473	5 744	4 694
PCBs	Sum PCB7 ^a	0.78	0.79	5.22	4.29	7.59	3.56	79	15.8	16.0	10.3
PBDEs	Sum PBDE ^b	0.38	1.49	26.1	4.75	8.80	1.13	14.6	4.99	40.2	22.0

475

^a PCBs analysed: CB 28; 52; 101; 118; 138; 153; 180

476

^b PBDEs analysed: BDE 28; 47; 66; 49+71; 77; 85; 99; 100; 119; 138; 153; 154; 183; 196; 206; 209; TBA

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Background level	No toxic effects	Chronic effects after long time exposure	Acute toxic effects after short time exposure	Extensive acute toxic effects
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Table 3 Organo-chlorine pesticides in sediments from the River Bosna. Concentrations exceeding the TEL or PEL are marked in bold, see text for details

(ng g ⁻¹)	Compound	STN1	STN2	STN3	STN4	STN5	STN6a	STN6b	STN6c	STN7	STN8
HCHs	α-HCH	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01
	β-HCH	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01
	γ-HCH (lindane)	0.01	0.02	0.02	0.02	0.03	0.02	0.03	0.02	0.10	0.02
	Sum HCH	0.01	0.02	0.02	0.02	0.03	0.02	0.05	0.02	0.10	0.02
DDTs	o,p'-DDE	0.02	<0.01	0.04	0.02	0.03	<0.01	0.02	0.01	0.04	0.03
	p,p'-DDE	1.1	0.39	1.5	0.57	1.0	0.31	0.97	0.37	1.8	1.2
	o,p'-DDD	0.17	0.05	0.35	0.13	0.18	0.08	0.29	0.09	0.52	0.25
	p,p'-DDD	0.49	0.17	1.0	0.37	0.56	0.20	0.50	0.29	0.95	0.61
	o,p'-DDT	0.05	0.03	0.09	0.14	0.12	0.05	0.11	0.03	0.11	0.12
	p,p'-DDT	0.15	0.07	1.6	0.48	0.50	0.20	2.1	0.18	0.49	0.51
	Sum DDT	1.9	0.71	4.6	1.7	2.4	0.85	4.0	0.97	3.9	2.8
Cyclodiene "Drins"	Dieldrin	<0.01	0.16	0.05	0.02	0.03	0.02	0.64	0.02	0.02	0.02
	Aldrin	0.01	0.17	0.01	0.016	0.02	0.02	1.3	0.03	0.02	0.01
	Isodrin	0.01	0.15	0.01	0.01	0.02	0.02	1.4	0.03	0.02	0.01
	Endrin	0.02	0.40	0.06	0.07	0.10	0.15	3.2	0.08	0.08	0.07
	Sum	0.04	0.87	0.13	0.13	0.16	0.21	6.7	0.16	0.14	0.11
Other Cyclodienes	Heptachlor	0.59	1.5	5.8	4.1	9.0	4.5	0.5	2.2	9.2	6.8
	Heptachlor-exo-epoxide	<0.01	0.27	<0.01	<0.01	<0.01	<0.01	0.15	0.01	<0.01	<0.01
	Heptachlor-endo-epoxide	0.05	0.62	0.05	0.07	0.12	0.10	2.1	0.28	0.11	0.05
	trans-Chlordane	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.05	<0.01	0.01	<0.01
	cis-Chlordane	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.13	<0.01	<0.01	<0.01
	Oxy-chlordane	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.33	0.01	0.01	<0.01
	Chlordene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.09	<0.01	<0.01	<0.01
	Sum	0.64	2.5	5.9	4.2	9.1	4.6	3.4	2.5	9.4	6.9

482

483 **FIGURE CAPTIONS**

484 **Fig. 1** Sampling locations. At Station 6 (Doboj), 3 sediment samples were taken and 2 SPMD
485 deployments made

486
487 **Fig. 2** Percentage of starting concentrations of PRCs remaining in all samplers after exposure
488 for 33 days. Symbols show average and standard deviation ($n = 10$). Dashed line represents
489 best nonlinear least squares model fit as described by (Booij and Smedes, 2010)

490
491 **Fig. 3** PAH ratio plots (Yunker et al., 2002) of Fluoranthrene (Fl)/Fluoranthrene + Pyrene
492 (Fl+Pyr) against; (a) anthracene (An)/ Anthracene+Phenathrene (178); (b)
493 Benzo[*a*]anthracene (BaA)/ Benzo[*a*]anthracene+Chrysene (228); (c) Indeno[1,2,3-*cd*]pyrene
494 (IP)/ Indeno[1,2,3-*cd*]pyrene + Benzo[*ghi*]perylene (IP+Bghi). Open symbols indicate
495 sediment samples and closed symbols, SPMDs. Indeno[1,2,3-*cd*]pyrene and/
496 Benzo[*ghi*]perylene not detected in all SPMD samples, hence fewer data points in (c).

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