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Potentially toxic elements in water and sediments of the Sava River under extreme flow events

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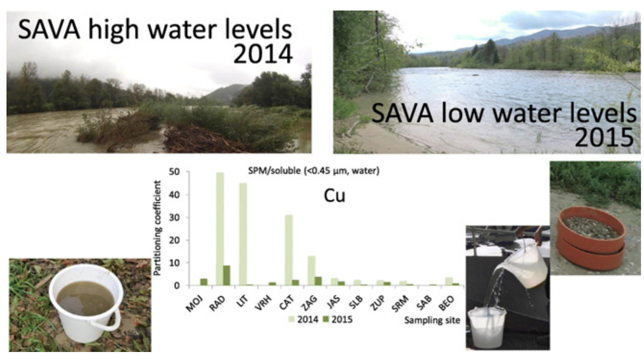
HIGHLIGHTS

- Extreme flow events greatly influenced contents of PTE in water and sediments of the Sava River.
- Under low discharges that followed big floods the contents of PTE in sediments were lower.
- PTE in sediments were during big floods partially remobilised into overlying waters.
- PTE exhibited different affinity to SPM in relation to different flow regimes.
- Potential ecological risk posed by the simultaneous presence of PET in Sava sediments was moderate.

GRAPHICAL ABSTRACT



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ABSTRACT

River ecosystems are exposed to various stressors. Among them, elements may contribute to overall pollution of riverine environments, in particular during the extreme flow events. To evaluate the influence of variable river flow conditions on the mobilization of potentially toxic elements (PTE) (Cr, Ni, Cd, Zn, Pb, As and Cu) from sediments into the overlaying waters of the Sava River, samples were collected in September 2014, during extremely high water discharges and in September 2015, under low water discharge conditions. In water samples the total element concentrations and the dissolved element contents (<0.45 μm) were determined. Sediment pollution was estimated by determination of the total element concentrations and mobile element fraction (0.11 mol L^{-1} acetic acid). Anthropogenic inputs of elements to sediments were evaluated by normalizing elemental against Al concentration. The results showed that concentrations of PTE in water were in general higher during high water discharges, while the soluble concentrations were higher during low water level conditions. Concentrations of PTE in the Sava sediments collected in 2015 were lower than those collected in 2014, mainly because during the extreme floods a mixture of bank sediment material and contaminated soil was sampled. Partitioning coefficients between suspended particulate matter (SPM) and soluble content of elements in the water under high and low flow conditions, indicated on different affinity of elements to SPM in relation to different flow regimes. The potential ecological risk posed by the simultaneous presence of PET in sediments was evaluated by Probable Effect Concentration Coefficient (PEC-Q) approach. Under high water level conditions, PEC-Qs were all above critical value 0.34 and derived mostly from anthropogenic inputs of Cr and Ni. Overall sediment toxicity was much lower under low water discharges. The data from this study importantly contribute to the knowledge regarding the behaviour of PTE under extreme flow events.

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1. Introduction

Water is indispensable for the existence of life on the Earth. About 97% of water on the globe water is saline, found mainly in oceans and seas and only 3% is freshwater. Nearly 69% of the total freshwater is held in continental and mountain glaciers, about 30% in groundwater reservoirs and the remaining portion is stored in surface waters (lakes, rivers and swamps) (McMichael, 2014). The freshwater is not evenly distributed on the Earth. The exploitation of water resources for industrial usage, agriculture, electricity generation, transport and other human activities, has created huge contamination problems and led to difficulties in the availability and accessibility of freshwater for the growing human population. To maintain the water at an adequate quality for humans and to preserve natural ecosystems and biodiversity, it is necessary to sustainably use, protect and manage the water resources. In countries of the European Union (EU), national water agencies, which follow EU policy and the requirements of the EU Water Framework and its Daughter Directives (Directive 2000/60/EC, 2000; Directive 2008/105/EC, 2008; Directive 2013/39/EU, 2013; European Communities Environmental Objectives 272/2009, 2009; European Communities Technical Report 2010-041, 2010), implement regular water monitoring with the aim to control and prevent pollution. For evaluation of the environmental status of sediments, various sediment quality guidelines have been proposed, based mainly on the biological effects approaches (MacDonald et al., 2000; CCME, 2001; McCready et al., 2006). MacDonald et al. (2000) developed and proposed consensus-based sediment quality guidelines for freshwater ecosystems, including a threshold effect concentration (TEC) below which harmful effects are unlikely to be observed, and a probable effect concentration (PEC) above which harmful effects are likely to be observed. Long et al. (2006) suggested Probable Effect Concentration Quotient (PEC-Q) approach, which allows an overall evaluation of the possible hazard posed by the simultaneous presence of several trace elements. Later, the PEC-Q analysis has been used by Vignati et al. (2013) to estimate the ecological risks due to trace element contamination of sediment in the Danube Delta.

By taking measures to reduce water pollution, the quality of surface waters was, in general, improved. Nevertheless, the contaminants, which have in the past accumulated in sediments, may be remobilized under certain conditions into overlying waters, where they can harm the freshwater environment (Kwok et al., 2014). The release of contaminants from river bottom sediments may occur during natural disturbance events, such as extreme rainfalls, which result in flash floods (Borga et al., 2014) and may also happen as a consequence of human activities like dredging (Ho et al., 2012) and waterway transport (Superville et al., 2014). Perturbation of sediments can change the redox potential and pH, which may significantly modify geochemical conditions in sediment that can lead to desorption of elements from sediment particles (Eggelton and Thomas, 2004). Mobilization of elements from sediments was studied in the laboratory-scale microcosm (Sun et al., 2016) and under environmental conditions during normal and high flow conditions (Vignati et al., 2003). During flood events sediments may be flushed into hydropower accumulation reservoirs and down the course of the river. Therefore, assessment of the sediment quality is of crucial importance for evaluating the temporal and spatial variations of elemental concentrations within the river ecosystem. Additional information on the input of contaminants into the riverine natural environment is obtained by determining the contents of dissolved elements in water (Dragun et al., 2009) and the amounts of elements associated with the suspended particulate matter (SPM) (Vidmar et al., 2016). Despite many rivers being under the pressure of changing discharge conditions, investigations on the behaviour of contaminants under different flow regimes are scarcely documented.

The Sava, which is 945 km long, flows through Slovenia, Croatia, Bosnia and Herzegovina and Serbia. It is the major drainage basin in Southeastern Europe and the biggest tributary of the Danube River (average discharge at mouth 1700 $m^3 s^{-1}$). In its upper reaches, the Sava has a steep riverbed with an average slope of >0.7‰ formed of coarse grained sediment (gravel, cobbles, sand) in prevailing limestone bedrock. Downstream from Slovenia it changes to a lowland river with flat riverbed (an average slope of 0.04‰) formed in alluvial sediments, igneous and prevailing Neogene siliciclastic rocks and sediments (Sommerwerk et al., 2009). The Sava River supplies groundwater aquifers that are the most important sources of drinking water for the 9 million riparian inhabitants. The main sources of pollution are industrial and intensive agricultural activities, high population density in big cities and, in the lower part of the Sava River, non-treated municipial sewage (Komatina and Grošelj, 2015).

In view of upcoming climate changes, flood flows and droughts are expected within the Sava River basin (Brilly et al., 2015). To evaluate the behaviour of pollutants during these extreme weather events, we investigate, for the first time, the influence of variable river flow conditions on mobilization of potentially toxic elements (PTE) (Cr, Ni, Cd, Zn, Pb, As and Cu) from sediments into the overlaying waters of the Sava River. Water and sediment samples were collected in September 2014 under high water levels, after a flood wave and in September 2015 under low water level conditions. For comparison, some of previously published data on elemental concentrations under high water levels (Vidmar et al., 2016) were re-used, which also enabled to calculate the partitioning coefficients between SPM and soluble content of elements in the water under high and low flow conditions and to estimate affinity of elements to SPM in relation to different flow regimes. PEC-Q approach (Long et al., 2006) was applied for overall evaluation of the possible risk posed by the simultaneous presence of PTE in sediments of the Sava River. This investigation was performed as a part of the EU 7th FW founded project GLOBAQUA, in which the Sava River is one of the river basins studied (Navarro-Ortega et al., 2015).

2. Materials and methods

2.1. Instrumentation

Total elemental concentrations were determined by ICP-MS (7700x, Agilent Technologies, Tokyo, Japan). ICP-MS operating parameters are presented in Table S1 (Supplementary). A CEM Corporation (Matthews, NC, USA) MARS 5 Microwave System was used for sample digestion. Mineralogical composition of sediments (fraction < 63 μm) were performed by X-ray Powder Diffraction (XRD) analyses on an Empyrean PANalytical diffractometer (PANalytical B.V., Almeo, The Netherlands) with Cu Kα irradiation ($\lambda = 1.54056$ Å), at 45 kV and a current of 40 mA, over the 2θ angular range from 5° to 70°, using a step size of 0.01° and a measuring time per step of 100 s. In the sediment fraction < 63 μm, mass portion of clay (particles with size < 2 μm) was determined by centrifugation procedure, as described by the U. S. Geological Survey (2001) and Moore and Reynolds (1989), using a VIBRA CELL sonication probe (SONICS, Newtown CT., U.S.A.) and Centric 322A centrifuge (Tehtnica, Železniki, Slovenia).

2.2. Reagents and materials

Ultrapure 18.2 MΩ cm water obtained from a Direct-Q 5 system (Millipore, Watertown, MA, USA) was used for preparation of samples and reagents. Merck (Darmstadt, Germany) suprapur acids were used. Samples were filtered using 0.45 μm Minisart cellulose nitrate membrane filters (Sartorius, Goettingen, Germany). The certified reference materials CRM 320 Trace Elements in River Sediment, Community Bureau of Reference (Geel, Belgium) and SLRS-5, River water reference material purchased from the National Research Council (Ottawa, Ontario, Canada) were used for accuracy check.