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

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ABSTRACT
The Stockholm Convention which aspires to manage persistent organic pollutants (POPs) at the international level was recently ratified in Bosnia and Herzegovina (BiH). Despite this fact, there is in general a paucity of data regarding the levels of POPs in the environment in BiH. In the present study screening for POPs was conducted in one of the country’s major rivers, the Bosna. A two pronged approach was applied using passive samplers to detect the freely dissolved and bioavailable concentrations in the water phase, and sediment analysis to provide an integrated measure of historical contamination. At several places along the river, concentrations of polycyclic aromatic hydrocarbons (PAH) were high, and exhibited potential for both chronic and acute effects to biota. River water also showed elevated
concentrations of PAH, up to 480 ng L\(^{-1}\) near the city of Doboj, and diagnostic ratios suggested combustion sources for the contamination present in both types of sample. Levels of the other contaminants measured; polychlorinated biphenyls (PCBs), organo-chlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs), were generally low in the water phase. However PCBs and some OCPs were present in river sediments at levels which breach international criteria and thus suggest potential for ecological damage. Additionally levels of heptachlor breached these criteria at many of the sites investigated. This study presents the first screening data for some of these Stockholm Convention relevant compounds in BiH and reveals both low concentrations of some chemical groups, but significant point sources and historic contamination for others.

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

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

In Bosnia and Herzegovina (BiH) the convention was recently ratified (March 2010) and the formulation of a national implementation plan is underway. It is therefore necessary to assess the environmental status of POPs in the country. Additionally BiH is a potential candidate country for EU accession, requiring (eventually) adherence to for example, the water framework directive (WFD) and its list of 33 priority pollutants (EU, 2006). There are
several challenges in this respect, not least of which is the complex socio-political situation in
the country. Some of these issues are inherent for many rivers in the Balkans in general. In a
recent review of the environmental state of rivers in the region, Skoulikidis (2009) states that
wars, political instability, economical crises, administrative and infrastructure constraints,
poor environmental planning and inspection, and a lack of environmental awareness in
general, results in significant environmental pressure on rivers. Thus in contrast to most EU
states there is almost no existing information concerning levels of POPs and other organic
pollutants in BiH waters. Additionally some of the compounds listed in the Stockholm
Convention or the WFD have never been measured in BiH at all. Limited data from the
Western Balkans region are available however, including neighbouring states that were
formerly part of Yugoslavia. For example, elevated levels of polychlorinated biphenyls (PCBs)
have been shown in aquatic biota from Serbia (Adamov et al., 2003; VojinovicMiloradov et
al., 1996) and in sediment samples from Croatia (Franciskovic-Bilinski et al., 2005) which is in
agreement with the general trend for Eastern Europe (Parlar et al., 2004; Ruzickova et al.,
2008). Several studies have considered human exposure to PCB concentrations, largely
utilising air monitoring (Turk et al., 2007) and including sites within BiH (Klanova et al., 2007).
Reasonably high concentrations of polycyclic aromatic hydrocarbons (PAH) have also been
reported, in air at urban locations within BiH (Skarek et al., 2007), and in water and
sediments following military operations in Serbia (Dalmacija et al., 2003). Despite what
appears therefore, to be a significant potential for elevated levels of POPs in BiH aquatic
systems the only relevant study available, in the Neretva River in the South of BiH, generally
showed low (pg/L) concentrations of those POPs which were detected (Djedjibegovic et al.,
2010). However, elevated concentrations of heavy metals in certain fish species in the
Neretva River have been reported (Djedjibegovic et al. 2011) and organo-chlorine pesticides
(OCPs) have also been detected in wastewater treatment effluents in BiH (Terzic et al.,
2008). In the present study concentrations of contaminants in the more industrial and more
polluted Bosna River which drains to the North of BiH were evaluated. Due to the assumed
low concentrations of many of the target compounds, passive sampling devices (PSDs) were
chosen as appropriate tools for measurement of the freely dissolved and bioavailable
fraction. Such devices accumulate chemicals by diffusive and partitioning processes and
provide integrative (time-averaged) measurements, and typically lower detection limits than
those achievable with traditional bottle sampling methods. Additionally they may offer
significant advantages over biomonitoring organisms (Harman et al., 2011). One such PSD is
the semipermeable membrane device (SPMD) (Huckins et al., 1990) which as been shown to
accumulate a wide range of relevant hydrophobic contaminants and has therefore been
applied to many different monitoring situations (Esteve-Turrillas et al., 2008). Sediment
samples were also taken in order to examine longer term contamination, as sediments
function as sinks for hydrophobic contaminants. Sediment analysis included therefore
certain pesticides which are now banned under the Stockholm Convention, in order to
ascertain their historical use in the region. Thus SPMDs and sediment samples may provide
complimentary information, one a measure of dissolved concentrations during the sampling
period, the other a measure of bound concentrations over a longer time period (Vrana et al.,
2001).

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

METHODS AND MATERIALS

Sampling rationale and deployment
The Bosna River is one of the major rivers in Bosnia and Herzegovina, flowing northwards for
271 km from its source just outside the capital Sarajevo. The Bosna River Valley is the
country's industrial centre with considerable metallurgical industry, coke plants, a thermal
power plant, an oil refinery and paper production. It is therefore considered to be the most
heavily polluted river in BiH today. The catchment has a population close to a million people,
and the river thus passes through several other large cities before eventually joining the Sava
River (a tributary of the Danube) at the border with Croatia. A total of eight sites were
strategically chosen along the river for sampling in 2008 (Fig. 1), from the source just outside
Sarajevo to the confluence with the Sava. At the industrial town of Doboj (STN 6), three
sediments and two SPMD sites were sampled, including a tributary (River Spreca, STN 6c)
with assumed high concentrations. This station (STN 6c) was sampled again in 2009, as was
the site assumed to be the most urban influenced, just after Sarajevo (STN 3, co-ordinates
for all stations provided in supporting information, S1: Sampling locations). This included the
deployment of extra SPMDs for extended analysis to include polybrominated diphenyl
ethers (PBDEs) and the use of small scale bioassays to ascertain in situ toxicity (results not presented). Passive samplers were deployed using simple rigs consisting of an anchored line with float (where appropriate) or tied to overhanging trees etc. Rigs were placed in order to minimise the chances of tampering as much as possible, which has been a problem in both previous and subsequent studies in the area. SPMDs were placed in commercially available stainless steel holders (EST labs, St Joseph, USA) which were attached to the ropes of rigs. Deployment lasted for 36 days in 2008 and in 22 days in 2009. The longer deployment time in 2008 was due to exceptional river flow which prevented the planned sampler collection. On retrieval samplers were kept frozen at -20°C until analysis at the Norwegian Institute for Water Research laboratory in Oslo, Norway.

**Sediment sampling**

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

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

In Norway, the Climate and Pollution Agency has guidelines for classifying the environmental quality of aquatic sediments (Bakke et al., 2010). The classification system has five quality classes that are based on the toxicity of individual prioritised contaminants and on the European Union system for defining environmental quality standards and performing risk assessment. Within the classification system, class I is considered to represent background conditions. The upper limits for class II and III are based on the PNEC (predicted no effect concentrations), for chronic and acute exposures to that compound. The upper limit of class
IV is defined as concentrations between 2 and 5 times the PNEC (depending on the compound) with class V representing concentrations above this level. The upper limit of class II represents the concentration of a contaminant which over time may have a negative effect on certain organisms in the aquatic environment. The upper limit of class III is the concentration at which acute effects to aquatic organisms may occur over a short time. The concentration in the upper limit of class IV will give rise to further effects, both in the degree of harm and the number of organisms affected. These classes are used as a tool for the management of the aquatic environment in Norway. However, since they are based on ecotoxicity, they may also be applied to other areas, including Bosnia. As some of the study pesticides were never used in Norway, guidelines for them do not exist. Thus Canadian environmental guidelines which are similar (CCME, 2002) were used for effects evaluation, in those cases. The Canadian guidelines operate with two levels; the threshold effect level (TEL, the concentration below which adverse biological effects are never or almost never observed) and probable effect level (PEL, above which adverse biological effects are usually or always observed).

**Chemicals and equipment**

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

**Extraction of SPMDs and organic chemical analysis**

Extraction, clean up and chemical analysis is given in detail elsewhere (Harman et al., 2008). Briefly, the surface of SPMDs were wiped clean using paper towels and pure water, before dialysis with 2 × 150 mL hexane (Huckins et al., 1990). Extracts were combined and reduced using nitrogen before clean-up using gel permeation chromatography (GPC) as described
previously (Harman et al., 2008). The resulting extracts were sent to either PAH (including the PRCs) or PCB/OCP analysis. The PCB fraction received further clean up by partitioning with concentrated sulphuric acid. The PAH fraction was analyzed by gas chromatography-mass spectrometry (GC-MS) and the PCB fraction by GC with electron capture detection (ECD). An Agilent Technologies 6890GC (Santa Clara, USA) was used in both cases with the inlet in splitless mode. The GC was equipped with either a 30 or 60 m column (PAH and PCB, respectively) with a stationary phase of 5% phenyl methylpolysiloxane (0.25 mm internal diameter and 0.25 µm film thickness, Agilent Technologies). Samples from 2009 that were also analysed for PBDEs were acid treated similarly to PCBs and also received an additional step of partitioning with acetonitrile (no GPC performed). The same GC-MS system as outlined above was used but with a Rtx-1614 30 m x 0.25 mm column with a 0.1 µm film (Restek, Bellefonte, USA) fitted, and used in negative chemical ionisation (NCI) mode.

Quantification of individual components was conducted by the relative response of internal standards. Analytical detection limits were set as the average value of triplicate procedural solvent blanks, plus 3 times the standard deviation of that average. Levels of target compounds in SPMD field controls (FCs) and laboratory controls (LCs) are considered separately.

**Extraction and analysis of sediments**

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

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

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

Where $N$ is the absorbed amount (ng), $V_s$ is the volume of the sampler (cm$^3$), $K_{sw}$ is the SPMD water partitioning coefficient (cm$^3$ cm$^{-3}$) and $R_s$ is the apparent water sampling rate (L d$^{-1}$).

Log $K_{sw}$ was estimated from log $K_{ow}$ of PRCs and target compounds using the quadratic equation from Huckins et al., (2006),

$$\log K_{sw} = a_0 + 2.321 \log K_{ow} - 0.1618 \left( \log K_{ow} \right)^2$$  \hspace{1cm} (2)

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

RESULTS AND DISCUSSIONS

**SPMD controls**

SPMDs are highly sensitive to contamination from air exposure during deployment and retrieval operations, and in subsequent laboratory procedures. Therefore each site had a dedicated field control (FC) which was exposed to air whilst deployment and retrieval took place. Additionally, laboratory controls (LCs) followed exposure from solvents, glass equipment, laboratory procedures, and were also used to determine initial concentrations of PRCs. Several target compounds were found in low concentrations in both types of control ($n = 12$); naphthalene, (81 ng SPMD$^{-1}$, RSD 13%), phenanthrene, (15 ng SPMD$^{-1}$, RSD 35%) and gamma-hexachlorocyclohexane ($\gamma$HCH, 2 ng SPMD$^{-1}$, RSD 22%). As both naphthalene
and γHCH are likely to be at equilibrium after the 33 d deployment period then
concentrations in exposed samplers are valid in theory. This assumption has however, not
been tested and both compounds have been reported in blanks elsewhere (Boehm et al.,
2005; Djedjibegovic et al., 2010; Harman et al., 2009; Short et al., 2008). For phenanthrene,
control concentrations were typically <1% of accumulated amounts in exposed samplers and
thus of little consequence. Contamination by phenanthrene may be due to impurities in the
deuterated phenanthrene spiked at 3 µg SMPD⁻¹ as a PRC. Additionally PBDE-47 and 99 were
found at low levels (<1 ng SPMD⁻¹) in controls from 2009 (n = 3). As these two compounds
will be in the linear stage of uptake at the end of the deployment period, then such
concentrations may be subtracted from results, assuming that blank values are consistent.

**SPMD derived concentrations of POPs**

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

Starting concentrations of PRCs showed little variation (RSD 2-5%, n = 9). The fraction
retained after deployment obviously varied depending on the exposure conditions at each
site, for example 4% of acenaphthene-d10 at L8, versus 40% at L9. This difference translated
to sampling rates of 2.4 and 7.8 L d⁻¹ for acenaphthene at those locations respectively. In
general however, differences in sampling rates between stations were small (Fig. 2) and the
average remaining fraction of both acenaphthalene-d10 and fluorene-d10 (15 and 18%,
respectively) means target compounds with a Log $K_{ow}$ <4.4 were approaching equilibrium at
the end of the deployment period. Photo-degradation of has been shown to cause an
underestimation of PAH concentrations in SPMDs by a factor of up to 5 (Komarova et al.,
As the retained percentage of Benzo[a]pyrene-d12, which is sufficiently hydrophobic to not be expected to be dissipated from SPMDs during typical deployment conditions, averaged 102% (RSD 18%, n = 9, Fig. 2), then we conclude that this has not been significant. PRC data was used to determine in situ sampling rates and then to calculate water concentrations as outlined in the methods section.

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

Additionally in 2009, SPMDs were analysed for PBDEs at these two stations. Only PBDEs 47, 99 and 100 were detected, at 0.3-3 ng SPMD\(^{-1}\), with the higher values coming from Station 3 (Sarajevo), the calculated water concentrations of these congeners was 2-19 pg L\(^{-1}\). For PBDE 100, accumulated amounts were only just above the detection limit of 0.2 SPMD\(^{-1}\) and thus must be treated cautiously. Due to the highly hydrophobic nature of these compounds reports of dissolved concentrations of PBDEs in natural waters are not
abundant. For comparison during a previous study in BiH, 0.7-7.3 and 0.4-6.8 ng L\(^{-1}\) (PBDEs 47 and 99, respectively) were shown using SPMDs (Djedjibegovic et al., 2010), and Bogdal et al. (2010) found concentrations of 17-78 pg L\(^{-1}\) using high volume water sampling equipment in lake Thun, Switzerland.

**Target chemical analysis in sediments**

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

The sediments were also analysed for a range of OCPs, including groups of HCH, DDT and its metabolites, and cyclodiene pesticides (aldrin, dieldrin, isodrin and endrin; heptachlor and clordane and some metabolites of the two last). The results are presented in Table 3. The concentrations of HCHs were very low, and with few exceptions, only the \(\gamma\)-isomer (lindane) was detected. The highest level observed was STN7 where 0.10 ng g\(^{-1}\) was detected. The levels of DDT ranged from 0.7-4.6 ng g\(^{-1}\), and the highest levels were observed at STNs 4, 6b and 7. The relative concentrations of the metabolites DDD and DDE and the parent DDT can be used for information regarding source and input history to the environment as well as the degradation pathways involved. A ratio of \((\text{DDE+DDD})/\Sigma \text{ DDT}angle 0.5 indicates that the DDT has been subject to long time weathering (Hites and Day, 1992; Wang et al., 2007). This ratio was above 0.5 (0.64-0.90) for all sites investigated except STN6b where the ratio was 0.45, indicating a less weathered DDT in these sediments and thus a more recent source. DDE is the aerobic degradation product of DDT, while DDD is the anaerobic degradation product. The ratio DDD/DDE were less than 1 in all the sites, indicating that the major part of DDT broke down under aerobic conditions before deposition into Bosna.
With regards to the “drin” cyclodiene pesticides (aldrin, dieldrin, isodrin and endrin), the levels ranged from < 0.01 to 3.3 ng g^{-1}, the highest level was observed for endrin at STN6b. Of the other cyclodiene pesticides, heptachlor was detected in all the sediment samples investigated with levels ranging from 0.48 to 9.2 ng g^{-1}. Also the endo-epoxidic metabolite was detected in all the samples investigated. The highest level of the epoxidic metabolite of heptachlor was observed in STN6b, exceeding the parent pesticide five times. This might indicate weathered heptachlor in this area (Wurl and Obbard, 2005). For the other stations, the ratio of metabolite to the sum of metabolite and parent compound was very low, possibly indicating a more recent release of heptachlor. Clordane and its metabolites were only detected in some stations at very low levels. These pesticides were not analysed for in SPMD samples due to financial constraints.

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

Ratios of parent PAH were determined in order to elucidate whether the observed concentrations could be attributed to pyrogenic or petrogenic sources. The ratio of the less thermodynamically stable PAH isomer relative to the more stable isomers was applied for the following compounds; Anthracene/ Anthracene + Phenanthrene (An/178); Fluoranthrene/ Fluoranthrene + Pyrene (Fl/Fl + Pyr); Benzo[a]anthracene/ Benzo[a]anthracene + Chrysene (BaA/228) and indeno[1,2,3-cd]pyrene/ indeno[1,2,3-cd]pyrene + benzo[ghi]perylene(IP/IP + Bghi) (Yunker et al., 2002). The sediment samples appear to be separated into two groups, most pronounced in Fig. 3(a), but also apparent in the other two ratio plots, with stations 1-4 (upstream) grouped lower and to the left than the other stations (5-8, further downstream), in all cases. This suggests (slightly) more influence from petroleum sources at these upstream sites and or increasing influence from combustion sources downstream, possibly the coal industry. The normal scenario is that the signal from combustion towards petroleum follows a gradient of increasing urbanisation (Yunker et al., 2002). However, in the present study this is hampered somewhat by the source of the Bosna, being located close to the capital city of Sarajevo. In either case the difference between these two ‘groups’ is small, and all of the four ratios used clearly suggest that combustion sources overall are dominating PAH accumulations in sediments throughout the course of the River.
Parent PAH ratios between SPMDs and sediment samples may be expected to be different as one measures an historical particle bound fraction and the other measures an exposure specific dissolved fraction. It is also important to note in the present study that we present ten sediment samples, with eight SPMD samples two of which are from a different year and that there was some distance between the two sampling points at some stations. Generally however, the ratios of Fl/FI + Pyr and BaA/228 were similar between SPMDs and sediment samples (Fig. 3), again suggesting primarily combustion sources. For the ratio of IP/IP + Bghi the comparison is likely hampered by some non-detects in SPMDs and analytical variability associated with those concentrations reported which were just above the D.L.

Results for SPMDs are influenced by specific events which may happen during the exposure period, such as accidents and spills, precipitation, etc. This is perhaps illustrated by the difference in the ratios at the same locations between subsequent years, for example 0.05 and 0.1 for An/178 at station 3 (2008 and 2009, respectively). Interestingly this difference is large for station 6c, where the highest concentrations of PAH were observed in 2008, with that sample being isolated from the others in Fig. 3 (a), whereas the 2009 sample is more closely grouped to the others to the far right of Fig. 3 (a). This may be further evidence that the concentrations in 2008 are not typical, but represent some significant contamination event. Conversely such differences are small when considering the spread in such ratios reported in the literature generally (Yunker et al., 2002).

**Ecotoxicological interpretation of findings**

For the dissolved fraction of PAH as measured by SPMDs, concentrations were below guideline values where these exist. For example even at the most polluted site in the River Spreca, levels of anthracene and fluoranthrene were 10 and 5-fold lower than the WFD EQS for these compounds (100 ng L\(^{-1}\)). It must be noted however that these guidelines are for total concentrations whereas we have measured only the freely dissolved fraction, which will be smaller due to binding with particulates and DOC (Gourlay-France et al., 2008). What proportion of the total is represented by the freely dissolved fraction will be dependent on both the amount of DOC and on the hydrophobicity of individual target compounds. Thus a two fold reduction in the freely dissolved fraction may be expected somewhere in the range of \(\log K_{ow} = 6.6\) at DOC concentrations of 1 mg L\(^{-1}\) (Huckins et al., 2006). As the sampling point was just before the confluence with the River Bosna, it is likely that concentrations are
higher upstream, nearer to the point sources in the Tuzla valley. Such concentrations are feasibly above WFD EQS values with associated potential for biological effects. The freely dissolved concentrations of individual congeners of PCBs, PBDEs and pesticides were low, typically tens of pg L\(^{-1}\) and thus assumed not to be of environmental significance. For example, for PBDEs it was well below the 500 pg L\(^{-1}\) environmental quality standard (EQS, \(\Sigma\) penta-brominated) defined for inland surface waters in the WFD (EU, 2006). Again it must be remembered that (especially) for highly hydrophobic compounds total concentrations (referred to in the EQS) will have been higher.

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

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

**CONCLUSIONS**
• The use of SPMDs and sediment analysis is complementary and provides a powerful screening approach for areas were little data is currently available.

• Freely dissolved concentrations of PAH were elevated in the Bosna River, with significant point source(s) around Doboj.

• Concentrations of PAH in sediments showed the potential for chronic and acute effects at several places along the watercourse, with the highest levels around Doboj.

• Diagnostic rations in PAH concentrations suggest that contamination is largely from combustion sources.

• Freely dissolved concentrations of PCBs, OCPs and PBDEs in the Bosna River were generally low.

• Several pesticides and PCBs at one site were present in sediments at levels which breach international criteria.

• The level of heptachlor breaches international criteria at many of the sites investigated in this study.

• Future work should focus on pinpointing the sources of contamination in the Doboj area, especially the contributions from the Tuzla valley.

ACKNOWLEDGEMENTS

This study was funded by the Norwegian Ministry of Foreign Affairs. Sediments were analysed at the Norwegian Institute for Air Research (NILU). We also thank Espen Lund for technical assistance.
**Table 1** Water concentrations (ng L\(^{-1}\)) of POPs in the Bosna River, derived from SPMDs. All PAH data shown, but totals only for PCBs, OCPs and PBDEs due to infrequent detections.

Where target compounds were not detected then the detection limit was used in calculations in order to provide a theoretical maximum average concentration (< ng L\(^{-1}\)).

Complete data tables are provided in supporting information (S2: SPMD derived water concentrations).

<table>
<thead>
<tr>
<th>Compound</th>
<th>ST 3</th>
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<th>ST 5</th>
<th>ST 6a</th>
<th>ST 6c</th>
<th>ST 8</th>
<th>ST 6c</th>
<th>ST 3</th>
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<td>&lt;7.639</td>
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<td>5.962</td>
<td>1.751</td>
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<tr>
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<td>0.851</td>
<td>19.334</td>
<td>17.402</td>
<td>256.572</td>
<td>80.539</td>
<td>13.746</td>
<td>1.150</td>
</tr>
<tr>
<td>Fluorene*</td>
<td>2.587</td>
<td>1.854</td>
<td>15.507</td>
<td>18.776</td>
<td>144.804</td>
<td>51.851</td>
<td>11.993</td>
<td>1.732</td>
</tr>
<tr>
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<td>0.695</td>
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<td>2.273</td>
<td>4.264</td>
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<td>17.402</td>
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<td>1.732</td>
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<td>0.098</td>
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<td>&lt;0.160</td>
<td>0.153</td>
<td>0.444</td>
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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 |
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<th>STN3</th>
<th>STN4</th>
<th>STN5</th>
<th>STN6a</th>
<th>STN6b</th>
<th>STN6c</th>
<th>STN7</th>
<th>STN8</th>
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</table>

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

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

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

<table>
<thead>
<tr>
<th>Background level</th>
<th>No toxic effects</th>
<th>Chronic effects after long time exposure</th>
<th>Acute toxic effects after short time exposure</th>
<th>Extensive acute toxic effects</th>
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</table>
**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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>STN1</th>
<th>STN2</th>
<th>STN3</th>
<th>STN4</th>
<th>STN5</th>
<th>STN6a</th>
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<td>&lt;0.01</td>
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FIGURE CAPTIONS

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

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

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

REFERENCES


Chemosphere, 20(5), 533-552.


