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Levels of regulated POPs in fish samples from the Sava River Basin. Comparison to legislated quality standard values

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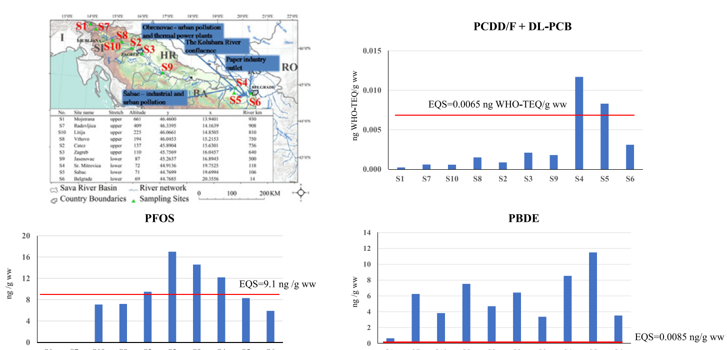
HIGHLIGHTS

- Fish samples from the lower stretch of the river showed PCDD/F+DL-PCB levels above the EQS.
- PCDD/Fs+DL-PCBs and NDL-PCBs exceeded the maximum levels for fish (as food product) in 20% of the samples.
- PBDE concentrations exceed the EQS up to more than a thousand times.
- Data suggest that anthropogenic impact is observed in the Sava River Basin.

GRAPHICAL ABSTRACT



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ABSTRACT

Fish samples of different species (i.e. rainbow trout (*Onchorhynchus mykiss*), barbel (*Barbus barbus*) and European chub (*Squalius cephalus*)) were collected from the Sava River Basin for a preliminary investigation of the levels of PCDD/Fs, PCBs, PBDEs and PFAS as a whole. Concentrations of PCDD/Fs, in terms of pg WHO-TEQ/g ww, were below the maximum limit established at the Commission Regulation (EU) No 1259/2011. On the contrary, when DL-PCBs were also included, levels increase up to 11.7 pg $\text{WHO-TEQ}_{\text{PCDD/Fs+DL-PCBs}}$/g ww in a particular case, with two samples out of a total of ten exceeding the maximum set at this EU Regulation and the EQS established at the European Directive regarding priority substances in the field of water policy (0.0065 ng $\text{WHO-TEQ}_{\text{PCDD/Fs+DL-PCBs}}$/g ww). A similar trend was also observed for NDL-PCBs, whit the same two samples, from the lower stretch of the river basin, exceeding the maximum limit allowed at the EU Regulation (125 ng/g ww). For PBDEs, levels found in all the samples exceeded the EQS (0.0085 ng/g ww) up to more than a thousand times and 40% of the samples presented PFOS values above the EQS. Data from this study were compared to values reported at the literature for fish from other geographical areas.

1. Introduction

Nowadays, there is a common position among the scientific community and the different competent authorities about the adverse effects of

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Persistent Organic Pollutants (POPs) on the environment and the exposed organisms, including human beings. The high toxicity, low degree of degradability and high persistence of these compounds have forced to adopt global measures for their control. In this sense, in 2001 the Stockholm Convention (SC) listed a number of chlorinated POPs as target compounds to be forbidden, eliminated or reduced by mean of the Best Available Techniques (BATs) (UNEP, 2001). Polychlorinated dibenzo *p* dioxins and polychlorinated dibenzofurans (PCDD/Fs), together with polychlorinated biphenyls (PCBs) were already included in the first list of substances. Later on, in 2009, the list of target chemicals of the SC was enlarged with 9 additional POPs, such as some polybromodiphenyl ethers (PBDEs) as well as perfluorinated compounds (PFASs) (i.e. perfluorooctane sulfonic acid (PFOS), its salts and its precursor perfluorooctane sulfonyl fluoride), among others (UNEP, 2009).

The particular concern about the unwanted effects of pollutants, including POPs, in the aquatic environment, is also reflected at the present European Directive regarding priority substances in the field of water policy (Directive 2013/39/EU). Environmental Quality Standards (EQS) have been set in the framework of this Directive for several substances, for some compounds not only in water but also in biota (e.g. fish). The Water Framework Directive (WFD) established EQS values for biota below which no harmful effects are expected to wildlife or humans. Monitoring conducted on biota is particularly important in the case of hydrophobic substances that tend to mostly accumulate in sediments and/or the fat tissues of living organisms. PCDD/Fs, PCBs and PBDEs are examples of lipophilic POPs that are hardly found in aqueous matrices and for which biota standards have been proposed. For PBDEs, biota EQS is referred to the sum of the concentrations of congeners BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 and has been set at 0.0085 ng/g wet weight (ww), while the EQS in inland surface waters for the same sum of congeners is 0.14 μg/L (maximum allowable concentration). These EQS should be taken into account in river basin management plans covering the period 2015 to 2021, and should be met by the end of 2021. On the other hand, PCDD/Fs and PCBs together with PFOS are among the new chemicals that were included in 2013 in the list of priority substances in the field of water policy. In this case, the EQS should be taken into account for monitoring programmes by the end of 2018, and should be met by the end of 2027. For PCDD/Fs and PCBs, EQS has only been established for biota and it is expressed in toxic equivalents according to the World Health Organisation 2005 Toxic Equivalence Factors (WHO-TEQ) for the sum of PCDD/Fs and "dioxin-like" PCBs (DL-PCBs) (0.0065 ng WHO-TEQ/g ww). The EQSs set for PFOS are 36 μg/L, as maximum allowable concentration in inland surface waters, and 9.1 ng/g ww in biota.

Apart from the environmental implications, the knowledge about POP levels in biota is also important from the point of view of human health. It is well known that at least 90% of the human exposure to PCDD/Fs and PCBs is estimated to come from food consumption, with fish and other related products contributing in an important way to this intake (Kiviranta et al., 2004; Bocio et al., 2007). In this sense, the WFD has derived EQS values in biota to ensure that humans are protected against adverse effects of consuming contaminated fish products. Therefore, the approach to derive these EQS is based on setting the same values already included in previous European Regulations as maximum levels for fish as food product. When these maximum levels are not available, human toxicological indicators (e.g. tolerable daily intake, reference dose) are considered to calculate the final EQS (EC. Guidance Document No. 27, 2011a).

In 1997 the International Agency for Research on Cancer (IARC) classified 2,3,7,8 tetra chlorodibenzo *p* dioxin carcinogenic to humans (Group 1) and more recently PCBs, as the whole family of compounds, have also been included in this group (IARC, 2016). Later on, in 2001, the European Union set maximum levels for PCDD/Fs at a wide range of food categories (e.g. fish) for the first time. These values have been revised along the last two decades and the latest update of the European Regulation also includes maximum levels for PCDD/Fs and DL-PCBs together and for the sum of the six most representative non-dioxin-like PCBs (NDL-PCBs) (Commission Regulation (EU) No 1259/2011). On the contrary, there are no limits established for PBDEs in food and the IARC has not classified the carcinogenicity of any PBDE congener. Despite there is an agreement that ingestion is one of the major routes of exposure to these compounds, particularly trough the consumption of fatty fish (Daso et al., 2010), the Panel on Contaminants in the Food Chain (CONTAM) of the European Food Safety Authority (EFSA) has not been able to set a tolerable daily intake (TDI) with the information available (EFSA, 2011). Therefore, based on the Opinion of this Expert Panel, the European Commission issued a Recommendation in 2014 with the aim to obtain more data about the concentrations of PBDEs in food in order to perform a further assessment (Commission Recommendation of 3 March, 2014). In regards to PFASs, fish consumption (Pérez et al., 2014) together with drinking water (Llorca et al., 2012a; Schwanz et al., 2016) have been identified as central sources of PFASs contamination in humans. In this sense, even though there is not a specific regulatory framework setting maximum allowable levels of PFASs in food products, a TDI of 150 ng/kg body weight per day for PFOS was established in 2008 as a result of the risk assessment on PFASs performed by the EFSA's CONTAM Panel (EFSA, 2008). However, nowadays these values are susceptible to be changed in order to be more restrictive, for instance the Environmental Protection Agency (US EPA) indicated in 2016 a reference dose of 20 ng/kg body weight per day (US EPA, 2016).

In this study, the levels of dioxin-like substances (PCDD/Fs and DL-PCBs), NDL-PCBs, PBDEs and PFASs were determined in fish samples collected along the Sava River Basin (SRB) during a sampling campaign performed in 2015. The SRB is one of the most significant sub basins of the Danube River Basin and, to the best of our knowledge, this is the first study reporting levels of this whole set of POPs in that geographical area. The main goal was to quantify the concentrations of all families of compounds and to discuss these preliminary findings from a regulatory point of view considering fish both, as biota as described in terms of the water policy Directive and as a food product that can be consumed by specific human sub-populations which obtain it from freshwater fishing. In addition, the POP levels have been compared to those reported in the literature for fish from other river basins and inland surface waters in order to assess the degree of contamination of the SRB.

2. Materials and methods

2.1. Study area and sample collection

The SRB covers a wide geographic area (Fig. 1) with a total of 97,713 km^2 and including population of about 8.5 million inhabitants. It is a macro region, an area that includes the territories of six countries – Slovenia (SI), Croatia (HR), Bosnia and Herzegovina (BA), Serbia (RS), Montenegro (ME), with a minor part of the basin also extending to Albania (AL).

The SRB is one of the most significant sub basins of the Danube River Basin, with a share of 12%. The landscape within the SRB is diverse, the elevation varying between approx. 69 m above sea level (m a.s.l.) at the mouth of the Sava River in Belgrade (Serbia) and 2864 m a.s.l. (Triglav, Slovenian Alps). Mean elevation of the basin is approximately 545 m a.s.l.

In terms of land cover/land use, most of the basin is covered by forest and semi-natural areas (54.7%) and agricultural surfaces (42.4%), while the share of artificial surfaces is 2.2%. The basin is affected by water scarcity, due either to climatic or societal reasons, and also by significant environmental pressures. The upper part is largely influenced by hydromorphological pressures, and central stretches by agricultural activities and biological processes related to eutrophication, while the lower part is influenced mostly by stressors related to high pollution