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Original scientific paper

Organic micropollutants in the Sava and Bosna river overbank and floodplain sediments during the May through June 2014 catastrophic flood

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Abstract
The aim of this study was to determine the presence and nature of organic micropollutants in river overbank and floodplain sediments from the border between Croatia and Bosnia and Herzegovina following the catastrophic 2014 flood. The study involved ten sediment samples from the Sava and Bosna river floodplain. The volatile aromatic compounds, i.e. benzene, toluene, ethylbenzene, and xylene (BTEX), together with alkanes (the linear straight-chain alkanes and the branched alkanes, C10-C28) were determined by GC-MS method. Their estimated amounts were from <0.054 to 3.886 mg/kg, and from 10 to 406 mg/kg, respectively. Hereby, they were below allowed concentration limits for total hydrocarbons in agricultural soil of lighter texture (sandy/loam soil) which is 1000 mg/kg, whilst for heavier clayey soils the limit is 2000 mg/kg. However, their presence in itself in the investigated sediment indicates oil spill problems, whilst their possible sources might be local oil refining industries located in the local cities of Brod and Modriča in Bosnia and Herzegovina.

Keywords
Catastrophic flood, oil refining industries, organic micropollutants (BTEX, alkanes), Sava and Bosna river sediment.

1. Introduction

Floods caused by rising rivers happen all the time, and they allways will. Whenever heavy rains come, water levels rise while threatening the population and hampering road traffic. It is well known that a 100-year flood has a 1% chance of occurring in any year. However, this probability could increase in the future due to climate change which is generally an accepted fact (**Kundzewicz et al., 2005**).

During the late spring 2014, catastrophic massive flooding inundated much of the middle Sava River Basin in the eastern part of Croatia (HR), and the northern part of Bosnia and Herzegovina (BH), as well as its lower course in the western part of Serbia (**Kuspilić et al., 2014**; **Vrančić, 2015**). The rainfall was the heaviest in 120 years of recorded weather measurements (**Kuspilić et al., 2014**). In the context of the hydrological conditions prior to the 2014 flood, the low pressure system called Donat lasted from 13th to 16th May. Water-levels, followed the rainfall, were significantly higher than the long span average (1961-1990) for the whole Sava river flow. The rainfall analysis for the May 2014 showed that the precipitation exceeded the average for that month by 200%. Water levels in the cities of Slavonski Brod and Županja abruptly raised by 2.6 m and 4.0 m, respectively, in only two days. The maximum, ever recorded water level in Slavonski Brod dating back to 1974 and equalling 883 cm, was exceeded by 56 cm during the 2014 flood. The Sava river bank was severely eroded and several levees failed (the villages of Rajevo Selo and Račinovci in particular), thus allowing the deposition of sediment over large areas of the basin's floodplain, even those that had not been affected by previous floods (**Kuspilić et al., 2014**; **Vrančić, 2015**). Such situations commonly rise concern about the transport and fate of sewage effluents as well as agricultural and industrial chemicals in the floodwaters, commonly known as organic micropollutants. Among them are

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BTEX (the term used for benzene, toluene, ethylbenzene, and xylene), volatile aromatic compounds typically found in petroleum products, such as gasoline and diesel fuel (**Cohen and Mercer, 1993; Medverec Knežević et al., 2001; Dukaj et al., 2015**). BTEX is known as the main source of environmental contamination caused by petroleum related pollution, such as gas tank leakage (**Koo, 2013**). In the region of Western Balkan (Croatia, BH, and Serbia), a study of over seventy individual wastewater contaminants, including some prominent classes of emerging contaminants was carried out a few years ago (**Terzić et al., 2008**). Their results indicate a widespread presence of these chemicals in municipal wastewaters. The authors conclude that most of the contaminants could be transferred from wastewaters into the ambient waters due to rather poor wastewater management practice in the abovementioned countries. To our best knowledge, there have been no published papers focused on organic micropollutants in the post-catastrophic-flood either overbank or floodplain sediment, at least in HR and BH. Therefore, this paper reports for the first time the micro-organic polluting effects of the 2014 catastrophic flooding in central HR and northern BH. The findings should contribute to flood-response measures, so as to improve awareness of the related processes.

2. Methods

2.1. Study area and sampling

The Sava River Basin is the largest drainage area in the countries Slovenia, Croatia, and Serbia, and the second largest tributary of the Danube River (**Prpić et al., 1997**). The Sava River together with its tributaries is characterised by nearly 2000 km of levees. Its total flow from Slovenia (originating in the Bohinj area) to Serbia (i.e. Belgrade, where it inflows into the Danube river) is nearly 1000 km. According to the published work (**Stec et al., 2011**), it is characterised by the scarcity of clean water due to the lack of treatment systems and the outdated water and sewage systems. In addition to that, the public in this region shows a high level of environmental concern, but a low level of environmental knowledge. Hereby, the sampling of the post-flood sediment was performed in HR and BH, a few days following the peak of the 2014 catastrophic flood (**Figure 1**). All the samples represent freshly deposited mud remained on places out of the river bed. The study area is under potential long-term detrimental influence of the oil refining industries in the cities of Modriča and Brod (south of the city of Slavonski Brod). The list of samples and the sampling location details are given in **Table 1**. Freshly deposited, wet overbank and floodplain sediment samples, and those slightly dried, were collected with a clean, stainless steel scoop, and put into plastic bags. Chemical analyses were carried out on the air-dried sediment that was sieved to size fraction <1 mm.

***Figure 1**: Simplified geographical map of the study area with sample locations (MI, SB, LI, SV, O1-04, M1, and M2).*

***Table 1**: The list of samples with sampling site descriptions*

No	Sampling site
M1	The Bosna River, left bank. Downstream of the city of Modriča, known for the oil refining industry. Sandy sample taken from the riverbank, 20 cm above the water level. No smell.
M2	The Bosna River, right bank. Downstream of the city of Modriča (oil refining industry). Clayey sample taken from the floodplain, below a bridge. No smell.
O1	The Bosna River, left bank. An abandoned channel, steep bank, sampling 2 m above the water level. No smell.
O2	The Bosna River, right bank. No smell. Location 10 m from the river channel. Mud remained on vegetation (1.5 m above the ground).
O3	The Bosna River, left bank. Desiccated sediment taken 50 m from the river channel, near local houses. No smell.
O4	The Bosna River, right bank. Location 20 m from the river channel. Wet sample left around a tree. No smell.
SV	The Sava River, right bank, Bosnian side (the county of Brod), the village of Svilaj. Wet, clayey mud sampled from a small pond. No smell.
LI	The Sava River, right bank, Bosnian side (10 km downstream of the city of Brod); the village of Liješće, in the vicinity of the Bosnian oil refining industry in the city of Brod. Wet, clayey mud sampled from a small pond. No smell.
SB	The Sava River, left bank, Croatian side (downstream of the city of Slavonski Brod). Bad smell (H_2S?). Wet mud left on the riverbank grass. Downstream of the Bosnian oil refining industry (Brod).
MI	The Sava River, left bank, Croatian side (upstream of the city of Slavonski Brod). No smell. Wet, sandy sample taken from the riverbank. Upstream of the Bosnian (Brod) oil refining industry.

2.2. Experimental

Due to instrumental obstacles, mineral composition was determined for only two samples (MI, SV) using Philips PW 3040/60 X'Pert PRO powder X-ray diffractometer (PANalytical; Almelo, The Netherlands) with a CuKλ line (λ=1.54055 Å) at 40 kV and 40 mA.

Cation exchange capacity (CEC) was determined by mixing the samples with the 0.01 mol/L solution of copper ethylenediamine complex $[Cu(en)_2]^{2+}$. The subsequent change in Cu^{2+} concentration due to sample sorption was determined with a ultraviolet-visible spectrophotometer Hach DR/4000 U (Hach Company, Loveland, CO, USA) at 548 nm.The pH of the $[Cu(en)_2]^{2+}$ solution upon mixing with each sample was around 7.

Carbonate content ($CaCO_3$) was determined gravimetrically by weight loss following the sample leaching with HCl. Loss on ignition (LOI), as an approximate indication of the organic matter content, was determined gravimetrically following the dry ashing at 375 °C during 24 h.

Analysis of micro-organic pollutants was carried out by twofold extraction in dichloromethane solvent in an ultrasonic bath. Following their concentration in a stream of nitrogen, the extracts were recorded with GC-MS technique (Shimadzu GC-MS system QP-2010, quadrupole mass analyzer, electron impact (EI) 70eV, capillary column Supelco SPB-5 TM 60 m x 0.32 mm x 0.25 μm, temperature: 40°C 5min/10°C/280°C 21 min; flow: 1.20 mL He/min). Measurement conditions involved relatively mild temperature programmed gas chromatographic conditions and the recording of full mass spectra with the standard conditions of ionization beam electron energy of 70 eV (electron impact, EI, 70 eV). To identify present micro-organic pollution, the separated mass spectra of unknown compounds were compared with the available databases (NIST, Wiley, PWM).

3. Results and Discussion

The predominant minerals present in the two analysed sediment samples are quartz, calcite, dolomite, illitic material, plagioclase, K-feldspar and kaolinite. They indicate weathering of heterogeneous upstream drainage bedrock composed of carbonate as well as silicate lithologies (**Pavlović et al., 2004**). **Figure 2** depicts variable lines vs. sampling sites. Generally, sediments characterised by a high CEC can sorb more radioactive and potentially toxic metal ions than those having a low CEC (**Kennedy, 1965**). Whilst some experiments regarding the sorption of BTEX by organo-clays have been published (**Sharmasarkar et al., 2000**), there have been no papers dealing with sorption of BTEX and alkanes by overbank/floodplain sediments. The measured CEC values (**Figure 2**) are rather low, reflecting probably coarser sediment grain fractions as well as non-swelling (kaolinite) clay minerals. The Kendall Tau correlation coefficients were found to be statistically significant ($P < 0.05$) as follows: LOI – $CaCO_3$ -0.47, LOI – CEC 0.64, BTEX – $CaCO_3$ 0.58, and alkanes – BTEX 0.63, whilst BTEX – CEC -0.13 ($P > 0.05$).

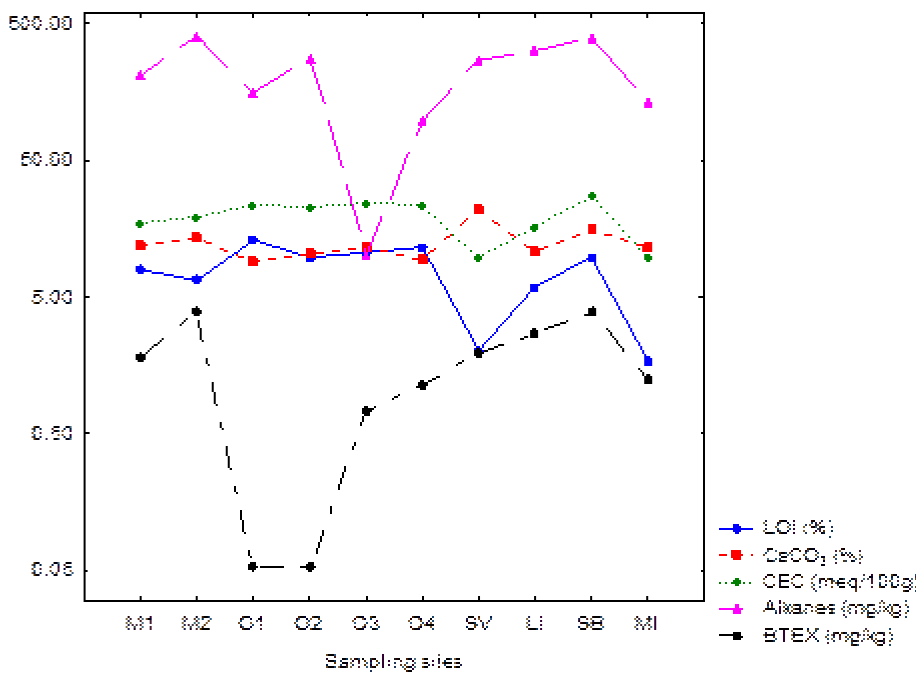

***Figure 2**: Geochemical properties of the post-flood sediment samples.*

Regarding organic micropollutants, they are listed where the similarity index was found to be ≥ 85. **Table 2** presents the list of common ingredients or ingredient groups for the majority of recorded extracts, whilst **Table 3** presents their concentrations. They belong to the BTEX group (benzene, toluene, ethylbenzene, and xylene), straight-chain and branched alkanes from C10 to C28 carbon atoms in the molecule, as well as the group of ortho-phthalic ester acid (diethyl phthalate - DEP dubutilphthalate - DBP, dietilheksilphthalate - DEHP, etc.). The estimated levels of the concentrations of BTEX and alkanes ranged from <0.054 to 3.886 mg/kg, and from 10 to 406 mg/kg, respectively (**Figure 2**, **Table 3**). Although they do not indicate pollution, as the allowed concentration limit for total hydrocarbons in agricultural soil of lighter texture (sandy/loam soil) is set to 1000 mg/kg, whilst for heavier clayey soils the limit is 2000 mg/kg (**NN, 2014**), the effect of dilution due to huge floodwater has to be taken into account. Moreover, **Figure 2** shows that the highest organic micropollutant levels were recorded at the sites M2 and SB, close to oil refining industries in the cities of Modriča and Brod, respectively.

***Table 2**: The list of identified organic micropollutants (RT – retention time; SI – similarity index)*

No	RT (min)	SI	Identified compound (BTEX)
1	12.36	80	C3-benzene
2	12.47	92	2-Ethylhexanol
3	15.22	86	Naphthene
4	15.43	91	n-Decanal
5	19.30	86	BHT-quinone-methide
6	19.63	80	2,6-Di-tert-butylphenol
7	19.70	89	4-Methyl-2,6-di-tert-butylphenol BHT
8	20.82	84	Hexadecanal Palmitaldehyde
9	20.95	85	isopropyl ester of lauric acid
10	22.18	88	2,6-Diisopropylnaphthalene
11	22.95	80	Anthracene
12	24.41	76	Cyclopentaphenanthrene
13	25.12	85	Isopropyl Palmitate
14	25.56	82	dihydro-neoclovene-(I)
15	25.67	91	octa-sulfur S8
16	25.81	92	Pyrene
17	26.33	88	Fluoranthene
18	27.21	70	1-Methyl-7-isopropylphenanthrene Reten
19	27.37	83	2,3-Benzofluorene
20	28.21	85	Oleamide Adogen 73
21	29.31	78	Triphenylene (CAS) Isochrysene
22	29.41	93	Chrysene Benzo[a]phenanthrene
23	32.53	83	Benzo[k]fluoranthene
24	32.78	89	farnesol isomer A
25	33.52	79	Benzo[a]pyrene
26			+ linear and branched alkanes (C10 - C25)
27			+ phthalates (dietil-,dibutil- and dietilhexil-phthalate)

Table 3: Concentrations of BTEX and alkanes in the investigated sediment (mg/kg)

	M1	M2	O1	O2	O3	O4	SV	LI	SB	MI
Benzene	<0.054	<0.054	<0.054	<0.054	<0.054	<0.054	<0.054	<0.054	<0.054	<0.054
Toluene	1.118	1.977	<0.054	<0.054	0.459	0.626	1.012	1.423	1.807	0.692
Ethylbenzene	0.403	0.334	<0.054	<0.054	<0.054	<0.054	0.141	0.214	0.412	0.155
Ksylene	0.264	1.575	<0.054	<0.054	0.367	0.510	0.806	1.064	1.652	0.418
Total BTEX	1.785	3.886	<0.054	<0.054	0.726	1.136	1.959	2.701	3.871	1.265
Alkanes	209	406	157	274	10.3	97.6	272	316	387	133

Herewith, dozens of microorganic contaminants were identified (**Figures 3, and 4**) whose presence could be explained by the flood water which could have probably transferred contaminants far away from primary sources of pollution. At least two plausible sources of micro-organic pollution might probably be the two oil refining industries in BH (**Table 1**), situated in the cities of Brod and Modriča (**Figure 1**).

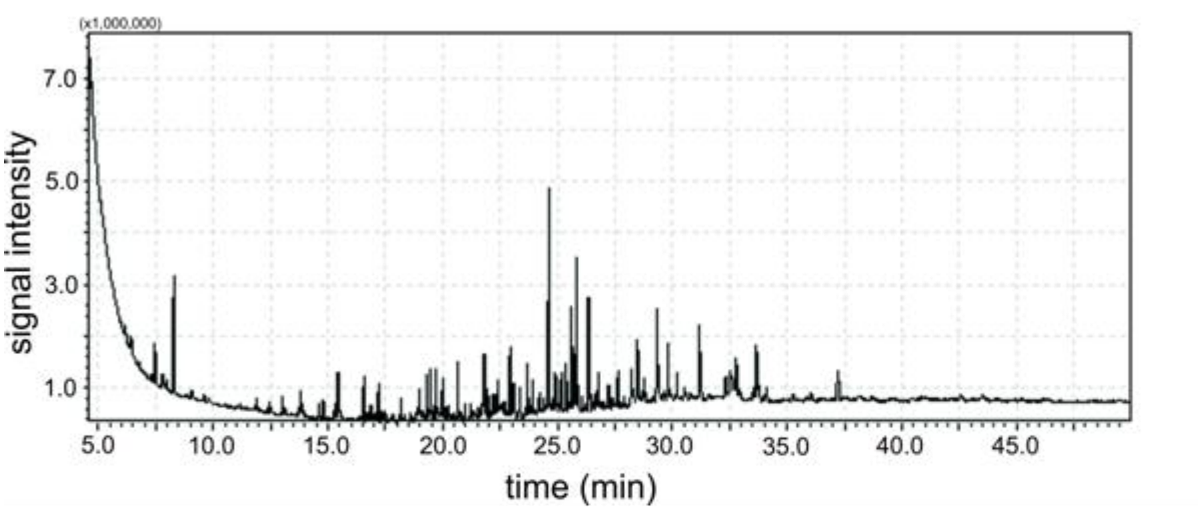

***Figure 3**: Total ion chromatogram of the sample M2.*

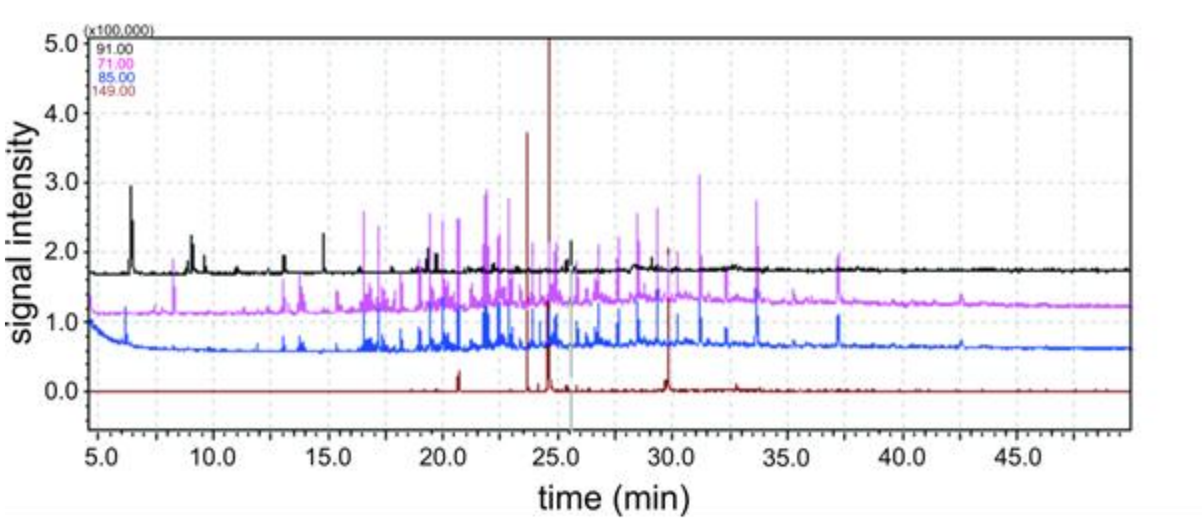

***Figure 4**: Identification of characteristic micro-organic pollutant fragments in the sample M2: m/z 91 (black - fragment characteristic for BTEX); m/z 71 and m/z 85 (pink and blue - fragments characteristic for alkane); and m/z 149 (brown - fragment characteristic for esthers of ortho-phthalic acid).*

Floodwater damages, erodes and washes everything on its way. Therefore, flood-plain sediments are prone to the accumulation of a great number of possible organic pollutants (**Ahel, 1991**). The results of this study unequivocally show the presence of organic micropollutants BTEX and alkanes in the Sava and Bosna river sediment following the 2014 catastrophic flood. Since they represent 'source-specific marker' compounds (**Wang et al., 1999**), regulative bodies in the abovementioned oil refineries (i.e. the cities of Modriča and Brod) as well as other local and regional industries are advised to either install or improve their wastewater treatment facilities in the near future.

4. Conclusions

The results of this study suggest that the 2014 catastrophic flood has caused not only economic and social, but also environmental effects. The specific problems include poor wastewater treatment facilities that are essentially lacking, poor legislative enforcement, and aging infrastructure, to name but a few. Oil refining industries in the northern BH should focus their conduct towards the better equipment so as not to affect the environment at all.

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Sažetak (abstract in Croatian)

Organska mikroonečišćenja poplavnog riječnog sedimenta rijeka Save i Bosne nakon katastrofalne poplave u proljeće 2014

Cilj ovog istraživanja bio je utvrditi prisutnost i prirodu organskih mikroonečišćenja u poplavnom riječnom sedimentu s manjeg područja uz granicu između Hrvatske i Bosne i Hercegovine neposredno nakon katastrofalne poplave u proljeće 2014. Istraživanje je obavljeno na deset uzoraka poplavnog sedimenta rijeka Save i Bosne. Hlapivi aromatski spojevi, tj. benzen, toluen, etilbenzen, i ksilen (BTEX), te alkani (ravnolančani i razgranati od C10 do C28) određeni su pomoću GC-MS metode. Unatoč tome što su njihove procijenjene vrijednosti bile ispod dopuštenih koncentracija, potrebno je uzeti u obzir učinak njihova razrjeđenja u uvjetima goleme količine vode. Budući da te tvari ukazuju na problem izlijevanja mineralnih

ulja, mogući izvori mikroorganskih onečišćenja zabilježenih u sedimentu vjerojatno su rafinerije nafte u gradovima Brod i Modriča u sjeverozapadnom dijelu Bosne i Hercegovine.

Ključne riječi: Katastrofalna poplava, industrija prerade nafte, organska mikroonečišćenja (BTEX, alkani), poplavni sediment (rijeke Sava i Bosna)