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ORIGINAL PAPER

Bedload sediment transport model for revealing the multi-year trend of polychlorinated biphenyl contamination in the river sediment (Kupa, Croatia)

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Abstract This article investigated the multi-year polychlorinated biphenyl (PCB) burden of the sediment collected along the Kupa River flow in Croatia using the bedload sediment transport model. Kupa, as the natural border between Croatia and Slovenia, belongs to the water system Krupa (Slovenia) → Lahinja (Slovenia) → Kupa (Croatia) → Sava → Danube → Black Sea. From 1962 to 1985, the total quantity of waste calculated for pure PCBs, released by a capacitor manufacturer into the environment within various locations of the Krupa River in Slovenia, was 70 tons. Krupa River (Slovenia) has become one of the most PCB-polluted rivers in Europe, and consequently, PCBs have been detected in the Kupa River (Croatia). Model application revealed that contamination of the Kupa River (Croatia) started significantly earlier than 1983, when a high concentration of PCB was detected for the first time in the Krupa River (Slovenia), with probably significantly higher sediment concentrations at the upstream boundary of the Kupa. A slow concentration changes and PCB accumulation in the sediment should be expected downstream compared to the upstream boundary, governed mainly by high flow events. The PCBs in sediments from 2020/2021 are markedly different after the Lahinja confluence with Kupa (0.2–0.6 µg kg^{-1} vs. 1.4–34.3 µg kg^{-1}). Measurements of PCBs in Kupa sediment suggest that the intake of PCB has not yet been completely stopped, which should be confirmed by detailed monitoring in the future. The contamination situation observed in

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the Kupa River represents an excellent example of the persistency of PCBs in the environment.

Keywords River sediment · Persistent organic pollutants (POPs) · Sediment modelling · Pollution transport

Introduction

Sediment is usually defined as a material settled at the bottom of a body of coastal water (stream, river, estuaries, or lake) that contains loose sand, clay, silt, or other soil particles. Sediment is moulded during soil erosion or by decomposition of living organisms that drain into the nearby water by wind and wet precipitation. Sediment formation is governed by complex physical, chemical, and biological processes, which depend on limnological, and hydrological changes induced by meteorological and climate conditions. Not less important parameter that shapes sediment is the status of surface water, which could be changed by human impacts (Thevenon et al., 2013).

Fresh surface waters could be enriched by environmental pollutants released into the atmosphere during anthropogenic activities and by direct discharge of contaminants into rivers or lakes. As the United States Environmental Protection Agency (USEPA, 2022) listed, sediment represents the most common source of pollutants in surface waters, while the environmental damage costs caused by sediment pollution account for $16 billion annually. Besides acting as a final sink for xenobiotics, sediment deposits play a crucial role in the translocation of pollutants through rivers/tributaries, basins, or watersheds (Marziali et al., 2021). Under conditions of certain hydrological, chemical and biotransformation processes, the contaminants bound to the particles from the water side or bottom could be remobilized making the sediment a source of pollution (Baran et al., 2019). If sediment pollution is not addressed and treated properly, the water body risk could be underestimated. Therefore, the European Science for Environment Policy proposed to target the status of both the water and underlying sediment when assessing the quality of surface water (European Commission, 2009; Tueros et al., 2009).

Multiple-source emissions of environmental pollutants that are highly variable at spatial and temporal scales could be reflected in the sediment composition. Sedimentary archives could serve as an excellent prerequisite to: (*i*) investigate variabilities of chemical or physical weathering, which is controlled by environmental factors; (*ii*) estimate the effects of human interventions for control and use of water systems; (*iii*) reconstruct the levels and distribution of contaminants (inorganic elements and organic compounds including persistent organic pollutants (POPs) released to aquatic environment over the years), and (*iv*) distinguish between anthropogenic and natural inputs of environmental pollutants (Bouwer et al., 2006; Thevenon et al., 2013). Organic contaminants including polychlorinated biphenyls (PCB) are minimally transformed during the sedimentation process. They are long-lived pollutants, which resist photolytic, chemical, and biological degradation. Because of their high lipophilicity, PCBs bind to fine particles in sediments, which are rich in organic matter. The affinity of PCBs toward the sediment also depends on the particle size. Highly chlorinated PCBs appeared to accumulate in fine sediment fractions (<63 μm), whereas low chlorinated PCBs tend to restrain coarse fractions (>63 μm) (Salvadó et al., 2013). Recent sediment records of polycyclic aromatic hydrocarbons (PAHs) and POPs in shallow lakes of the Selenga River (Siberia) implied the influence of both local and regional sources of pollution in the twentieth and twenty-first century (Adams et al., 2018). Temporal variations in contaminant profiles and abundance were associated with economic and industrial growth in the former Union of Soviet Socialist Republics (USSR) after the Second World War and the economic decline of Russia in the 1980s and 1990s, as well as global trends in industrialization and development (Adams et al., 2018). Similarly, Gardes et al. (2020) recorded PCB temporal trends in sediment cores downstream of the Eure River (major Seine estuary tributary) watershed that were mainly linked with the production, consumption, and banning of PCBs in France. High levels of congeners from the 1950s to the 1970s were associated with discharges of technical mixture of low chlorinated congeners into waterways, while PCB levels after the 1970s were the result of atmospheric deposition.

In the present study, we investigated the multi-year PCB burden of sediment collected along the Kupa River in Croatia using the sampling analyses and bedload sediment transport model as a tool for qualitative long-term processes interpretation. Kupa represents a natural border between north-west Croatia and south-east Slovenia, a part of Dinaric karstic region. The basic features of the karst area are carbonate aquifers, groundwater flows, occurrences of karst springs with a wide range of outflows and sensitivity to external influences due to its permeability (Kogovšek, 1995). Kupa River belongs to the water system Krupa (Slovenia) → Lahinja (Slovenia) → Kupa (Croatia) → Sava → Danube → Black Sea. Waste contained PCB technical blends was deposited in various Iskra factory's landfills located in shallow karst of the Krupa River hinterland, Slovenia. As a consequence of an improper handling of PCB waste material, according to inventory of PCB use in the Iskra factory from 1962 to 1985, the total quantity of waste calculated for pure PCBs released into the environment was approximately 70 tonnes (NIP, 2009). High concentrations of PCBs were the first detected in river water in 1983 and afterwards in air, sediment and living organisms (Pezdirc et al., 2011; Polič et al., 2000). After the remediation of the landfill, it is estimated that more than 13 tonnes of PCB seeped into the Krupa River karstic hinterland (NIP, 2009). Although a gradual reduction of the POP burden in the river's surrounding compartments (air, water, sediment, and soil) after the main disposal sites were cleaned and systematically removed by protective measures and a remedial environmental programme, increased PCB concentrations are still observed occasionally (NIP, 2009; Pezdirc et al., 2011).

If the contaminated sediment from primary water flow has a significant impact on the downstream rivers and having in mind the protective and remedial measures taken in the endangered zone of the Krupa River (Slovenia), we aimed to reconstruct the historical abundance of PCBs and characterize their temporal dynamics in the sediment of the Kupa River (Croatia) using pollution transport modelling.

Modelling the transport and fate of contaminants in sediment is highly dependent on the hydrodynamic and morphodynamic conditions and processes. The physical description of these processes advanced significantly in the last century, enabling the development of highly advanced and complex numerical models (i.e., Lesser et al., 2004, Warner et al. 2008, Shakibaeinia et al., 2017). Despite the progress and availability of modelling tools for the prediction of these processes, the degree of accuracy of morphodynamic models remains difficult to assess and is certainly less than that of hydrodynamic models (Syvitski et al., 2009; Villaret et al., 2013). These models include many parameters that are rarely available for specific riverine environment. In addition, all models utilize sediment transport rates based on approximate semi-empirical concepts.

Modelling of sediment mobilization is in most cases based on the riverbed shear stress estimation and its excess over critical values. A distinction is made between cohesive and non-cohesive sediment mixtures since the governing processes of erosion and deposition are significantly different. Silts and clays are usually considered as cohesive (grain size smaller than < 63 µm), while larger particles are considered non-cohesive (sand and gravel). Due to a lack of sediment measurements, in this study the bedload transport capacity rates are calculated under the assumption of erosion equilibrium, with the goal to qualitatively describe the dynamics of the contaminant long-term transport.

Material and methods

Study area

The Kupa River is a transboundary river and a significant water resource for both Croatia and Slovenia. The nearly 200 km long reach of interest for this study is located downstream of the tributary Lahinja (Slovenia), until its confluence to the river Sava (Croatia). The average flow near the confluence (period 1983−1990 and 2000−2020) is 185 $m^3 s^{-1}$, with a minimal daily flow of 13 $m^3 s^{-1}$ (August 2000) and maximum daily flow of 1315 $m^3 s^{-1}$ (December, 2015). Obviously, due to high peak flows the hydraulic conditions and processes form the primary input for large-scale dispersion of historically contaminated sediments (Westrich and Forstner, 2005).

River bathymetry data were obtained from the Slovenian Environment Agency for the hydrometric stations in Slovenia and from the Croatian Meteorological and Hydrological Service for the rest. In total, 10 bathymetry profiles (for each hydrometric station) were available, while numerical profiles were linearly interpolated in terms of hydraulic parameters. It is assumed that during the simulation period there were no significant changes in the bathymetry, so the change of hydraulic parameters for sediment transport were solely the function of the recorded daily hydrologic conditions.

Sediment sampling

The Krupa→Lahinja→Kupa water system belongs to karstic region. The Kupa River passes through two different areas, the karst area where it springs, and near Karlovac, Kupa crosses into a non-karst area—the Pannonian Basin (Fig. 1). As indicated on Fig. 1, sediment samples of the Kupa River were collected along the river water course at sampling sites starting from the spring of the Kupa River to the confluence with the Sava River: Kuželj→Kupica→Klanac→Lahinja River confluence-Jurovski Brod→Ozalj→Karlovac→Korana→Kupčina→Sisak (Sisak-confluence with the Sava River). Consequently, the sampling sites Kuželj, Klanac, Jurovski Brod, Ozalj, Kupica, Korana belong to the karst part of Kupa, and Kupčina and Sisak to the lowland part of Kupa, while Karlovac represents a boundary section between karst and lowland. Kupica, Korana and Kupčina are tributaries of the Kupa River. Samples were collected between May 2020 and September 2021, during stable weather and when the water flow was at its lowest. At each sampling location, four sediment samples were taken at vertices of a square with side lengths of 1 m. At Jurovski Brod—the site of Lahinja's confluence with the Kupa River, the abundance and levels of PCBs were evaluated with respect to the sediment depth. The sediments were sampled using hand-driven vertical plastic corers of 5 cm inner diameter and 25 cm length. Four sediment core samples were taken along the riverbank at a distance of 10 m. The collected sediment cores were only 16 cm long because there is a stone layer under the sediment layer. Before analysis, the frozen sediment cores were divided by the depth of the sediment in 13 segments. Segments of the same depth of

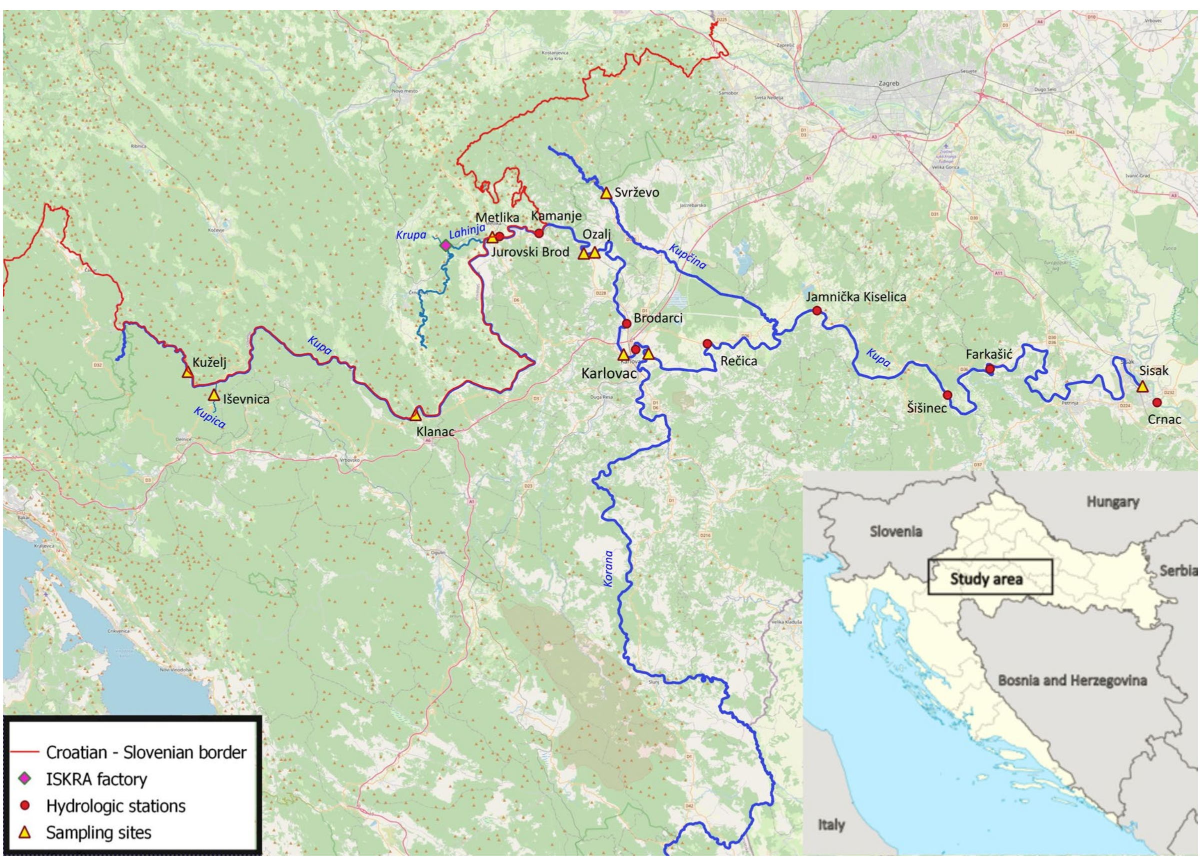

Fig. 1 Study area and the model domain with the hydrologic stations (HS). The Kupa River section considered for the transport model is between HS Metlika and its confluence to river Sava (HS Crnac), which is 178.5 km of Kupa River

four sediment samples were combined and thoroughly mixed to prepare composites representative of a certain sediment depth. All sediment samples were stored at − 18 °C. Prior to analysis, the river sediments were defrosted and then combined and thoroughly mixed to prepare composites representative for each sampling location. Due to the high moisture content, the composite sediment samples were dried at room temperature and additionally homogenized by mixing.

Chemical analyses

The PCB extraction procedure was extensively described in our previous study (Dvoršćak et al., 2019). Briefly, compounds were extracted from 5 g of wet sediment sample using a microwave-assisted extraction procedure with 30 mL of a mixture of *n*-hexane and acetone in a 1:1 volume ratio at 80 °C. After cooling the extract to room temperature, a 25-mL aliquot of the extract was decanted and reduced under a gentle stream of nitrogen to 1 mL.

The obtained extracts were purified according to a previously described procedure (Dvoršćak et al., 2019). Three purification steps were included in the procedure. Solid phase extraction (SPE) on the Florisil Bakerbond cartridge and mixing with concentrated sulphuric acid were used for elimination of fats and matrix components interfering in gas chromatographic (GC) analysis of target analytes. Additionally, samples were treated with Hg for sulphur removal.

Final analysis of PCB was performed on an Agilent 7890B gas chromatograph equipped with two micro electron-capture detectors (GC_ECD) and two gas chromatographic columns, HP-5 and SDB-1701, both 30 m × 0.25 mm i.d., 0.25 µm film thickness (Agilent, USA). The column temperature ranged from 90 °C (with 1 min hold) up to 180 °C at 30 °C min^{-1} (1 min hold), and then up to 240 °C at 2 °C min^{-1} with a hold of 20 min and finally up to 260 °C at 5 °C min^{-1} with 8 min hold. The injector and detector temperatures were 270 °C and 300 °C, respectively. The carrier gas was helium with a flow rate of 1.2 mL min^{-1}. The injection volume was 1 µl. Stock solutions were prepared in acetone and further diluted with *n*-hexane as required by the experiment. The mass concentration of a single compound in GC-ECD standards ranged from 0.1 to 5.0 ng mL^{-1}. Calibration lines were obtained in triplicate at five different concentration levels and were linear in this range.

All sediment samples were analysed in duplicate on two gas chromatographic columns of different polarity. Only compounds confirmed on both columns were evaluated. The mass fractions were reported as an average of the result obtained on two different gas chromatographic columns. Solvent and reagent blanks were prepared and analysed in the same manner as the sediment extracts.

The estimated limits of detection (LOD) for PCB congeners, based on a signal-to-noise ratio of 3 in real samples, ranged between 0.02 µg kg^{-1} d.m.

The performance of the applied analytical method was checked by analysis of each sediment spiked with target analytes. The average values of PCB recoveries from all investigated sediments containing 0.08–4.34% total organic carbon ranged from 59 to 77%.

Although it seems that recovery values linearly decrease with the increase of the total organic content and electric conductivity of sediment, the obtained slopes were not statistically significantly different from zero, and correlation factors were less than 0.5 for most compounds.

All mass fractions of each PCB congener in individual sediment samples were corrected according to the procedure efficiency obtained for a specific congener and sediment.

The PCB congener standards (PCB-28, PCB-52, PCB-60, PCB-74, PCB-101, PCB-105, PCB-114, PCB-118, PCB-123, PCB-138, PCB-153, PCB-156, PCB-157, PCB-167, PCB-170, PCB-180, PCB-189) were supplied either by LGC Promochem (Wesel, Germany) or by Ultra Scientific (North Kingstown, RI, USA) as standards of 97% to 99.9% chemical purity. Acetone and *n*-hexane for gas chromatography, sulphuric acid (95–97%, p.a.), and mercury 99.9999 Suprapur® were products of Merck KgaA, Darmstadt, Germany. Florisil Bakerbond SPE cartridges (1000 mg, 6 mL) were from J.T. Baker, Avantor Performance Materials, Deventer, Netherlands. Helium (99.9999% pure) and nitrogen (99.9995% pure) were supplied by SOL SPA, Monza, Italy.

According to the number and position of chlorine atoms in the PCB molecule, there are a total of 209 isomers and homologues called congeners. We analysed seven indicator PCB congeners (IUPAC number: 28, 52, 101, 118, 138, 153, 180), whose selection was based on their dominant presence in technical mixtures, environment, and animal and human tissues; and 10 toxicologically relevant congeners: 8 mono-*ortho* substituted PCBs (IUPAC numbers: 60, 74, 105, 114, 123, 156, 157, 167, 170, 189). Summary data for several major groups of contaminants were presented: ΣIndPCB as the sum of 7 indicator PCBs, Σ17PCB as the sum of all analysed congeners.

Modelling

One-dimensional transport model, based on daily river flow and water level data, is used to qualitatively evaluate the long-term transport of contaminated bedload sediment. The deterministic numerical model developed in this study provides a tool for investigating the mobility and temporal and spatial distribution of associated chemicals (PCB) adsorbed on the bedload sediment. Considering the time scale of the process, in this study it is assumed that contaminated non-cohesive sediment is the main carrier of the PCB contaminants. This was implicitly confirmed by sample analyses, where mainly lower chlorinated PCB congeners were present (as described below).

The model utilizes the daily hydrologic data from hydrologic stations along the river reach and geometric properties of river section to estimate the river bedload capacity and consequently the transport of related adsorbed contaminants. The obtained concentrations are compared with the results from measurement campaigns (Drevenkar et al., 1985; Polič et al., 1991; Frančišković et al., 2005) occasionally reported during the nearly 40-year modelling period (1983–2020).

The governing equation solved numerically in this model is formulated as:

$$\frac{\partial M_{bs}}{\partial t} = -\frac{\partial\left(C_{bs}q_{bx}\right)}{\partial x}\Delta x - R \tag{1}$$

where M_{bs} is the mass of the PCB in the bed sediment in the river reach of length Δx, C_{bs} is the concentration of PCB in the non-cohesive bedload, q_{bx} is the bedload mass flux and the R is the sink/source term. For calculation of the bedload flux, two empirical models are considered. The first one is the based on the critical velocity concept, where Goncharov (1954) proposed:

$$q_{bx} = 2(1+\varphi)d_{50}\widetilde{u}_c\left(\frac{\widetilde{u}}{\widetilde{u}_c} - 1\right)\left[\left(\frac{\widetilde{u}}{\widetilde{u}_c}\right)^3 - 1\right] \tag{2}$$

where φ is the empirical coefficient depending on the sediment particle size, d_{50} is the corresponding sediment particle size, $\widetilde{u}_c$ is the critical velocity, and $\widetilde{u}$ is the depth averaged flow velocity.. Here, the critical velocity is defined as:

$$\widetilde{u}_c = 0.535log\left(\frac{8.8h}{d_{95}}\right)\sqrt{2g(s-1)d_{50}} \tag{3}$$

where h is the water depth.

The second one is based on the excess of the bed shear stress approach, the Meyer–Peter–Muller (1948) formulation of the bedload flux:

$$q_{bx} = c_{mpm}\sqrt{g(s-1)d^3}\left(\theta - \theta_c\right)^{3/2}\left(\theta > \theta_c\right) \tag{4}$$

where c_{mpm} is the Mayer-Peter-Muller parameter, s is the sediment relative density and θ_c is the critical Shields number. The Shields number is defined as a dimensionless shear stress:

$$\theta = \frac{\tau_0}{\rho(s-1)gd} \tag{5}$$

with critical value for initiation of non-cohesive sediment erosion:

$$\theta_c = \frac{0.3}{(1+1.2d_*)} + 0.055\left(1 - e^{-0.02d_*}\right) \tag{6}$$

where d_* is dimensionless sediment particle diameter, defined as:

$$d_* = d\left[\frac{g(s-1)}{\nu^2}\right]^{\frac{1}{3}} \tag{7}$$

Figure 2 shows the flowchart of numerical simulation which is coded in C++programming language. In the first step, the program reads prepared geometry tables of each HS cross section. Tables contain discretized dependency of cross section area and hydraulic radius on water depth. Table data is prepared based on the cross-section geometry with water depth interval between 5 and 10 cm.

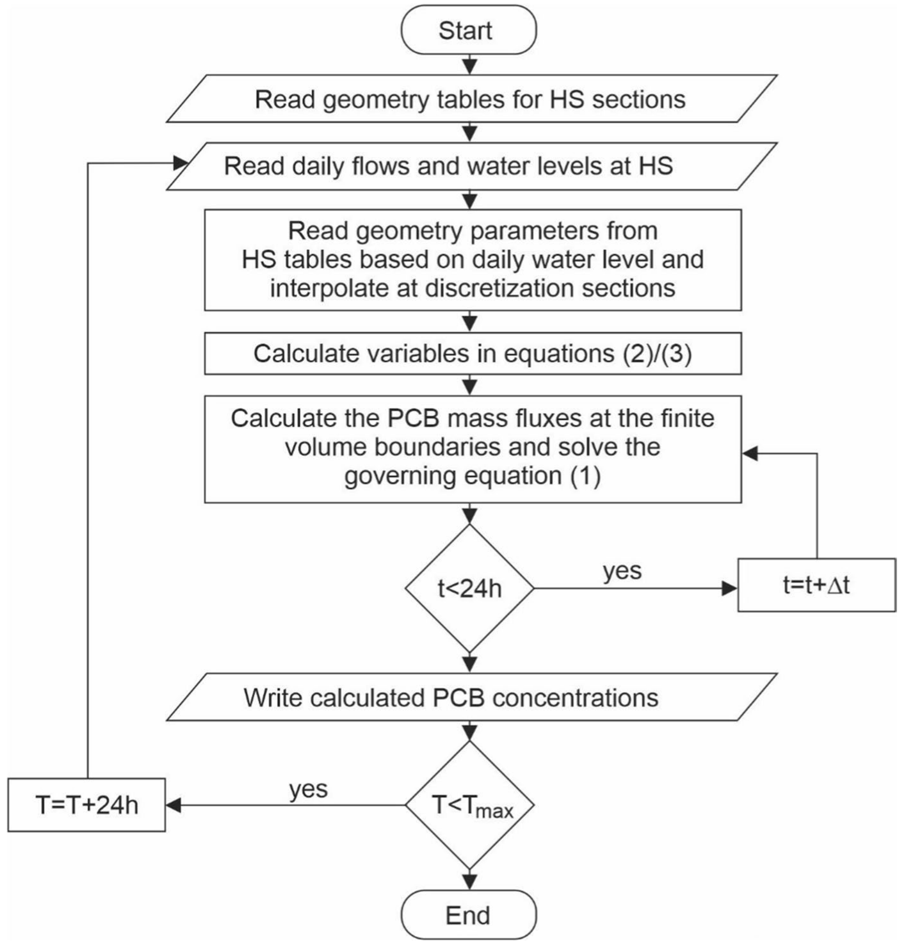

Fig. 2 Flowchart of numerical simulation. The T_{max} corresponds to simulation period and $\Delta t = 5$ s

The outer time loop (24 h step) starts with reading the daily water level and discharge data at each HS. The water level is converted to water depth and HS geometry table is utilized to obtain the hydraulic properties of HS cross sections. These properties are in the next step interpolated at discretization sections along the river. The river domain is discretized by sections (finite volumes) between 100 and 250 m in length. Discharges, water levels and cross-section hydraulic properties enable calculation of variables in Eqs. (2) or (4) to obtain bedload fluxes at discretization sections, i.e., at the finite volume boundaries.

Numerically, Eq. (1) is solved by a finite volume method, where the second order approach approximation of the advective term is utilized by a linear interpolation of the PCB concentrations with the application of TVD limiters (Hirsch, 1990) to prevent oscillations and minimize numerical dispersion effects. The time step of 5 s is utilized in the inner time loop (Fig. 2) since the finer discretization had no significant effect on calculated results.

The sediment particle size and density have significant influence on sediment transport modelling results (e.g., Lepesqueur et al., 2019). The d_{50} certainly changes along the considered river reach. However, we had no data regarding the bedload sediment granulometry relevant for the PCB transport. Therefore, it may be considered as a calibration parameter. In this study, for qualitative analysis, we assumed the values which provided relatively good agreement with observed PCB concentrations during the simulation period of 30 years. Utilized model parameters are shown in Table 1.

Boundary and initial conditions

For the transport model, the upstream boundary condition is imposed as the specified PCB bed

Table 1 Model parameters used in simulation analyses

Parameter	d_{50} (mm)	d_{95} (mm)	s (–)	φ (–)	c_{mpm}	R(mg/s)
Value	0.25	2.5	2.65	1.25	8.0	0

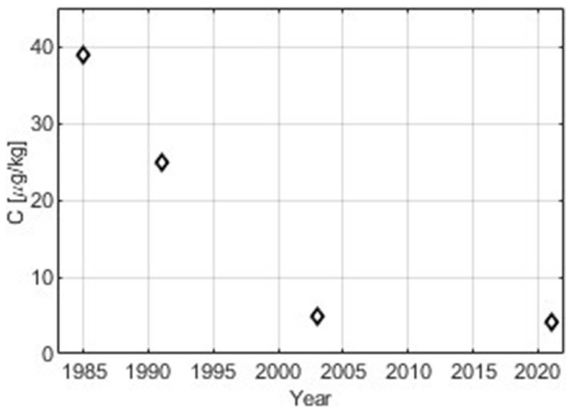

Fig. 3 Recorded concentration in the Kupa River bed sediment near the Lahinja River confluence utilized as the upstream boundary condition through the linear interpolation

sediment concentration according to reported measurements near the Lahinja River confluence. Figure 3 shows measurements at this location reported chronologically (Drevenkar et al., 1985; Polič et al., 1991; Frančišković et al., 2005; and this study). Linear interpolation was used to obtain continuous boundary conditions. There were no data about bedload or suspended sediment transport during the considered period. Therefore, analysis was conducted with the bedload potential as a qualitative estimate.

Regarding the initial concentration of the PCB along the Kupa River, there were only two measured values available in 1985. Near the HS Karlovac, a sediment concentration of 7 μg kg^{-1} was measured (Drevenkar et al., 1985) and near the Sisak one (confluence of the Kupa River) of 8 μg kg^{-1}. However, a number of simulations revealed that the initial condition (distribution of initial concentrations along the Kupa River) has a significantly lower influence on the long-term distribution of PCBs along the Kupa River in comparison with the upstream boundary condition. The change of concentrations at the upstream boundary had a dominant impact on long term PCB concentration values along the Kupa River. The concentrations measured near Karlovac and Sisak in 1985, according to model results, indicate significantly higher concentrations than the ones measured at the upstream boundary before 1985.

Results and discussion

Measured PCB levels in sediment collected in 2020/2021

Due to worldwide public concern about adverse outcomes upon human health and wildlife, the use of PCBs was banned or restricted during the 1970s and 1980s in many industrial countries. PCB levels decline in primary sources, but in deeper horizons of soils, oceans and sediments they are inherently persistent. Scientific research in the last few decades has focused on the harmful effects of PCBs on both the environment and human health. The International Agency for Research on Cancer (IARC) classified them as group 1 carcinogens for humans in 2015. In industrially developed parts of the world, the increase in cases of various cancers is associated with exposure to organochlorine compounds (breast, testicular, prostate and thyroid cancer) (Zhang et al., 2015). This is why they are still intensely in scientific focus across the globe, causing constant toxicological and public health concerns. Measures of the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2017) and EU legislation (Regulation (EU) 2019/1021 of the European Parliament and of the Council, 2019) should minimize contamination. Due to their lipophilicity and resistance to metabolic degradation in biota, PCBs enter and accumulate in the food chain, causing predatory species at the top of the food chain to have the highest levels of PCB.

In aquatic environments, owing to their lipophilic character, PCBs are prone to adsorption to suspended matter and subsequent sedimentation (Josefsson et al., 2011). Consequently, higher levels are in the sediment than in the overlying water. This is why sediment is a secondary source of PCB contamination

Table 2 PCB content (μg kg^{-1}) in the sediment samples of Kupa River collected between May 2020 and September 2021

KUPA	Tributary	Length of Kupa (km)	∑ 17 PCB (μg kg^{-1})	Mutual distance between sites (km)
Kuželj		275	0.2	
	Kupica	269	0.6	6
Klanac		226	0.6	43
Jurovski Brod		178	5.2	48
Ozalj upstream		163	31.2	15
Ozalj downstream		163	3.7	0
Karlovac		139	1.4	24
	Korana	135	1.2	4
	Kupčina	105	0	30
Šišinec*		76	34.3	29
Sisak		1	5.4	75

*Sediment sampled in 2019 (Report, 2021; In Croatian)

for aquatic life. For example, studies conducted in the lakes of northern Italy showed that the fish species *Silurus glanis* was not for consumption (Squadrone et al., 2016), while sediment analysis showed the presence of PCBs at high levels for more than 20 years (Marziali et al, 2021).

After 1960 and nowadays, the Krupa River (Slovenia) and its environment is ill-reputed because of its PCB pollution. In this study, we analysed the sediment sampled at different sites along Kupa's flow since PCBs absorbed in suspended particles in water, which present a long-term source of water system Krupa (Slovenia) –Lahinja (Slovenia)—Kupa (Croatia).

As shown in Table 2, PCB levels are markedly different after the Lahinja confluence (Jurovski Brod). Also, it is noticeable that the karst tributaries of the Korana and Kupica differ from the lowland tributaries of the Kupčina, where there were no PCBs.

Kuželj, Kupica and Klanac are in sparsely populated area with no known anthropogenic influences. At Jurovski Brod—the site of Lahinja's confluence with the Kupa, the sediments were sampled using hand-driven vertical plastic corers and sediment cores were divided by the depth of the sediment in 13 segments. PCB concentrations were equal in all layers, except for the layers where gravel predominated and where consequently PCB levels were lower (Fig. 4). At the sampling site Ozalj, two samples were taken at a distance less than 1 km. The sample with a higher level (31.2 μg kg^{-1}) was upstream of the sampling site with lower PCB levels (3.7 μg kg^{-1}). Differences between sampling sites with a small distance from

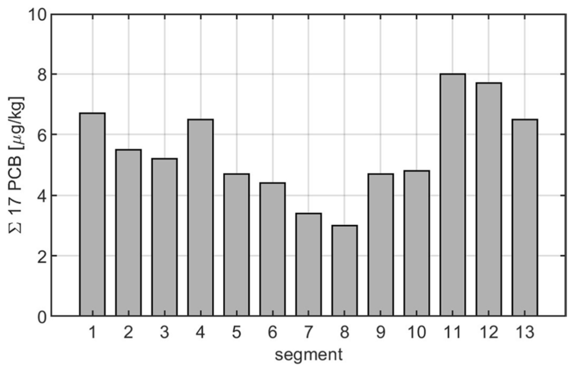

Fig. 4 PCB content (μg kg^{-1}) at sampling site Jurovski Brod where the Lahinja confluence with the Kupa River is. Sediment cores were divided by the depth of the sediment in 13 segments (16 cm), where 13 is the deepest layer and 1 represents a surface layer

each other were found in Krupa`s sediment (Slovenia) (Pezdirc et al., 2011), and explained by interactions of various translocation processes. In the lowland part of Kupa, at the Šišinec sampling site (Fig. 1), a PCB level of 34.3 μg kg^{-1} was measured in the sediment sampled in 2019 (Report, 2021; in Croatian). According to the best of our knowledge, there is no known source of contamination that could be directly associated with the concentration peaks at the sampling points Ozalj and Šišinec, besides pollution translocation from Krupa (Slovenia). It was found that the level of PCB in chub fish caught in 2019 from Kupa was quite high (107.8 μg kg^{-1}) (Report, 2021; in Croatian). PCB distribution in all of the analysed samples (Fig. 5) showed that trichlorobiphenyl (PCB-28)

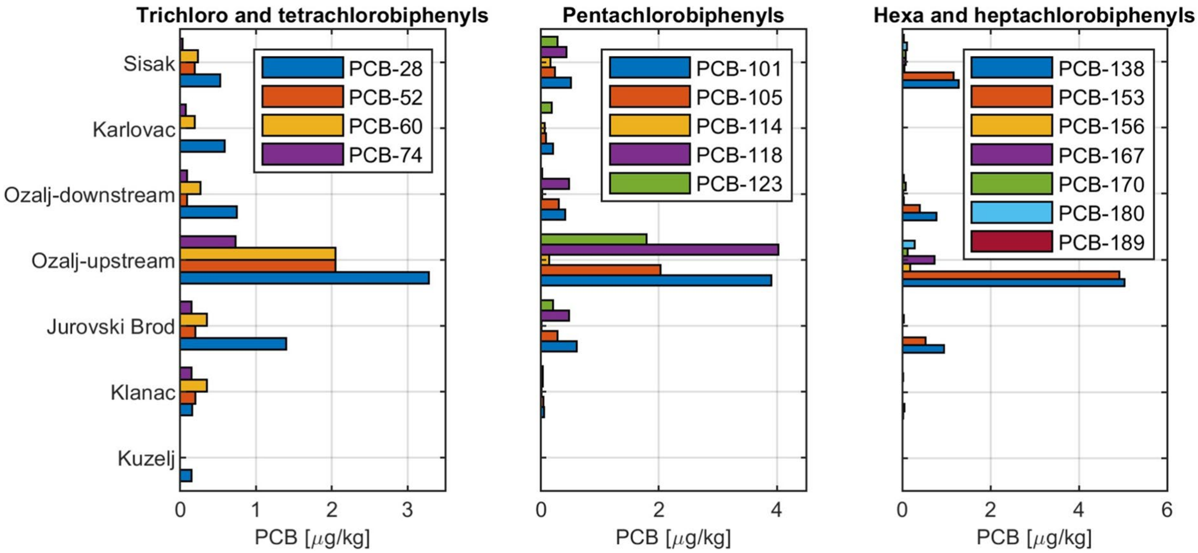

Fig. 5 PCB congener (μg kg^{-1}) profile at all of the sampling sites at Kupa

are present in all samples as prominent, following are tetrachlorobiphenyls (PCB-52, -60, -74) and pentachlorobiphenyls (PCB-101, -105, -114, -118, -123). Following are hexachlorobiphenyls (PCB 138, -153), and in some extent other hexachlorobiphenyls (PCB-156, -167) and heptachlorobiphenyls (PCB-170, -180, -189). Clophen A-30, Pyralene 3010 and Pyralen 1500 mainly consist of trichlorobiphenyls and tetrachlorobiphenyls while Clophen A-50 of tetrachlorobiphenyls and pentachlorobiphenyls. Clophen A-30, Clophen A-50, Pyralene 1500 and Pyralene 3010 were mostly used in "Iskra" (Polič et al., 2000). PCB congener distribution in Kupa sediments from 2020/21 (this study, Fig. 4) is very similar to PCB congener distribution in Krupa (Slovenia) sediments collected in 1985 (Jan & Tratnik, 1988) and in 2008 (Pezdirc et al., 2011). Results for Kupa is in accordance with Krupa (Slovenia) where increased PCB concentrations are still observed occasionally (NIP, 2009; Pezdirc et al., 2011), as shown by the results presented in the National Implementation Plan for the management of POPs in the period from 2009 to 2013, the sediment of surface waters of Slovenia and the Krupa River particularly is overloaded with PCBs, and consequently, the sediment in the Kupa River (NIP, 2009). Besides, drainage and irrigation from surrounding landfills and polluted soil, as well as air transmission are significant paths of PCB dispersion. In 2002, the average PCB concentration measured in the sediment of the Kupa did not exceed 200 μg kg^{-1}, while PCB levels in the water were not above 20 ng L^{-1} (NIP, 2009). In addition, the Krupa sediment was occasionally more burdened by PCB congeners (-28, -52, -101, -118, -138, -153, -180, and -194) in 2005 (380 μg kg^{-1}) and 2008 (minimum value: 455 μg kg^{-1}) than the samples presented herein, as shown by Polič (2005) and Pezdirc et al. (2011), respectively.

Despite relatively low levels at some sampling sites, the results in this study imply the need for detailed PCB monitoring in the Kupa.

Model output

We considered that the fate of adsorbed sediment contaminants is mainly dependent on the sediment mobility in the river environment. As a measure of bedload mobility, the duration of the excess of the bed shear stress may be considered. Figure 6 qualitatively shows the bedload transport potential of the Kupa River segments. It generally shows different characteristics of the upstream section (HS Kamanje—HS Brodarci), upstream from the HS Karlovac, and downstream sections until the Sava confluence. Upstream sections show significant bedload transport capacity most of the time, while the downstream part is generally flood event-dependent. The exception is the reach HS J. Kiselica—HS Sisinec

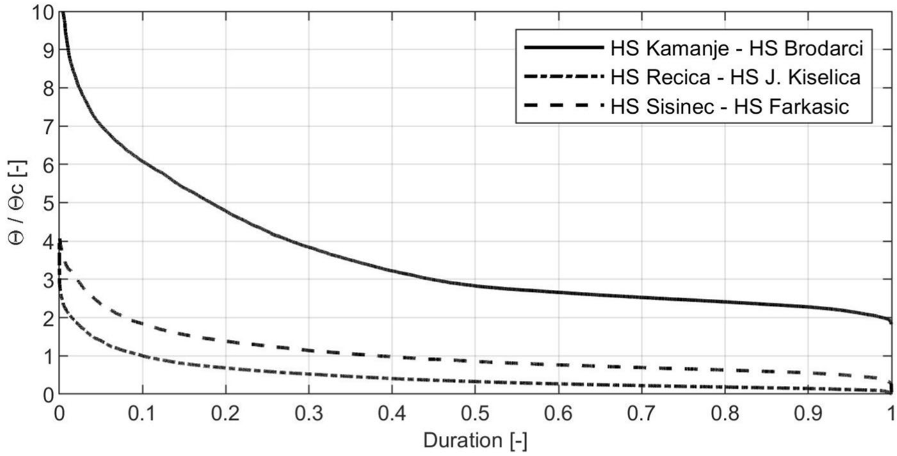

Fig. 6 Duration curve of the bed shear stress excess along three Kupa River sections in the period 1983–2020 for dimensionless sediment particles diameter $d_* = 96$

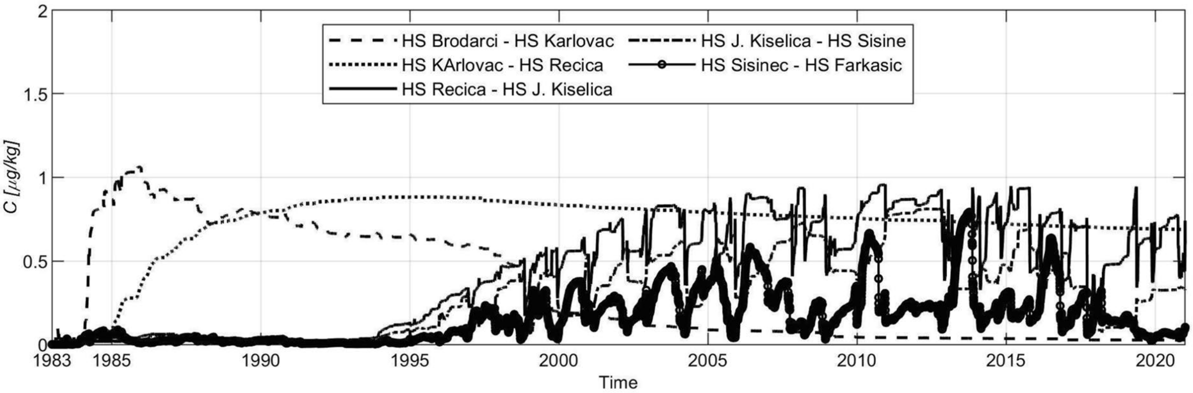

Fig. 7 Calculated reach-averaged PCB concentrations along the river Kupa sections in the period 1983–2020 for the "zero" initial condition simulation

which also has significant bedload transport potential most of the time. The lowest bedload potential can be attributed to the reach HS Karlovac—HS Rečica, where accumulation of the contaminants can be expected. Based on this analysis, it could be assumed that relatively fast transport may be expected until HS Karlovac, with accumulation and slow concentration change at the HS Karlovac—HS Rečica reach. Downstream from the HS Rečica, hydraulic conditions are mainly prone to flood event transport where intensity highly depends on the local hydraulic and morphodynamical conditions. Between flood events, the contaminated sediment may reside for a relatively long period before the occurrence of conditions for further transport. Similarly, Polič (2005) reported that PCB concentrations in the Krupa River were significantly elevated at the banks, contributing to the increase of pollutant in water after lengthy periods of precipitation and flooding events.

The described effects of hydraulic conditions on pollutant transport are presented in Fig. 7. The figure shows simulation results with "zero" initial conditions as the averaged PCB concentrations along the specific river reach. The reach HS Karlovac − HS Rečica had the lowest bedload capacity and therefore, it accumulated and stored contaminants for a longer period. As expected, the downstream part was more prone to flood event transport with occasional peaks in concentrations with a similar amplitude and general decrease of the peak concentrations in downstream directions.

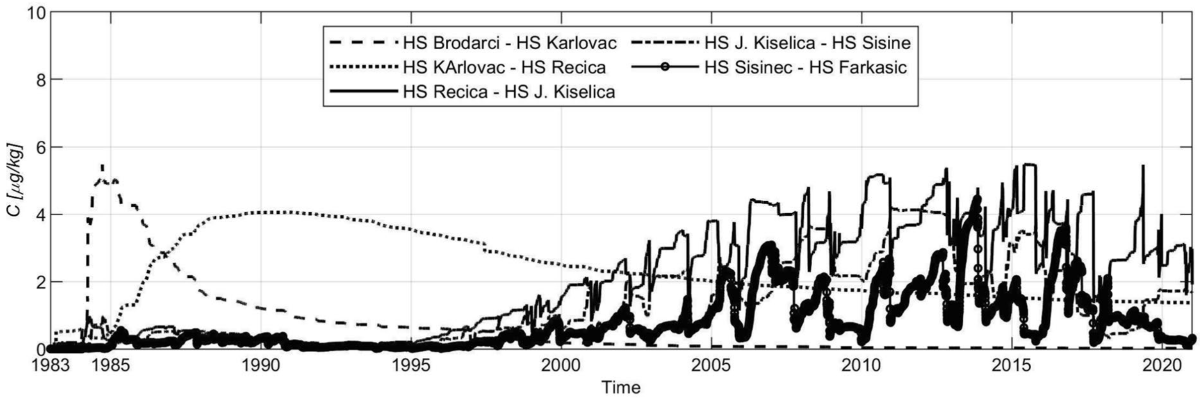

Fig. 8 Calculated reach-averaged PCB concentrations along the river Kupa sections in the period 1983–2020 for the "zero" initial condition simulation and increased the upstream boundary PCB concentration in the period 1983–1985

Calculated peak concentrations are of the same order, however, lower than the measured ones. For example, at Karlovac and Sisak in 1985, the measured values were 7 μg kg^{-1} and 8 μg kg^{-1}, respectively, while in the simulation the contaminant wave had only reached Karlovac, but not the Sisak (HS Crnac). Obviously, the contamination of the Kupa River started significantly earlier than in 1983 with probably significantly higher sediment concentrations at the upstream boundary. In this simulation, the boundary PCB concentrations in the period from 1983 to 1985 is assumed as a linear extrapolation of measurements from 1985 to 1991.

The effects of the boundary concentration in the period 1983–1985 is shown in Fig. 8, where the PCB concentration was assumed as 500 μg kg^{-1} at the upstream boundary in 1983. This was a reasonable assumption since the measured values in the river Lahinja, not far from the confluence with the Kupa River, were in the period 1983–1984 between 4 500 and 9 000 μg kg^{-1} (Drevenkar et al., 1985). The dynamics of the contaminant propagation were very similar as in the previous case, with peak concentrations very similar to the ones measured in this study.

To the best of our knowledge, no similar models or studies have aimed to reconstruct PCB patterns over multiple years in the sediment of Kupa River. A model based on artificial neural networks was used previously to investigate the dynamics, transport, and mass balance of PCB pollution of the karst water system of the Krupa River (NIP, 2009). The results were obtained with a certainty value higher than 90% and provided the verification of the measurements taken to remediate the endangered zone of the river, but also to forecast the dynamics of the River Krupa source pollution prior to 1980 and up to 2015. As indicated, PCB levels were expected to be reduced by 83, 66 and 800 times in the water, air above the water and edible fish species, respectively, from 1980 to 2010. The findings also suggested that the transfer of PCB concentrations that have remained in the affected environment up to the present is far less (up to 100 times smaller) than before the rehabilitation measures had been carried out.

PCB trends in the world sediment

Recently, many studies have investigated sediment samples as a means to reconstruct the burden of terrestrial waters by POPs, usually searching for a relation between the intensification of anthropogenic sources and their apportionment. Adams et al. (2018) used paleolimnological techniques to explore temporal changes in the PAH and POP levels in the Selenga River basin over the past 70 years. Variations in the pollutant content were related to global trends in industrialization and economic growth after World War II as well as the economic decline in the late 1980s and 1990s. Similarly, the sediment analyses (Lake Brêt) showed that PCB emissions in Switzerland reached maximums between 1960 and 1970 in accordance with global emission peaks, while a rapid reduction was observed after the first regulatory measurements were taken (Thevenon et al., 2013).

Apart from global sources and long-range transports, local polluters were noticed including agricultural activities and the melt down of surrounding glaciers. Gardes et al. (2020) characterized PAH and PCB pollution in the sediment cores from the Eure River (Seine tributary, France) and linked it with previously reported global trends of contamination as proven by a comprehensive literature review. In addition, Marziali et al. (2021) concluded that significant levels of POP were present in Lake Maggiore (Italy) from 2001 and 2018 compared to other waters in Europe and Asia, and highlighted that a tributary played a crucial role in the transport of polluted sediment.

Conclusion

Based on the results of the sediment transport model and measured PCB levels in sediment samples collected in 2020/2021, we can conclude that the application of the bedload sediment transport model is a valuable concept for the evaluation and interpretation of the multi-year PCB burden of sediment collected along the Kupa. Our model application revealed that the contamination of the Kupa sediment started significantly earlier than 1983, when a high concentration of PCB was the first time detected in the Krupa (Slovenia), with probably significantly higher sediment concentrations at the upstream Kupa boundary. Furthermore, according to the model, the accumulation and slow concentration change of PCBs should be expected in the downstream part of Kupa because it is generally flood-event dependent, while its upstream sections show significant bedload transport capacity most of the time. The determination of PCBs in sediment samples from 2020/2021 implied that the intake of PCB has not yet been completely stopped, which should be confirmed by detailed monitoring in the future. At the upstream boundary of the Kupa (sampling location Ozalj) at a distance of less than 1 km, PCB levels of different orders of magnitude were measured (31.2 µg kg^{-1} vs. 3.7 µg kg^{-1}) similarly to the Šišinec sampling location (34.3 µg kg^{-1}) at the downstream section. Sampling sites at the beginning and at the end of the investigated flow of the Kupa (Lahinja River confluence—Jurovski Brod and Sisak) had similar levels (5.5 µg kg^{-1} vs. 5.4 µg kg^{-1}).

The contamination situation observed in the Kupa represents an excellent example of the persistency of PCBs in the environment.

Suggestion for further actions: In the case of the Kupa, detailed monitoring of sediment and biota is necessary. According to the results of our model and the measured PCB levels, the downstream part of the Kupa deserves more attention and detailed sediment sampling, in addition to the upstream part around Ozalj. It would be important to include the analysis of edible fish in future research, such as carp and catfish. Carp and catfish are demersal fish that mainly feed on aquatic invertebrates from the sediment and are long-lived species whose age can be more than 60 years (Jakšić, 2019), which is why they can accumulate considerable concentrations of PCBs within their tissues over time.

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Author contributions Snježana Herceg Romanić conceived of the presented idea and developed the theory. Nenad Jaćimović performed the model. Sanja Fingler verified the analytical methods. Gordana Mendaš and Sanja Stipičević carried out the experiments. Goran Jakšić collected samples and data. Aleksandar Popović and Gordana Jovanović interpreted the results. Snježana Herceg Romanić, Nenad Jaćimović, and Gordana Jovanović wrote the manuscript. All authors discussed the results and contributed to the final manuscript.

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Declarations

Conflict of interest The authors declare no conflict of interest. The authors have no relevant financial or non-financial interests to disclose.

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