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Seasonal variability of organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and benzene, toluene, ethylbenzene and xylenes in the Sitnica River, Kosovo, under contrasting hydrological conditions

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ABSTRACT

This study assessed the seasonal variability of physicochemical conditions and selected organic pollutants in the Sitnica River, Kosovo, under contrasting hydrological conditions. Surface water samples were collected from 15 monitoring stations during a high-flow campaign in February/March 2023 and a low-flow campaign in September 2023. The investigated pollutants included organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), BTEX compounds, and chlorobenzenes. Physicochemical parameters indicated stronger anthropogenic pressure during the low-flow period, with increased organic load, nutrients, ionic content, and suspended solids. Organic pollutants were detected during both campaigns, but their seasonal behavior differed among contaminant groups. Total PCB concentrations were significantly higher during the high-flow campaign ($p = 0.004$), suggesting hydrological mobilization or resuspension of particle-associated residues. In contrast, total BTEX concentrations were significantly higher during the low-flow campaign ($p = 0.005$), indicating stronger recent local inputs under reduced dilution conditions. OCPs, PAHs, and chlorobenzenes showed pronounced spatial variability, with localized peaks rather than uniform seasonal trends. Screening-level comparison with European environmental quality standards indicated that selected legacy pesticides, PAHs, benzene, pentachlorobenzene, hexachlorobenzene, and trichlorobenzenes reached concentrations of potential environmental concern at specific stations. These findings confirm the coexistence of legacy and recent contamination signals in the Sitnica River and demonstrate that hydrological conditions influence pollutant transport, redistribution, and detectability. The study provides baseline information for seasonal monitoring, source identification, and risk-oriented management of organic pollution in the Kosovo Plain.

Keywords: seasonal variability, organic contaminants, Sitnica River, environmental monitoring, Kosovo.

INTRODUCTION

Rivers draining mixed-use catchments are particularly vulnerable to organic pollution because they receive combined inputs from agriculture, urban wastewater, transport corridors, mining areas, and industrial activities. In such systems, seasonal hydrology influences contaminant concentrations, transport pathways, partitioning behavior, and the detectability of local pollution sources. High-flow conditions may enhance runoff-driven mobilization of contaminants from soils, urban surfaces, and river sediments, whereas low-flow periods may reduce dilution capacity and increase the influence of point-source discharges.

The Sitnica River is the main river system of the Kosovo Plain, draining a catchment of approximately 2.9×10^3 km² and flowing northwards for about 90 km before joining the Ibar River. It is a lowland river with pronounced seasonal hydrological variability, with higher discharge generally occurring in late winter and lower flow conditions during late summer (Kajtazi and Floqi, 2021). The river basin is exposed to multiple anthropogenic pressures, including municipal wastewater discharges, agricultural runoff, coal mining activities, industrial emissions, fuel-handling operations, and dense transport activity. These pressures make the Sitnica River an important case for assessing the seasonal behavior of organic pollutants in surface waters.

Persistent organic pollutants, including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), remain environmentally relevant because of their chemical stability, persistence, bioaccumulation potential, and ability to be remobilized from contaminated soils and sediments (Jones and de Voogt, 1999). Although many OCPs have been banned or restricted, residues may persist for decades and re-enter aquatic systems through runoff, erosion, atmospheric deposition, or sediment–water exchange (Wilhelm et al., 2002). PCBs, historically used in electrical and industrial applications, may similarly continue to occur in rivers through legacy contamination and secondary emissions from contaminated environmental reservoirs (Nuro et al., 2017).

Polycyclic aromatic hydrocarbons (PAHs) are another important group of organic contaminants in river systems and originate from both petrogenic sources, such as fuel and oil leakage, and pyrogenic sources, including incomplete combustion from traffic and industrial activities (Akkanen et al., 2005). Their occurrence in surface waters is strongly influenced by hydrological conditions, suspended particulate matter, and interactions between water and sediments. In contrast, BTEX compounds are more volatile and biodegradable and are commonly used as indicators of recent or ongoing petroleum-related and urban–industrial inputs. Chlorobenzenes represent another relevant group of chlorinated aromatic compounds because they may occur in aquatic environments through industrial, urban, or legacy contamination pathways. Combining POPs, PAHs, BTEX compounds, and chlorobenzenes in the same monitoring framework therefore allows a broader interpretation of both persistent historical contamination and more recent pollution pressures.

Previous studies from the Balkan region have reported the occurrence of OCPs, PCBs, PAHs, and other organic pollutants in aquatic environments, confirming the relevance of these contaminants in catchments affected by combined agricultural, urban, and industrial pressures (Nuro et al., 2014; Vryzas et al., 2009). Despite restrictions on many legacy compounds, OCP residues continue to be detected in surface and groundwater because of their persistence and resistance to degradation (Navarrete et al., 2018). However, for lowland rivers in Southeast Europe, integrated monitoring of OCPs, PCB marker congeners, PAHs, BTEX compounds, and chlorobenzenes under contrasting hydrological conditions remains limited.

For the Sitnica River, available information has been fragmented across contaminant groups and sampling periods, limiting the understanding of co-occurrence patterns, localized hotspots, seasonal shifts, and potential ecological implications relevant for environmental monitoring and river-basin management. Therefore, this study aimed to assess the seasonal variability of physicochemical parameters and selected organic pollutants in Sitnica River surface waters. Specifically, it evaluated the occurrence and concentration levels of OCPs, PCB marker congeners, PAHs, BTEX compounds, and chlorobenzenes at 15 monitoring stations during the high-flow campaign in late February/early March 2023 and the low-flow campaign in September 2023, assessed spatial and seasonal differences, compared measured concentrations with relevant European environmental quality standards, and provided baseline information for long-term monitoring of surface waters in the Kosovo Plain.

MATERIALS AND METHODS

Study area and sampling design

Water sampling was conducted at fifteen (15) monitoring stations distributed along the Sitnica River, Kosovo, during two sampling campaigns representing contrasting hydrological conditions: the high-flow campaign in late February/early March 2023 and the low-flow campaign in September 2023 (Figure 1). The Sitnica River is the principal river system of the Kosovo Plain and flows through an area affected by combined

agricultural, urban, transport-related, mining, and industrial pressures. The selected monitoring stations covered upstream, midstream, and downstream sections of the river in order to capture longitudinal changes and possible differences in contaminant occurrence along the river course.

The land-use categories presented in Table 1 are intended to provide general spatial context for the interpretation of pollutant distribution. They are based on the position of each station along the river course and the surrounding land-use characteristics. These categories should therefore be interpreted as descriptive background information and not as direct source attribution for individual contaminants.

The two sampling periods were selected to represent contrasting hydrological conditions. The high-flow campaign reflected greater dilution capacity and potential runoff-driven transport, whereas the low-flow campaign represented conditions under which pollutant concentrations may increase due to reduced dilution and cumulative inputs from agricultural, industrial, urban, and transport-related sources (Grünberger et al., 2024). Seasonal hydrological contrasts are recognized as important factors influencing contaminant dynamics in surface waters (Abdel-Wareth and Abd El-Hamid, 2023).

Sampling stations were selected to represent upstream, midstream, and downstream river sections affected by urban, agricultural, and industrial pressures. This design enabled assessment of longitudinal variability and potential point and non-point source contributions, consistent with river-monitoring strategies for integrated surface-water assessment (International Organization for Standardization [ISO], 2018).

At each station, 2.5 L of surface water was collected in pre-cleaned amber glass bottles with Teflon-lined caps to minimize photodegradation, volatilization, and sorption losses. Sampling, preservation, and handling followed water-quality guidelines (ISO, 2018). Samples were transported at approximately 4 °C, refrigerated upon arrival, and processed within recommended holding times for trace organic pollutant analysis (ISO, 2018; U.S. Environmental Protection Agency [U.S. EPA], 2007).

In situ measurements

At each monitoring station, in situ measurements were performed immediately after water collection to characterize the physicochemical status of the river at the time of sampling. The following parameters were measured directly in the water column: pH, electrical conductivity (EC), and temperature. Additional physicochemical indicators were determined in the laboratory as described below.

Measurements were carried out using a calibrated portable multiparameter probe (Hanna Instruments HI98194). Instrument calibration was performed prior to field deployment according to

Table 1. Geographic location and general land-use context of the Sitnica River sampling stations

Station	Latitude (°N)	Longitude (°E)	River section	General land-use context
WS1	42.5047060	21.1219483	Upstream	Agricultural/rural
WS2	42.5261214	21.0955410	Upstream	Agricultural/local settlement
WS3	42.6088487	21.0619632	Upper-midstream	Agricultural/peri-urban
WS4	42.6271761	21.0724370	Upper-midstream	Peri-urban/agricultural
WS5	42.6420713	21.0665364	Midstream	Settlement/agricultural/transport
WS6	42.6695752	21.0762906	Midstream	Urban/peri-urban/transport
WS7	42.7067198	21.0384675	Midstream	Urban/industrial/transport
WS8	42.7231792	21.0219837	Midstream	Urban–industrial/transport
WS9	42.7824287	20.9919064	Lower-midstream	Agricultural/settlement/cumulative
WS10	42.8242140	20.9552893	Lower-midstream	Settlement/transport/cumulative
WS11	42.8420180	20.9240534	Downstream	Agricultural/settlement/cumulative
WS12	42.8776290	20.8747332	Downstream	Urban/peri-urban/cumulative
WS13	42.8890689	20.8771270	Downstream	Urban/peri-urban/cumulative
WS14	42.8936166	20.8823112	Downstream	Urban/peri-urban/transport
WS15	42.9007714	20.8740238	Downstream	Terminal downstream section

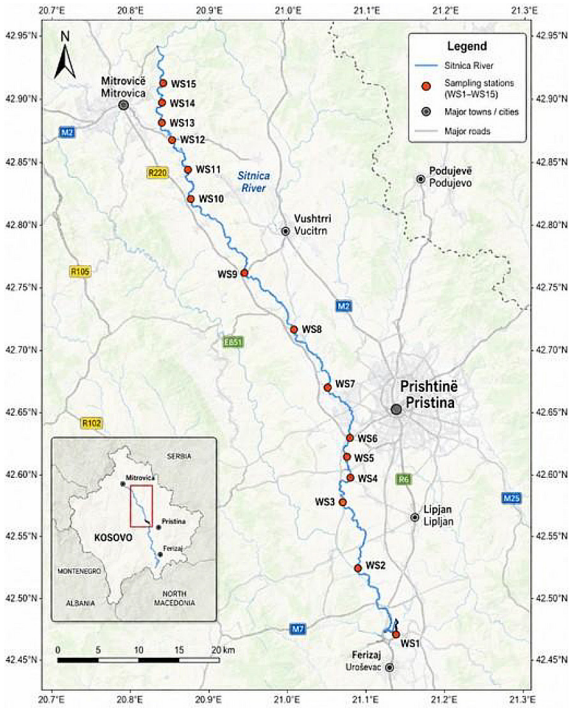

Figure 1. Location of the Sitnica River sampling stations (WS1–WS15) in Kosovo
Note: Sampling stations are arranged along the Sitnica River corridor from the southern upstream section (WS1) towards the northern downstream section near Mitrovica (WS15)

the manufacturer's instructions, using certified calibration buffers and standards appropriate for each parameter. Measurements were taken directly in river water to minimize alterations related to transport, storage, or atmospheric interaction.

Seasonal variation in physicochemical parameters is recognized as an important factor influencing contaminant mobility, partitioning behavior, and degradation dynamics in surface waters (Abdel-Wareth and Abd El-Hamid, 2023).

Laboratory determination of physicochemical indicators

Biochemical oxygen demand (BOD_5)

Five-day biochemical oxygen demand (BOD_5) was determined using VELP automatic respirometric sensors under controlled laboratory conditions. Samples were incubated in sealed respirometric bottles at 20 °C for 5 days, and oxygen consumption was continuously recorded. Final BOD_5 values were obtained directly from the respirometric system according to the manufacturer's specifications.

Chemical oxygen demand (COD)

COD was determined using pre-prepared SPEC COD digestion tubes (16 mm) containing $HgSO_4$. A 2 mL aliquot of each water sample was added to the digestion tube, mixed thoroughly, and digested in an ECO 16 thermoreactor at 150 °C for 2 h. After cooling to room temperature, absorbance was measured using a PF-3 spectrophotometer at the wavelength corresponding to the selected COD range. COD values were calculated according to the manufacturer's calibration specifications.

Nutrients and sulfate (UV-VIS spectrophotometry)

Nutrients and sulfate were quantified using a SCAN ONDA UV 31 spectrophotometer in accordance with ISO-based protocols. Nitrite was determined according to ISO 6777:1984 (ISO, 1984b). Ammonium was determined according to ISO 7150-1:1984 (ISO, 1984a). Nitrate was determined according to ISO 7890-3:1988 (ISO, 1988). Total nitrogen (N-total) was determined after digestion with potassium persulfate ($K_2S_2O_8$), with absorbance measured at 220 and 275 nm, and results expressed as NO_3^- equivalents. Total phosphorus (P-total) was measured after oxidative digestion to orthophosphate and subsequent spectrophotometric determination at 880 nm. Sulfate (SO_4^{2-}) was determined using the turbidimetric Method 9038 (U.S. EPA, 1986) at 420 nm. Reagent blanks and calibration standards were included in each analytical sequence to ensure analytical accuracy and reliability.

Major ions (Cl^-, Ca^{2+}, Mg^{2+})

Chloride was determined using the argentometric Mohr method (4500-Cl^- B). Calcium and magnesium were determined by complexometric titration with EDTA according to Standard Methods (APHA, AWWA, & WEF, 2017). Three replicate titrations were performed for each sample, and the mean value was reported.

Total suspended solids (TSS)

Total suspended solids (TSS) were determined gravimetrically. Water samples were filtered under vacuum through pre-weighed 32-mm glass fiber filters (0.45 µm pore size). Filters were dried at 105 °C for 8 h both before and after filtration. TSS was calculated from the mass difference relative to the filtered sample volume.

Organic pollutants were determined following extraction, chromatographic separation, and instrumental detection procedures. Concentrations are reported in µg/L.

Organic pollutants – organochlorine pesticides (OCPs) and PCBs (GC-ECD)

Extraction and cleanup

A 1.0 L aliquot of each water sample was subjected to liquid-liquid extraction using n-hexane (2 × 40 mL). The combined organic extracts were dried over 5 g of anhydrous Na_2SO_4.

Cleanup was performed using a Florisil column (20 cm × 1.2 cm i.d.) packed with 10 g of Florisil pre-conditioned with n-hexane. Elution was carried out with n-hexane/dichloromethane (4:1, v/v; 20 mL). Extracts were concentrated to 2.0 mL using a Kuderna-Danish concentrator at 70 °C.

GC–ECD analysis

Analysis was performed using a Varian 450 GC equipped with a ^63Ni electron capture detector (ECD) and an Rtx-5 capillary column (30 m × 0.33 mm × 0.25 µm).

The injector and detector temperatures were set at 280 °C and 300 °C, respectively. A 1 µL injection volume was introduced in split mode (1:50). Nitrogen was used as the carrier gas at 1 mL/min and as the make-up gas at approximately 25 mL/min.

The oven temperature program was as follows: initial temperature 70 °C, held for 2 min; increased to 200 °C at 7 °C/min; then to 280 °C at 40 °C/min; and finally to 300 °C at 10 °C/min, with a final hold of 10 min.

Compound identification was based on retention-time matching with certified reference standards, while quantification was performed by six-level external calibration in the concentration range of 5–250 µg/L.

Polycyclic aromatic hydrocarbons (PAHs) (GC-FID)

Thirteen PAHs were determined following liquid-liquid extraction. Samples were first extracted with dichloromethane and subsequently with n-hexane. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated to 2.0 mL.

Analysis was carried out using a Varian 450 GC equipped with a flame ionization detector (FID) and a VF-1ms column (30 m × 0.33 mm × 0.25 µm).

The injector and detector temperatures were set at 280 °C and 300 °C, respectively. Injections were performed in splitless mode. Helium was used as the carrier gas at a flow rate of 1 mL/min, while hydrogen (30 mL/min) and air (300 mL/min) served as flame gases. Nitrogen was used as the make-up gas. Identification and quantification were based on retention-time matching and external calibration using certified PAH mixtures.

GC–ECD method for the determination of chlorobenzenes

For the analysis of chlorobenzenes, 5 mL water samples were transferred into 10 mL SPME vials. All vials were fitted with Teflon-lined caps suitable for headspace analysis. Sampling was performed using a manual SPME syringe equipped with a 100 µm PDMS (polydimethylsiloxane) fiber through the Teflon septum. The vial was maintained at 50 °C for 30 min. Desorption of chlorobenzenes was carried out in the gas chromatograph injector at 260 °C for 10 s.

Qualitative analysis and quantitative determination of chlorobenzenes were performed using a Varian GC 450 gas chromatograph equipped with an electron capture detector (ECD). Separation of chlorinated benzene derivatives was achieved using an RTX-5 capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness), which is suitable for their separation (Nuro et al., 2017; Camaj et al., 2024).

Calibration curves for chlorobenzenes were established using standard solutions at concentrations of 12.5, 25, 50, 100, and 250 µg/L.

Determination of BTEX compounds (HS-SPME-GC/FID)

Benzene, toluene, ethylbenzene, and xylene isomers (BTEX) were determined by headspace solid-phase microextraction coupled with gas chromatography and flame ionization detection (HS-SPME-GC/FID). The method followed GC/FID principles for non-halogenated volatile organic compounds (U.S. Environmental Protection Agency, 2003) and standardized or previously reported HS-SPME approaches for BTEX analysis in water (Halo et al., 2023; International Organization for Standardization, 2016).

Analyses were performed using a Varian 450 GC system equipped with an FID and PTV

injector. Separation was achieved on a VF-1ms capillary column (30 m × 0.33 mm i.d., 0.25 µm film thickness). The injector and detector temperatures were maintained at 280 °C and 300 °C, respectively, and samples were introduced in splitless mode. Hydrogen and air were used as flame gases, while nitrogen served as the carrier and make-up gas.

Headspace extraction was performed under controlled analytical conditions using an SPME fibre, with three parallel injections for each sample. Method performance was assessed in terms of repeatability, linearity, LOD, and LOQ. Calibration curves were prepared using certified BTEX standards at 12.5, 25, 50, 100, and 250 µg/L, and the 50 µg/L standard was used for retention-time confirmation (Halo et al., 2023).

Quality assurance and quality control (QA/QC)

Sampling, preservation, and handling procedures followed ISO 5667-3:2018 guidelines to ensure sample integrity and minimize contamination during collection, transport, and storage. All glassware used for extraction and chromatographic analysis was solvent-rinsed and oven-dried before use. Quality assurance and quality control included calibration with certified reference standards, verification of instrumental performance, and evaluation of linearity, limits of detection and quantification, and recovery for each analyte group.

The applied methods showed satisfactory analytical performance, with coefficients of determination ranging from 0.9925 to 0.9983, LODs from 0.005 to 0.1 µg/L, LOQs from 0.015 to 0.3 µg/L, and recoveries from 73.6% to 101.7%, depending on the analyte group. The main validation characteristics are summarized in Table 2.

Data treatment and statistical analysis

Physicochemical parameters and nutrients were expressed in mg/L, whereas organic pollutants, including OCPs, PCBs, PAHs, chlorobenzenes, and BTEX compounds, were reported in µg/L. All datasets were checked for completeness, transcription errors, outliers, and analytical consistency prior to interpretation.

Descriptive statistics, including mean, median, minimum, maximum, and standard deviation (SD), were calculated for each sampling campaign and analyte group. For organic contaminants, values below the limit of quantification (LOQ) were reported as <LOQ. For descriptive statistical purposes only, concentrations below the LOQ were substituted with LOQ/2 in order to reduce bias in summary statistics.

Seasonal differences between the high-flow and low-flow campaigns were evaluated using station-level paired data from the 15 monitoring stations, because the same stations were sampled during both campaigns. The normality of paired differences was assessed using the Shapiro–Wilk test. When the paired differences were normally distributed, a paired t-test was applied; otherwise, the Wilcoxon signed-rank test was used. Statistical significance was considered at $p < 0.05$.

Table 2. Summary of validation parameters for the determination of organic pollutants in Sitnica River water samples

Analyte group	Target analytes (n)	Preparation method	Instrumental method	Calibration range/levels (µg/L)	R^2	LOD (µg/L)	LOQ (µg/L)	Recovery (%)
OCPs	21	LLE, Na_2SO_4 drying, Florisil cleanup	GC–ECD	5–250	0.9965	0.009–0.021	0.03–0.07	77.1–95.8
Indicator PCBs	7	LLE, Na_2SO_4 drying, Florisil cleanup	GC–ECD	5–250	0.9983	0.015–0.05	0.05–0.15	78.8–96.5
PAHs	13	LLE, Na_2SO_4 drying, alumina cleanup	GC–FID	12.5–250	0.9970	0.005–0.008	0.015–0.025	73.6–101.7
Chlorobenzenes	1	HS-SPME, PDMS fiber	HS-SPME–GC–ECD	12.5–250	0.9925	0.005–0.05	0.02–0.15	91.6
BTEX	4	HS-SPME, triplicate injections	HS-SPME–GC–FID	12.5–250	0.9952	0.01–0.1	0.03–0.3	78.7

RESULTS AND DISCUSSION

Physicochemical characteristics of river water

A summary of mean physicochemical parameters for the two sampling campaigns is presented in Table 3. The river showed slightly alkaline conditions during both campaigns, with mean pH values of 8.18 during the high-flow campaign and 8.22 during the low-flow campaign. Water temperature varied only slightly, increasing from 16.22 °C to 16.61 °C.

Several parameters were higher during the low-flow campaign. Electrical conductivity increased from 967.17 to 994.09 µS/cm, while BOD_5 and COD increased from 19.14 to 26.54 mg/L and from 123.99 to 134.67 mg/L, respectively. TSS also increased from 138.78 to 149.79 mg/L. Nutrient-related parameters followed the same general pattern, with nitrate increasing from 42.71 to 44.59 mg/L and slight increases also observed for total nitrogen and total phosphorus.

Overall, the physicochemical results indicate persistent anthropogenic influence in the Sitnica River, with more pronounced effects during the low-flow campaign. The higher conductivity, organic load, suspended solids, and nutrient levels under reduced-flow conditions suggest lower dilution capacity and provide an important context for interpreting the seasonal occurrence and distribution of organic pollutants.

Table 3. Summary of mean physicochemical parameters of Sitnica River water during the high-flow and low-flow sampling campaigns in 2023

Parameter	February/March 2023	September 2023
pH	8.18	8.22
Temperature (°C)	16.22	16.61
Conductivity (µS/cm)	967.17	994.09
BOD_5 (mg/L)	19.14	26.54
COD (mg/L)	123.99	134.67
TSS (mg/L)	138.78	149.79
NO_3^- (mg/L)	42.71	44.59
NO_2^- (mg/L)	0.39	0.43
NH_4^+ (mg/L)	0.05	0.06
N-total (mg/L)	17.64	18.44
PO_4^{3-} (mg/L)	0.73	0.80
P-total (mg/L)	1.64	1.80
SO_4^{2-} (mg/L)	50.32	50.63
Cl^- (mg/L)	105.12	111.86
Ca^{2+} (mg/L)	59.34	62.82
Mg^{2+} (mg/L)	25.43	27.37

Organochlorine pesticides in surface water

Descriptive statistics for individual OCPs and grouped pesticide classes detected in Sitnica River water during the high-flow and low-flow sampling campaigns are summarized in Table 4. Concentrations are expressed in µg/L. The spatial distribution of total OCP concentrations and the seasonal profile of grouped OCP classes are presented in Figures 2 and 3.

Legacy organochlorine pesticides were detected during both sampling campaigns, but their composition differed between the high-flow and low-flow periods (Table 4). During the high-flow campaign, the highest mean concentrations among individual compounds were observed for δ-HCH (3.419 µg/L), Endosulfan I (3.063 µg/L), and Heptachlor (2.845 µg/L). The maximum values reached 10.250 µg/L for δ-HCH, 9.210 µg/L for Heptachlor, and 16.848 µg/L for Endosulfan II. For several compounds, low median values together with elevated maximum values indicated right-skewed distributions and localized concentration peaks along the river course.

During the low-flow campaign, the OCP profile shifted toward higher mean concentrations of α-Chlordane (1.302 µg/L), Endosulfan sulfate (1.098 µg/L), 4,4′-DDE (0.728 µg/L), and Dieldrin (0.683 µg/L). The highest maximum values during this campaign were recorded for α-Chlordane and Endosulfan sulfate, both reaching 12.455 µg/L, while 4,4′-DDE and Methoxychlor reached 5.058 µg/L. These results indicate that localized concentration peaks occurred under both hydrological conditions.

When OCPs were grouped into pesticide classes, the seasonal shift became more evident (Table 4; Figure 3). During the high-flow campaign, the grouped OCP profile was dominated by ΣEndosulfanes (4.457 µg/L), ΣHCHs (4.242 µg/L), ΣHeptachlors (3.160 µg/L), and ΣAldrins (2.581 µg/L). In contrast, during the low-flow campaign, the highest grouped concentrations were observed for ΣChlordanes (2.047 µg/L), followed by ΣDDTs (1.588 µg/L), ΣEndosulfanes (1.545 µg/L), and ΣAldrins (1.462 µg/L). This change suggests that hydrological conditions influenced not only the total concentration of OCPs, but also the relative contribution of different pesticide classes.

Table 4. Descriptive statistics of individual and grouped OCPs in Sitnica River water during the high-flow and low-flow campaigns (μg/L)

OCPs	High-flow mean ± SD	High-flow min–max	High-flow median	Low-flow mean ± SD	Low-flow min–max	Low-flow median
Individual OCPs						
α-HCH	0.507 ± 0.808	0.000–2.745	0.079	0.129 ± 0.174	0.009–0.621	0.060
β-HCH	0.250 ± 0.427	0.007–1.559	0.034	0.123 ± 0.171	0.013–0.651	0.049
Lindane	0.066 ± 0.165	0.000–0.658	0.024	0.051 ± 0.089	0.000–0.232	0.000
δ-HCH	3.419 ± 3.233	0.017–10.250	2.580	0.140 ± 0.182	0.004–0.570	0.063
Heptachlor	2.845 ± 3.236	0.000–9.210	2.210	0.327 ± 0.603	0.000–2.288	0.034
Aldrin	0.314 ± 0.450	0.000–1.373	0.046	0.098 ± 0.178	0.000–0.528	0.000
Heptachlor epoxide	0.315 ± 0.714	0.000–2.745	0.032	0.003 ± 0.011	0.000–0.044	0.000
γ-Chlordane	0.891 ± 2.702	0.000–10.553	0.034	0.745 ± 1.451	0.000–5.009	0.110
Endosulfan I	3.063 ± 2.784	0.000–7.258	2.580	0.054 ± 0.158	0.000–0.616	0.000
α-Chlordane	0.369 ± 1.013	0.000–3.739	0.000	1.302 ± 3.228	0.000–12.455	0.019
4,4′-DDE	0.082 ± 0.226	0.000–0.882	0.004	0.728 ± 1.481	0.000–5.058	0.032
Dieldrin	0.464 ± 0.871	0.000–2.751	0.021	0.683 ± 1.163	0.000–2.973	0.033
Endrin	0.102 ± 0.223	0.000–0.876	0.019	0.160 ± 0.323	0.000–1.140	0.033
Endosulfan II	1.240 ± 4.336	0.000–16.848	0.000	0.393 ± 1.154	0.000–4.484	0.005
4,4′-DDD	0.411 ± 1.041	0.000–3.739	0.012	0.139 ± 0.310	0.000–1.120	0.021
Endrin aldehyde	0.088 ± 0.273	0.000–1.071	0.005	0.410 ± 0.844	0.016–3.325	0.088
4,4′-DDT	0.244 ± 0.700	0.000–2.751	0.014	0.130 ± 0.199	0.000–0.616	0.067
Endosulfan sulfate	0.153 ± 0.306	0.000–1.104	0.054	1.098 ± 3.215	0.008–12.455	0.108
Methoxychlor	0.047 ± 0.064	0.000–0.193	0.017	0.591 ± 1.391	0.000–5.058	0.081
Endrin ketone	1.613 ± 1.814	0.000–4.360	0.077	0.111 ± 0.156	0.000–0.548	0.046
Mirex	0.014 ± 0.031	0.000–0.102	0.000	0.102 ± 0.286	0.000–1.120	0.000
Grouped OCP classes						
ΣHCHs	4.242 ± 3.180	0.114–10.306	3.439	0.443 ± 0.443	0.072–1.490	0.298
ΣHeptachlors	3.160 ± 3.247	0.052–9.517	2.405	0.330 ± 0.602	0.000–2.288	0.035
ΣChlordanes	1.260 ± 3.659	0.000–14.292	0.121	2.047 ± 3.828	0.000–13.267	0.119
ΣAldrins	2.581 ± 1.980	0.055–6.498	2.694	1.462 ± 1.544	0.103–3.904	0.572
ΣDDTs	0.784 ± 1.247	0.000–3.846	0.239	1.588 ± 1.953	0.009–5.329	0.362
ΣEndosulfanes	4.457 ± 6.043	0.043–24.221	2.663	1.545 ± 4.314	0.008–16.939	0.190
ΣOCPs	16.499 ± 12.953	6.461–49.294	12.588	7.517 ± 9.469	0.569–30.792	2.566

Total OCP concentrations, calculated as the sum of all individual OCP compounds at each station, were higher during the high-flow campaign, with a mean value of 16.499 μg/L, compared with 7.517 μg/L during the low-flow campaign (Table 4). The maximum ΣOCPs reached 49.294 μg/L during the high-flow campaign and 30.792 μg/L during the low-flow campaign. The spatial distribution of ΣOCPs across stations WS1–WS15 showed clear variability along the river course (Figure 2), indicating that OCP contamination was not uniform and was influenced by site-specific inputs or remobilization processes within the catchment.

The occurrence of both parent OCP compounds and transformation products confirms the persistence and mobility of legacy pesticides in the Sitnica River basin (Table 4; Figures 2 and 3). The dominance of ΣEndosulfanes, ΣHCHs, and ΣHeptachlors during the high-flow campaign may reflect runoff-driven mobilization of historically contaminated soils, riverbank deposits, and suspended particulate matter, as high-flow conditions can promote the remobilization and downstream transport of hydrophobic organic pollutants.

During the low-flow campaign, the increased relative contribution of ΣChlordanes, ΣDDTs,

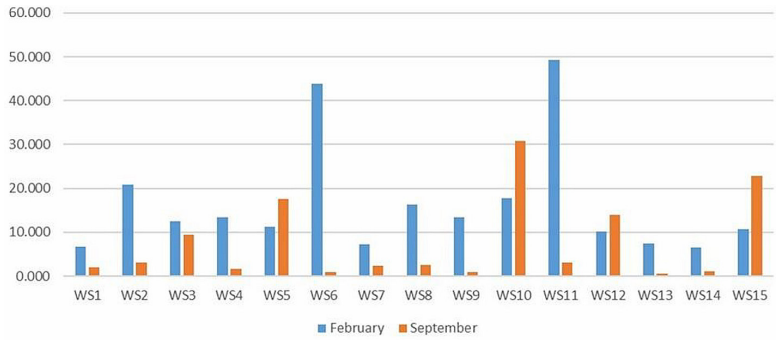

Figure 2. Total organochlorine pesticide concentrations (ΣOCPs, µg/L) at monitoring stations WS1–WS15 in the Sitnica River

and selected degradation products such as DDE, Endosulfan sulfate, and Heptachlor epoxide suggests the influence of aged residues, transformation processes, and sediment–water exchange. Similar seasonal shifts from parent compounds toward metabolites have been reported in Mediterranean and Balkan river systems (Vryzas et al., 2009; Nuro et al., 2014).

Comparison with EU Environmental Quality Standards (Directive 2008/105/EC, as amended by Directive 2013/39/EU) suggests that selected OCP concentrations may be environmentally relevant, particularly at stations with elevated peak values. Overall, OCP occurrence in the Sitnica River is consistent with reports from other Western Balkan river systems, where legacy pesticides remain detectable long after restriction or prohibition (Nuro et al., 2014).

Polychlorinated biphenyls (PCBs)

PCB marker congeners were detected in water samples from the Sitnica River during both sampling campaigns. Descriptive statistics for the seven PCB marker congeners and total PCB concentrations are summarized in Table 5. The spatial distribution of total PCB concentrations across stations WS1–WS15 is shown in Figure 4, while the mean congener profile is presented in Figure 5.

During the high-flow campaign, total PCB concentrations were considerably higher than during the low-flow campaign. The mean ΣPCB concentration was 14.296 µg/L in February/March, compared with 1.941 µg/L in September. The highest ΣPCB value was recorded during the high-flow campaign, reaching 60.712 µg/L, while the maximum value during the low-flow campaign was 4.885 µg/L. These results indicate strong spatial variability and suggest that PCB occurrence was influenced by localized inputs and hydrological mobilization processes.

As shown in Figure 4, total PCB concentrations varied substantially among sampling stations. During the high-flow campaign, the highest values were observed at WS7 and WS10, followed by WS8, WS11, WS9, WS6, and WS14. During the low-flow campaign, concentrations were generally lower, although moderate elevations were observed at selected stations, particularly WS4, WS12, WS10, and WS1. This spatial

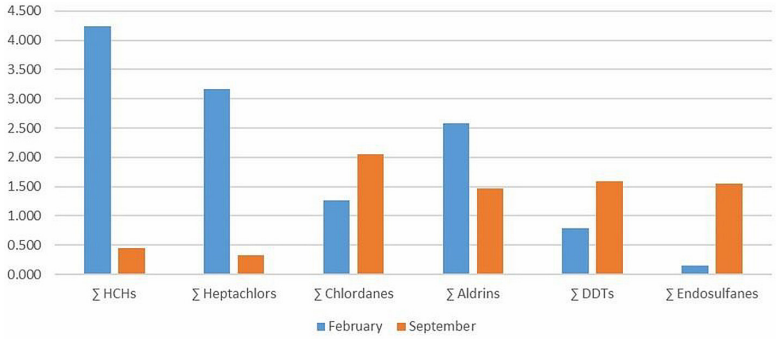

Figure 3. Mean concentrations of grouped OCP classes (ΣHCHs, ΣHeptachlors, ΣChlordanes, ΣAldrins, ΣDDTs, and ΣEndosulfanes) during the high-flow and low-flow campaigns (µg/L)

Table 5. Descriptive statistics of PCB marker congeners in Sitnica River water during the high-flow and low-flow campaigns

PCB congener	High-flow mean ± SD	High-flow min–max	High-flow median	Low-flow mean ± SD	Low-flow min–max	Low-flow median
PCB 28	5.505 ± 5.094	0.016–15.470	4.699	0.285 ± 0.512	0.005–1.869	0.067
PCB 52	3.639 ± 6.134	0.000–21.257	0.947	0.430 ± 0.553	0.000–2.132	0.278
PCB 101	0.867 ± 2.084	0.000–7.916	0.074	0.005 ± 0.018	0.000–0.069	0.000
PCB 118	2.114 ± 4.474	0.000–13.591	0.028	0.199 ± 0.239	0.000–0.817	0.110
PCB 153	0.977 ± 2.891	0.000–11.250	0.015	0.489 ± 0.955	0.000–2.973	0.054
PCB 138	1.189 ± 3.304	0.000–12.580	0.021	0.432 ± 1.121	0.000–4.346	0.053
PCB 180	0.005 ± 0.015	0.000–0.056	0.000	0.101 ± 0.231	0.000–0.817	0.000
ΣPCBs	14.296 ± 16.226	0.546–60.712	7.142	1.941 ± 1.523	0.213–4.885	1.283

Note: Concentrations are expressed in µg/L. ΣPCBs represents the summed concentration of the seven PCB marker congeners for each monitoring station.

pattern suggests that PCB contamination was not uniform along the river course and may reflect site-specific inputs, runoff-related transport, or resuspension of contaminated particles during higher-flow conditions.

The congener-specific distribution also differed between the two campaigns (Table 5; Figure 5). During the high-flow campaign, PCB 28 and PCB 52 showed the highest mean concentrations, reaching 5.505 µg/L and 3.639 µg/L, respectively. PCB 118, PCB 138, PCB 153, and PCB 101 were also detected, but with lower mean values. During the low-flow campaign, overall PCB concentrations decreased markedly; however, PCB 153, PCB 138, and PCB 52 showed relatively higher contributions compared with the other congeners. PCB 180 remained low in both campaigns, although its mean value was slightly higher during the low-flow period.

The coexistence of lighter congeners, such as PCB 28 and PCB 52, with heavier congeners, such as PCB 138, PCB 153, and PCB 180, suggests mixed contamination patterns in the Sitnica River basin. The higher PCB levels observed during the high-flow campaign may indicate enhanced mobilization of particle-associated residues, runoff-driven transport, or resuspension of historically contaminated material. Similar PCB profiles have been reported in Balkan and European river systems affected by historical industrial activity and sediment-bound contamination (Nuro et al., 2017; Breivik et al., 2002). Although PCB concentrations were not uniformly elevated across all stations, their spatial variability and persistence remain environmentally relevant due to the potential for bioaccumulation and biomagnification in aquatic food webs.

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) were detected in water samples from the Sitnica River during both sampling campaigns. Descriptive statistics for individual PAH compounds and total PAH concentrations are summarized in Table

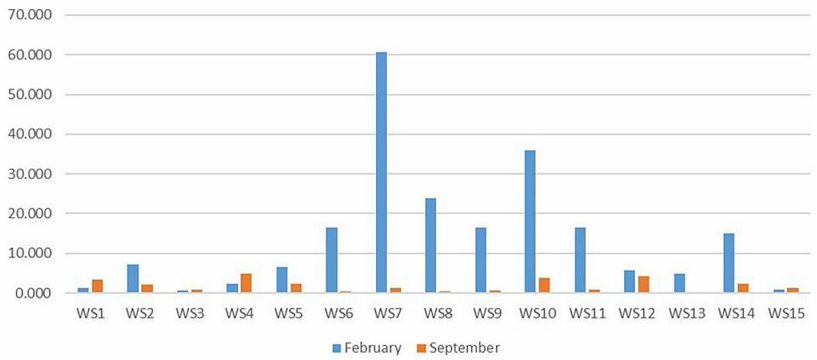

Figure 4. Total PCB marker concentrations (µg/L) measured at monitoring stations WS1–WS15 along the Sitnica River

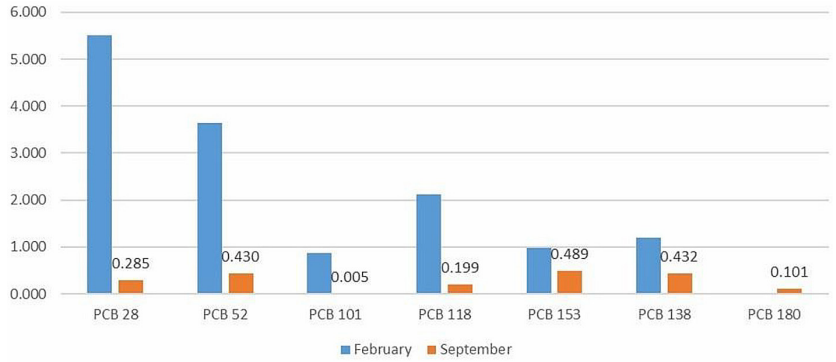

Figure 5. Comparative congener profile of PCB markers (mean concentrations, µg/L) detected in Sitnica River water during February and September 2023

6. The spatial distribution of total PAH concentrations across stations WS1–WS15 is presented in Figure 6, while the mean profile of individual PAH compounds is shown in Figure 7.

Total PAH concentrations were higher during the low-flow campaign than during the high-flow campaign. The mean ΣPAH concentration increased from 4.726 µg/L in February/March to 10.862 µg/L in September. The maximum ΣPAH value was also substantially higher during the low-flow campaign, reaching 42.829 µg/L, compared with 11.494 µg/L during the high-flow campaign. These results indicate that PAH occurrence in the Sitnica River was influenced by both seasonal hydrological conditions and localized inputs.

As shown in Figure 6, total PAH concentrations varied both spatially and seasonally. During the high-flow campaign, the highest concentrations were observed mainly at WS4, WS2, WS3, and WS5, indicating moderate PAH occurrence along the upper-midstream and midstream sections. During the low-flow campaign, more pronounced peaks were recorded at WS12, WS1, WS13, and WS11, suggesting site-specific inputs or episodic contamination under reduced-flow conditions. The observed variability indicates that PAH contamination was not uniform along the river course and may reflect differences in runoff, local anthropogenic inputs, and sediment–water interactions.

Table 6. Descriptive statistics of individual and total PAHs in Sitnica River water during the high-flow and low-flow campaigns

PAH compound	High-flow mean ± SD	High-flow min–max	High-flow median	Low-flow mean ± SD	Low-flow min–max	Low-flow median
Acenaphthylene	0.352 ± 0.391	0.000–1.115	0.185	2.403 ± 5.924	0.000–21.961	0.194
Fluorene	0.486 ± 0.465	0.005–1.493	0.373	2.253 ± 4.590	0.000–13.890	0.399
Phenanthrene	0.344 ± 0.289	0.000–0.819	0.398	0.602 ± 1.043	0.000–3.535	0.074
Anthracene	0.816 ± 1.016	0.000–3.813	0.490	0.627 ± 1.192	0.000–4.022	0.115
Pyrene	0.259 ± 0.320	0.000–0.970	0.094	1.105 ± 3.109	0.000–11.974	0.023
Benzo[a]anthracene	0.379 ± 0.458	0.000–1.759	0.259	2.023 ± 5.065	0.000–19.286	0.030
Chrysene	0.531 ± 0.574	0.000–1.349	0.392	0.656 ± 1.077	0.000–3.582	0.008
Perylene	0.268 ± 0.365	0.000–1.125	0.016	0.262 ± 0.577	0.000–2.204	0.000
Benzo[b]fluoranthene	0.317 ± 0.402	0.000–1.312	0.127	0.147 ± 0.304	0.000–1.012	0.000
Benzo[k]fluoranthene	0.328 ± 0.484	0.000–1.322	0.000	0.647 ± 1.625	0.000–5.751	0.000
Indeno[1,2,3-cd]pyrene	0.262 ± 0.478	0.000–1.587	0.000	0.088 ± 0.210	0.000–0.750	0.000
Dibenzo[a,b]anthracene	0.161 ± 0.382	0.000–1.377	0.000	0.049 ± 0.191	0.000–0.738	0.000
Benzo[ghi]perylene	0.223 ± 0.489	0.000–1.595	0.000	0.000 ± 0.000	0.000–0.000	0.000
ΣPAHs	4.726 ± 3.160	0.777–11.494	3.501	10.862 ± 12.873	0.060–42.829	3.487

Note: Concentrations are expressed in µg/L. ΣPAHs represents the summed concentration of all measured PAH compounds for each monitoring station.

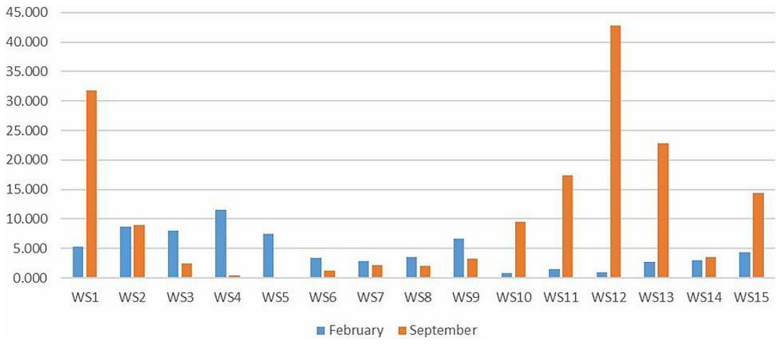

Figure 6. Spatial distribution of total polycyclic aromatic hydrocarbons (PAHs) (µg/L) in water samples from the Sitnica River during February and September 2023

The compound-specific profile showed the presence of both low molecular weight (LMW) and high molecular weight (HMW) PAHs (Table 6; Figure 7). During the high-flow campaign, the highest mean concentrations were observed for Anthracene, Chrysene, Fluorene, Benzo[a]anthracene, and Acenaphthylene. During the low-flow campaign, the highest mean concentrations were observed for Acenaphthylene, Fluorene, Benzo[a] anthracene, Pyrene, and Chrysene. The pronounced increase of selected PAHs during the low-flow campaign, particularly Acenaphthylene, Fluorene, Benzo[a]anthracene, and Pyrene, indicates localized enrichment under reduced dilution conditions.

LMW PAHs are generally associated with petrogenic inputs, including fuel-related contamination, lubricants, urban runoff, and direct hydrocarbon discharges, whereas HMW PAHs are commonly linked to pyrogenic sources such as incomplete combustion, traffic emissions, industrial activities, and open burning. The simultaneous occurrence of LMW and HMW PAHs therefore suggests mixed petrogenic and pyrogenic sources within the Sitnica River basin. This pattern is consistent with urban areas, traffic corridors, fuel-related activities, small industrial facilities, and mechanical workshops along parts of the catchment, and is comparable to mixed-source PAH patterns reported in Balkan surface waters (Magi et al., 2002).

Because several PAHs are persistent, hydrophobic, and strongly associated with suspended particles and sediments, their localized increases remain environmentally relevant even when contamination is not uniformly distributed along the river course. A detailed comparison with European Environmental Quality Standards and potential exceedances is provided in the regulatory comparison section.

BTEX compounds (benzene, toluene, ethylbenzene and xylenes)

BTEX compounds were detected in water samples from the Sitnica River during both sampling campaigns. Descriptive statistics for individual BTEX compounds and total BTEX concentrations are summarized in Table 7. The spatial distribution of total BTEX concentrations across stations WS1–WS15 is presented in Figure 8, while the mean profile of individual BTEX compounds is shown in Figure 9.

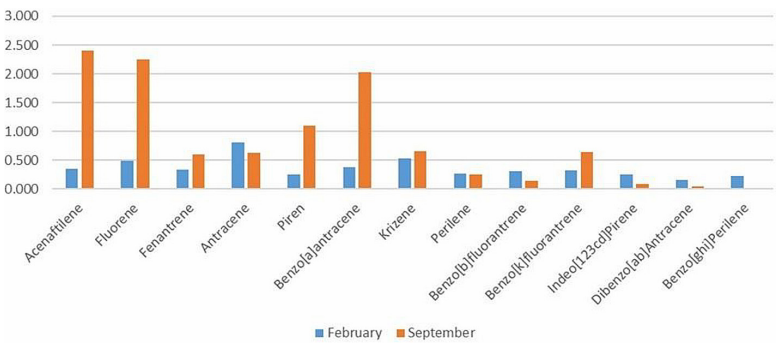

Figure 7. Comparative profile of individual PAH compounds (mean concentrations, µg/L) in Sitnica River

Total BTEX concentrations were higher during the low-flow campaign than during the high-flow campaign. The mean ΣBTEX concentration increased from 3.144 µg/L in February/March to 9.879 µg/L in September. The maximum ΣBTEX value also increased markedly, from 7.013 µg/L during the high-flow campaign to 33.063 µg/L during the low-flow campaign. These results indicate a stronger influence of recent or ongoing urban, transport-related, or petroleum-associated inputs under reduced-flow conditions.

As shown in Figure 8, total BTEX concentrations varied both spatially and seasonally. During the high-flow campaign, concentrations were moderate and relatively more evenly distributed, with the highest values observed at WS4, WS5, WS9, WS12, and WS1. During the low-flow campaign, substantially higher concentrations were recorded at selected stations, particularly WS10, WS13, WS11, and WS14. This pattern suggests localized petroleum-related, transport-related, or urban–industrial inputs under reduced dilution conditions.

The individual BTEX profile also changed between the two campaigns (Table 7; Figure 9). During the high-flow campaign, benzene showed the highest mean concentration, followed by toluene and m-xylene. During the low-flow campaign, benzene and ethylbenzene showed the highest mean concentrations, while o-xylene and m-xylene also increased compared with the high-flow period. The pronounced increase in benzene, ethylbenzene, and xylene isomers during September indicates seasonal enrichment of volatile aromatic hydrocarbons under reduced-flow conditions.

BTEX compounds are commonly associated with petroleum products, vehicle emissions, fuel handling, solvent use, mechanical workshops, and accidental hydrocarbon releases. Considering the land-use context summarized in Table 1, the elevated BTEX values at WS10, WS11, WS13, and WS14 are consistent with site-specific urban, transport-related, or peri-urban influences along the lower river course. Unlike more persistent contaminants such as OCPs and PCBs, BTEX compounds are more volatile and biodegradable; therefore, their presence generally indicates recent or ongoing contamination rather than historical residues.

Although BTEX compounds are less persistent than OCPs, PCBs, and many PAHs, their localized increases remain environmentally relevant, particularly because benzene is toxic and carcinogenic. The low-flow campaign therefore appears to represent a more critical period for BTEX accumulation in the Sitnica River, most likely due to reduced dilution capacity and the stronger influence of local inputs. A detailed comparison with relevant environmental guideline values and potential exceedances is provided in the regulatory comparison section.

Chlorobenzenes in surface water

Chlorobenzenes were detected in Sitnica River water during both sampling campaigns. Descriptive statistics for individual chlorobenzene compounds and total chlorobenzene concentrations are summarized in Table 8. The spatial distribution of total chlorobenzenes across stations WS1–WS15 is presented in Figure 10, while the mean compound profile is shown in Figure 11.

Total chlorobenzene concentrations showed clear spatial variability during both campaigns. The mean ΣChlorobenzene concentration was slightly higher during the high-flow campaign,

Table 7. Descriptive statistics of individual and total BTEX compounds in Sitnica River water during the high-flow and low-flow campaigns

BTEX compound	High-flow mean ± SD	High-flow min–max	High-flow median	Low-flow mean ± SD	Low-flow min–max	Low-flow median
Benzene	1.096 ± 1.039	0.005–3.654	0.901	2.656 ± 3.727	0.109–14.579	0.940
Toluene	0.730 ± 0.985	0.003–3.698	0.334	0.847 ± 1.134	0.000–3.864	0.354
Ethylbenzene	0.145 ± 0.195	0.000–0.659	0.056	2.434 ± 3.273	0.000–11.626	1.111
m-Xylene	0.480 ± 0.609	0.000–1.978	0.188	1.356 ± 1.403	0.000–3.899	0.910
p-Xylene	0.391 ± 0.492	0.000–1.615	0.154	0.766 ± 1.177	0.000–4.142	0.267
o-Xylene	0.304 ± 0.459	0.000–1.401	0.004	1.820 ± 1.627	0.000–4.972	2.026
ΣBTEX	3.144 ± 1.847	0.061–7.013	3.066	9.879 ± 8.763	1.394–33.063	7.444

Note: Concentrations are expressed in µg/L. ΣBTEX represents the summed concentration of benzene, toluene, ethylbenzene, and xylene isomers for each monitoring station.

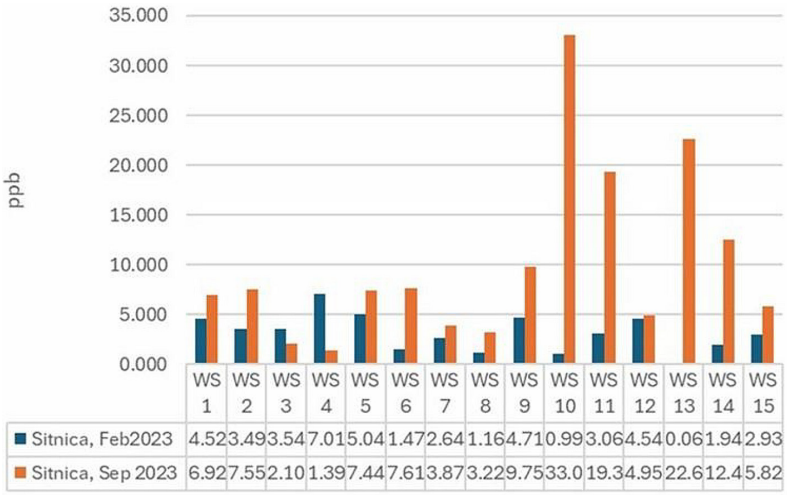

Figure 8. Spatial distribution of total BTEX compounds (µg/L) in water samples from the Sitnica River

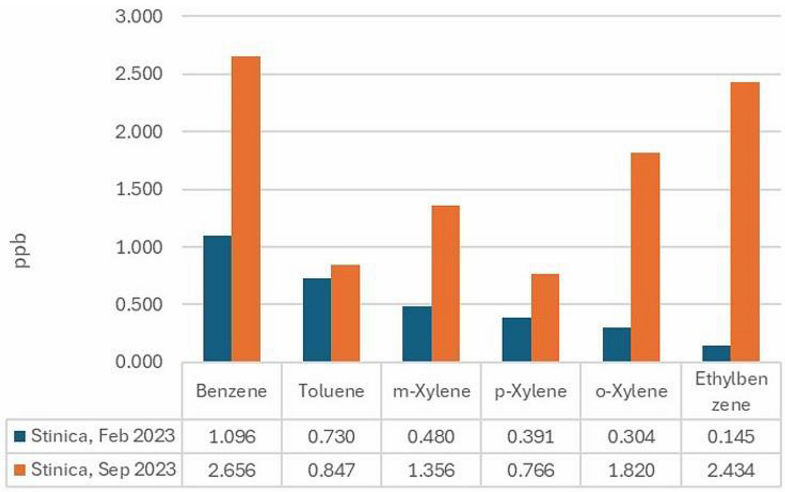

Figure 9. Comparative profile of individual BTEX compounds (mean concentrations, µg/L) in Sitnica River water during February and September 2023

with a value of 2.850 µg/L, compared with 2.156 µg/L during the low-flow campaign. However, the highest localized value was observed during the low-flow campaign, reaching 5.537 µg/L, compared with 4.760 µg/L during the high-flow campaign. This indicates that chlorobenzene contamination was not uniformly distributed along the river and was influenced by localized inputs or site-specific transport processes.

As shown in Figure 10, the highest total chlorobenzene concentrations during the high-flow campaign were observed at WS3, WS6, WS10, WS7, WS8, and WS12. During the low-flow campaign, the most pronounced values were recorded at WS8, WS4, WS15, WS3, and WS11. This distribution suggests that chlorobenzene occurrence was controlled by localized contamination patterns rather than a uniform longitudinal increase along the river course.

The compound-specific profile also differed between the two campaigns (Table 8; Figure 11). During the high-flow campaign, the highest mean concentrations were observed for 1,4-Dichlorobenzene, 1,2-Dichlorobenzene, Chlorobenzene, and 1,3-Dichlorobenzene. During the low-flow campaign, the profile shifted toward higher mean concentrations of Pentachlorobenzene, 1,3,5-Trichlorobenzene, 1,2,3-Trichlorobenzene, and HCB. This pattern indicates that both lower-chlorinated and higher-chlorinated benzene derivatives were present in the river water, with seasonal differences in their relative contribution.

The detection of chlorobenzenes together with OCPs, PCBs, PAHs, and BTEX confirms

Table 8. Descriptive statistics of individual and total chlorobenzenes in Sitnica River water during the high-flow and low-flow campaigns

Chlorobenzene compound	High-flow mean ± SD	High-flow min–max	High-flow median	Low-flow mean ± SD	Low-flow min–max	Low-flow median
Chlorobenzene	0.371 ± 0.304	0.000–0.875	0.408	0.171 ± 0.408	0.000–1.613	0.038
1,2-Dichlorobenzene	0.394 ± 0.467	0.000–1.615	0.224	0.151 ± 0.304	0.000–1.100	0.022
1,3-Dichlorobenzene	0.352 ± 0.547	0.000–1.910	0.053	0.139 ± 0.156	0.013–0.527	0.089
1,4-Dichlorobenzene	0.542 ± 0.589	0.000–1.349	0.392	0.195 ± 0.415	0.016–1.658	0.057
1,3,5-Trichlorobenzene	0.272 ± 0.326	0.000–1.091	0.122	0.361 ± 0.583	0.009–1.797	0.131
1,2,3-Trichlorobenzene	0.258 ± 0.507	0.000–2.007	0.083	0.261 ± 0.443	0.018–1.797	0.158
1,2,4-Trichlorobenzene	0.233 ± 0.206	0.000–0.633	0.280	0.113 ± 0.139	0.010–0.446	0.051
Tetrachlorobenzene	0.149 ± 0.158	0.000–0.456	0.111	0.164 ± 0.240	0.010–0.719	0.067
Pentachlorobenzene	0.183 ± 0.268	0.000–0.948	0.047	0.401 ± 1.100	0.000–4.346	0.044
Hexachlorobenzene (HCB)	0.097 ± 0.111	0.000–0.350	0.038	0.200 ± 0.206	0.007–0.653	0.140
ΣChlorobenzenes	2.850 ± 1.368	0.217–4.760	2.627	2.156 ± 2.007	0.254–5.537	1.028

Note: Concentrations are expressed in µg/L. ΣChlorobenzenes represents the summed concentration of all measured chlorobenzene compounds for each monitoring station.

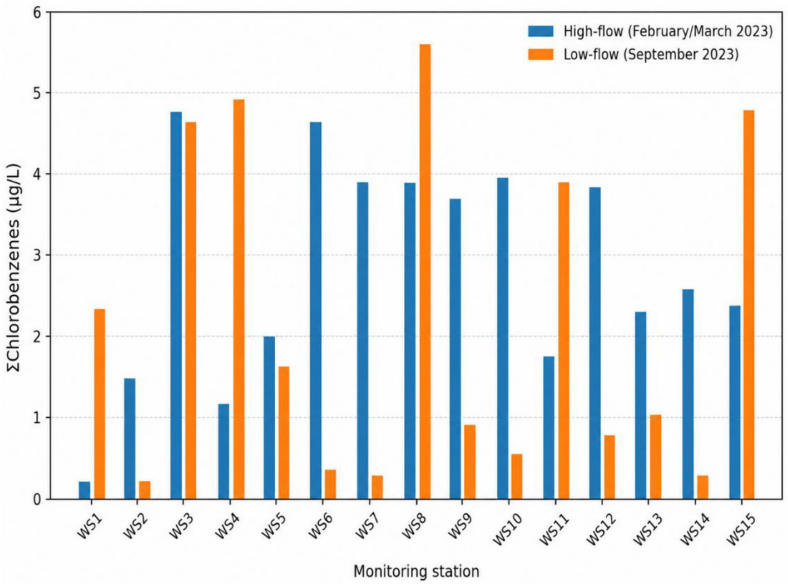

Figure 10. Spatial distribution of total chlorobenzene concentrations (ΣChlorobenzenes, µg/L) measured at monitoring stations WS1–WS15 along the Sitnica River during February/March and September 2023

the presence of multiple classes of organic pollutants in the Sitnica River. Lower-chlorinated compounds may indicate more recent or more mobile inputs, whereas higher-chlorinated compounds such as Pentachlorobenzene and HCB are more persistent and may reflect legacy contamination, sediment interaction, or remobilization processes. Although chlorobenzene concentrations were not uniformly elevated across all stations, their occurrence remains relevant because these compounds can contribute to cumulative organic pollutant exposure in the aquatic environment. A detailed comparison with relevant environmental quality standards and potential ecological implications is provided in the following section.

Seasonal statistical comparison of major pollutant groups

To evaluate whether the observed differences between the high-flow and low-flow campaigns were statistically meaningful, the summed concentrations of the major pollutant groups were compared between the two sampling periods using

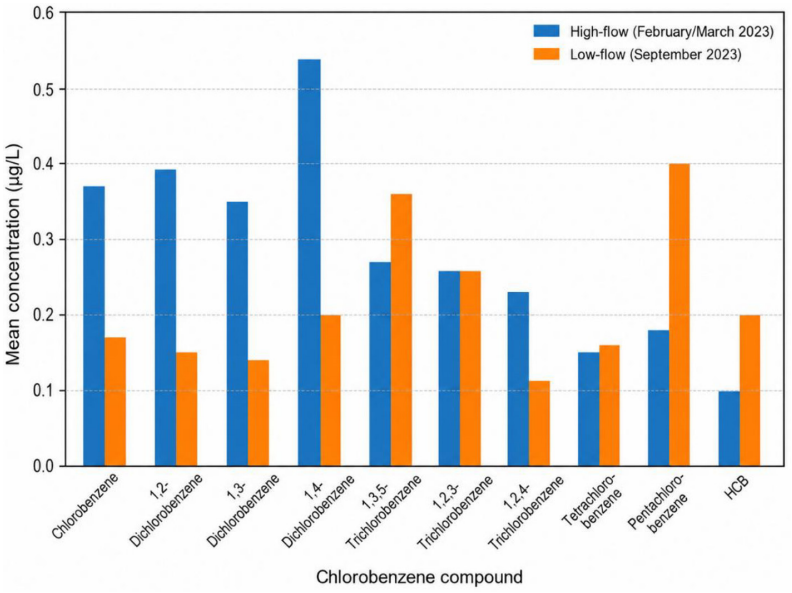

Figure 11. Comparative profile of individual chlorobenzene compounds (mean concentrations, µg/L) in Sitnica River water during February/March and September 2023

paired statistical tests. Since the same monitoring stations were sampled during both campaigns, the comparison was performed on paired station-level data. Normality of paired differences was assessed, and either a paired t-test or a Wilcoxon signed-rank test was applied as appropriate. Statistical significance was considered at $p < 0.05$ (Table 9).

The statistical comparison showed that not all observed seasonal differences were significant. Total PCB concentrations were significantly higher during the high-flow campaign ($p = 0.004$), indicating that PCB occurrence was strongly influenced by hydrological mobilization, runoff-related transport, or resuspension of contaminated particles. Total OCP concentrations were also higher during the high-flow campaign; however, this difference was not statistically significant at the $p < 0.05$ level ($p = 0.061$), suggesting a strong increasing tendency but considerable spatial variability among stations.

In contrast, total BTEX concentrations were significantly higher during the low-flow campaign ($p = 0.005$). This result supports the interpretation that volatile aromatic hydrocarbons were more strongly influenced by recent or ongoing local inputs under reduced dilution conditions. Although total PAH concentrations were higher during the low-flow campaign, the difference was not statistically significant ($p = 0.124$), mainly because PAH concentrations were strongly affected by localized peaks at selected stations. Total chlorobenzene concentrations did not differ significantly between the two campaigns ($p = 0.316$), indicating that their distribution was more site-specific than seasonally uniform.

Overall, the statistical results confirm that seasonal hydrological conditions influenced the distribution of organic pollutants in the Sitnica River, but the response differed among pollutant groups. PCBs were more associated with the high-flow period, BTEX compounds were more characteristic of the low-flow period, while OCPs, PAHs, and chlorobenzenes showed pronounced spatial variability with localized concentration peaks.

Comparison with environmental quality standards and ecological implications

To address the environmental relevance of the measured concentrations, selected compounds were compared with available European Environmental Quality Standards (EQS) for inland surface waters, mainly those established under Directive 2008/105/EC and Directive 2013/39/EU. Only compounds or compound groups for which relevant water-column EQS values were available and comparable with the measured analytes were included in this assessment. The comparison should be interpreted as a screening-level evaluation rather than a formal compliance assessment, because the EU annual average EQS values are based on long-term monitoring data, whereas the present study was based on two seasonal sampling campaigns (Table 10).

Table 9. Seasonal statistical comparison of major organic pollutant groups in Sitnica River water

Pollutant group	High-flow mean ± SD	Low-flow mean ± SD	High-flow median	Low-flow median	Statistical test	p-value	Seasonal pattern
ΣOCPs	16.499 ± 12.953	7.517 ± 9.469	12.588	2.566	Paired t-test	0.061	Higher in high-flow, not significant
ΣPCBs	14.296 ± 16.226	1.941 ± 1.523	7.142	1.283	Wilcoxon signed-rank test	0.004	Significantly higher in high-flow
ΣPAHs	4.726 ± 3.160	10.862 ± 12.873	3.501	3.487	Paired t-test	0.124	Higher in low-flow, not significant
ΣBTEX	3.144 ± 1.847	9.879 ± 8.763	3.066	7.444	Wilcoxon signed-rank test	0.005	Significantly higher in low-flow
ΣChlorobenzenes	2.850 ± 1.368	2.156 ± 2.007	2.627	1.028	Paired t-test	0.316	No significant seasonal difference

Note: Concentrations are expressed in µg/L. Statistical comparisons were performed using paired station-level data from the 15 monitoring stations. Differences were considered statistically significant at $p < 0.05$.

The comparison with environmental quality standards showed that several measured organic pollutants reached concentrations of potential environmental concern. The most pronounced exceedances were observed for legacy organochlorine pesticides, particularly ΣHCHs, heptachlor and heptachlor epoxide, ΣEndosulfanes, cyclodiene pesticides, and ΣDDTs. These exceedances were not limited to a single isolated location, suggesting that historical pesticide residues remain widely distributed within the Sitnica River system. Their persistence, hydrophobicity, and potential association with suspended particles and sediments may support their remobilization during high-flow conditions.

For PCBs, a direct water-column comparison with the selected EU EQS list was not applied to the seven PCB marker congeners, because the available European regulatory framework does not provide directly comparable water-column EQS values for these individual marker congeners in the same way as for several other priority substances. Nevertheless, the elevated ΣPCB values observed during the high-flow campaign remain environmentally relevant because PCBs are persistent, bioaccumulative, and capable of biomagnification in aquatic food webs.

Among PAHs, exceedances were observed for selected compounds, particularly anthracene and high-molecular-weight PAHs such as benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[ghi]perylene. These compounds are generally associated with combustion-related sources, traffic emissions, industrial activities, and particle-bound transport. Their localized peaks indicate that PAH contamination in the Sitnica River is not uniformly distributed, but may be linked to specific inputs or sediment-associated remobilization.

For BTEX compounds, benzene exceeded the annual average EQS at one low-flow station, while the maximum allowable concentration was not exceeded. This pattern suggests localized and probably recent petroleum-related or urban input rather than widespread BTEX contamination. Because BTEX compounds are relatively volatile and biodegradable compared with OCPs, PCBs, and several PAHs, their occurrence is more indicative of ongoing or recent contamination.

Chlorobenzenes also showed environmentally relevant patterns. Pentachlorobenzene and hexachlorobenzene exceeded their annual average EQS values at several stations, while trichlorobenzenes also exceeded the relevant EQS at selected locations. These results indicate that chlorinated aromatic compounds contribute to the overall burden of organic pollution in the Sitnica River, together with OCPs, PCBs, PAHs, and BTEX.

Overall, the regulatory comparison indicates that the Sitnica River is affected by a mixture of legacy and more recent organic pollutants. Legacy pesticides, PCBs, and chlorinated aromatic compounds point to persistent historical contamination and possible sediment-related remobilization, whereas PAHs and BTEX indicate ongoing urban, transport-related, petroleum-related, and combustion-derived inputs. The occurrence of multiple pollutant classes, together with localized exceedances and seasonal shifts, suggests potential cumulative ecological pressure on the aquatic environment. These findings support the need for continued seasonal monitoring, source identification, sediment assessment, and risk-oriented river-basin management in the Kosovo Plain.

Table 10. Screening-level comparison of selected measured organic pollutants with European environmental quality standards for inland surface waters

Compound / group	Relevant EQS value used for comparison (µg/L)	Maximum measured concentration (µg/L)	Exceedance pattern	Environmental interpretation
Benzene	AA-EQS: 10; MAC-EQS: 50	14.579	AA-EQS exceeded at one low-flow station; MAC-EQS not exceeded	Localized petroleum-related or urban input
ΣHCHs	AA-EQS: 0.020; MAC-EQS: 0.040	10.306	Exceeded in all samples from both campaigns	Widespread legacy pesticide contamination
Heptachlor + heptachlor epoxide	AA-EQS: 2×10^{-7}; MAC-EQS: 3×10^{-4}	9.517	Exceeded in nearly all samples	High environmental concern due to very low EQS values and persistence
ΣEndosulfanes	AA-EQS: 0.005; MAC-EQS: 0.010	24.221	Exceeded in almost all samples	Persistent pesticide residues and possible remobilization from soils or sediments
Measured cyclodiene pesticides (aldrin + dieldrin + endrin)	AA-EQS: 0.010	3.735	Exceeded in most samples	Legacy cyclodiene pesticide contamination
Measured DDT-related compounds (DDE + DDD + DDT)	AA-EQS: 0.025	5.288	Exceeded in most samples	Aged residues and transformation products of historical DDT use
Anthracene	AA-EQS: 0.100; MAC-EQS: 0.100	4.022	Exceeded at several stations in both campaigns	PAH-related ecological concern, especially at localized peaks
Benzo[b]fluoranthene	MAC-EQS: 0.017	1.312	Exceeded at selected stations	Indicates potential influence of pyrogenic PAH sources
Benzo[k]fluoranthene	MAC-EQS: 0.017	5.751	Exceeded at selected stations	Localized high-molecular-weight PAH enrichment
Benzo[ghi]perylene	MAC-EQS: 0.0082	1.595	Exceeded at selected high-flow stations	Particle-associated PAH contamination
Pentachlorobenzene	AA-EQS: 0.007	4.346	Exceeded in most samples	Persistent chlorinated aromatic contamination
Hexachlorobenzene	AA-EQS: 0.050; MAC-EQS: 10	0.653	AA-EQS exceeded at several stations; MAC-EQS not exceeded	Legacy chlorinated pollutant signal
ΣTrichlorobenzenes	AA-EQS: 0.400	3.854	Exceeded at several stations	Localized chlorinated aromatic contamination

Note: AA-EQS = annual average environmental quality standard; MAC-EQS = maximum allowable concentration environmental quality standard. The comparison is intended as a screening-level assessment based on the measured concentrations from two seasonal sampling campaigns and should not be interpreted as a formal annual compliance assessment. For compound groups, the comparison was based on the summed concentration of the measured analytes included in each group.

CONCLUSIONS

This study provides a seasonally resolved assessment of physicochemical conditions and selected organic contaminants in the Sitnica River under contrasting hydrological conditions. The results showed that the river remains under continuous anthropogenic pressure, particularly during the low-flow campaign, when higher organic load, nutrient-related parameters, ionic content, and suspended solids indicated reduced dilution capacity and stronger influence of local inputs.

The detection of OCPs, PCB marker congeners, PAHs, BTEX compounds, and chlorobenzenes confirms the coexistence of multiple classes of organic pollutants in the Sitnica River basin. OCPs, PCBs, and chlorobenzenes indicate the persistence and possible remobilization of legacy pollutants from historically contaminated soils, sediments, or riverbank deposits. In contrast, PAHs and BTEX compounds reflect more recent or ongoing inputs related to petroleum activities, combustion sources, traffic, urban runoff, and other local anthropogenic pressures.

The seasonal statistical comparison showed that pollutant groups responded differently to hydrological conditions. Total PCB concentrations were significantly higher during the high-flow campaign, suggesting enhanced mobilization or resuspension of particle-associated residues. In contrast, total BTEX concentrations were significantly higher during the low-flow campaign, indicating stronger influence of recent local inputs under reduced dilution conditions. OCPs, PAHs, and chlorobenzenes showed pronounced spatial variability, with localized concentration peaks rather than uniform seasonal changes along the entire river course.

The comparison with environmental quality standards indicated that selected compounds, particularly legacy organochlorine pesticides, selected PAHs, benzene, pentachlorobenzene, hexachlorobenzene, and trichlorobenzenes, reached concentrations of potential environmental concern at specific stations. These findings highlight that the Sitnica River is affected by both historical and ongoing sources of organic pollution. Although contamination was not uniform along the river course, the occurrence of multiple pollutant classes and localized exceedances suggests potential cumulative ecological pressure on the aquatic environment.

Overall, this study provides important baseline information for interpreting seasonal organic pollution in the Sitnica River and supports risk-oriented river-basin management in the Kosovo Plain. The findings also highlight the environmental relevance of combined legacy and recent pollutant inputs under contrasting hydrological conditions.

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