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Effects of persistent organic pollutants and mercury in protected area „Obrenovački zabran"

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Abstract: This study aims to assess and monitor the health of an urban protected area by analyzing the levels of persistent organic pollutants (POPs) and mercury (Hg) in soil and sediments. Based on the results, the detected concentrations of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and Hg are above the threshold maximum values for soils, and the prescribed target values for sediments. In the investigated protected area PCBs pose a very high ecological risk. The presence of 16 priority PAHs in analyzed soils and sediments poses a moderate to high cancer risk and Hg poses a considerable health risk to children. The research suggests that preserving urban protected areas is crucial for environmental and urban sustainability. In urban environments these areas should be evaluated in terms of their environmental, eco-geochemical, economic, and socio-cultural dimensions. The value of the existence of this natural oasis lies in its aesthetic and psycho-hydrological impact, local climate regulation, residential isolation, and significant art-architectural and horticultural shaping. The connection between eco-geochemical and management practices, planning, and urban green spaces policy should become an adopted innovation in the cities in the future.

Keywords: mercury; organochlorine pesticides; polybrominated diphenyl ethers; polychlorinated biphenyls; polycyclic aromatic hydrocarbons.

INTRODUCTION

Today half of humanity lives in urban areas. According to the prediction, the urban population will increase to 68 % by 2050.[1] Protected areas with distinct environmental qualities in urban areas require special protection measures. They provide ecosystem services such as nutrient cycling, climate regulation, infiltration

and stabilization of groundwater levels, retention of flood waters, and recreational activities.[2]

When pollutants reach the environment, the effects on the ecosystems and their services will depend on a range of factors, such as persistence, mobility, and their bioavailability. Monitoring of polluting substances can contribute to prevention and elimination of the consequences of degradation processes. The presence of persistent organic pollutants (POPs) and mercury (Hg) in the environment is of great concern due to their toxicity and ability to accumulate in organisms.[3] The POPs and Hg can biomagnify in the food chain, leading to increased concentrations and potential adverse effects in organisms at the top of the food chain.[3]

Among the most important synthetic POPs, organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants.[4] As agricultural chemicals, especially disease control chemicals, OCPs are widely used worldwide. Due to high toxicity and long-term environmental accumulation, OCPs are prohibited from use.[5,6] Since the 1930s, PCBs, due to their properties have found wide application as ideal additives for insulators in electrical equipment.[7] Although PCBs production was banned from the 1970s to the 1980s in most countries, their environmental concentrations are still high in many areas worldwide.[8] In the environment PCBs lead to a public health concern and a decline in wildlife since they are highly persistent, bioaccumulative, and toxic.[9,10,11] Polybrominated diphenyl ethers (PBDEs) are industrial chemicals (flame retardants) that have been used for over 40 years. There are 209 congeneric PBDEs.[12] PBDEs can cause environmental pollution and human health problems.[13,14] Polycyclic aromatic hydrocarbons (PAHs) are of particular concern among pollutants, especially in urban areas. The PAHs have been intensively studied in various parts of the environment as a group of organic pollutants that are carcinogenic, mutagenic, and teratogenic. [15,16]

Hg is released into the environment from natural and anthropogenic sources.[17] The Hg undergoes chemical transformations (primarily by microbiological processes) in the environment and can be changed from inorganic into methylmercury, which can accumulate in living organisms (bioaccumulation) and concentrate up the food chain (biomagnification), especially in the aquatic one.

This study aims to assess and monitor the health of an urban protected area by analyzing the levels of POPs and Hg in soil and sediments. The research hypothesis is that preserving urban protected areas is crucial for environmental and urban sustainability. This research chose a protected area „Obrenovački zabran" (OZ) (Fig. S-1), Serbia, as a case study.

EXPERIMENTAL

Following a combination of a sieve and sedimentation test determination of particle size distribution was done.[18] Soil organic matter (OM) weight percent was determined using the loss

on ignition (LOI) method.[19] Sharing OM content with the conventional "Van Bemmelen factor" of 1.724 total organic carbon (TOC) content was calculated.[20]

For the simultaneous analysis of multiple compounds (OCPs, PCBs, PBDEs, and PAHs) QuEChERS analysis was used. Into 50 ml polypropylene centrifugal tubes were weighed 5 g of sample, 10 ml of water, and 10 ml of acetonitrile. To the suspension were added CHROMABOND QuEChERS Mix I, Extraction, EN 15662, 6.5 g. The tube was centrifuged and the aliquot was placed in the freezer. The cold extract was purified by CHROMABOND QuEChERS Mix VI, Clean-up, EN 15662, 1.2 g. The aliquot was evaporated to almost dry and reconstituted with acetone for gas chromatography (GC) analysis and acetonitrile for liquid chromatography (HPLC) analysis. The OCPs and PBDEs were analyzed by GS with an electron capture detector (GC–ECD). Analysis of PCBs was performed by GC with a mass spectrometry detector (GC–MS). The PAHs were analyzed by HPLC with a diode array detector (HPLC–DAD). The methodology of the sample preparation, quantification of POPs, and quality control assurance was described in detail in a previous publication.[20]

For total Hg content, samples were analyzed using Direct Mercury Analyzer DMA 80 Milestone. The Mercury Atomic Absorption Standard (ref. N: AA34N-1) from AccuStandard manufacturer was used as certified reference material.

To test the differences between studied sites in the content of POPs, TOC values, as well as particle size distribution Principal Component Analysis (PCA) was performed. A more profound comprehension, of the perspective trend of the POPs content feature profile, was realized by embracing the grouped samples' PCA plot. The unrooted cluster tree was performed to visually investigate the likenesses among various samples. Origin 2021 software (OriginLab Corporation, Northampton, MA, USA) was used for the statistical study of the data.

RESULTS AND DISCUSSION

Soil and sediment properties

The TOC content ranged from 8.69 % to 13.58 % with a mean value of 11.59 % and a median value of 12.16 % in soil samples, and from 4.92 % to 5.76 % with a mean value of 5.37 % and a median value of 5.41 % in sediment samples. Particle size data for the 12 sites showed that the majority of samples comprise fine sands (≈ 70 %), silt (≈ 20 %), and clay (≈ 10 %).

Organochlorine pesticides (OCPs) in soil and sediments

The total concentrations of $\sum_{20}$OCP in soil samples in the study area range from not detected (n.d.) to 740 µg kg^{-1}, and in sediment samples from 120 µg kg^{-1} to 330 µg kg^{-1}. The coefficient of variation (CV) of $\sum_{20}$OCP in soil and sediment samples was 58.82 %, which indicates that there is no considerable variation in the content of OCPs in the OZ region.

Among total concentrations of $\sum_{20}$OCP, endrin aldehyde, and endrin ketone accounted for the largest share. Endrin aldehyde and endrin ketone were found in concentrations of n.d. to 190 µg kg^{-1} and n.d. to 120 µg kg^{-1} in soil, and of 40 to 180 µg kg^{-1} and n.d. to 70 µg kg^{-1} in sediment samples. Endrin aldehyde and endrin ketone were never commercial products but occurred as impurities of endrin or as degradation products.[22] In 1951, endrin was first used as a rodenticide, insecticide, and avicide to control voles, cutworms, grasshoppers, and other pests on tobacco,

cotton, sugarcane, grain, and apple orchards.[23] However, endrin has never been used for termite proofing or other applications in urban areas, unlike aldrin/dieldrin.[23] The main reason for discontinuing its use is endrin's toxicity to non-target populations of raptors (birds of prey) and migratory birds. The detected concentrations of endrin in the samples may indicate their earlier application.[22] Aldrin was determined on sites M3 and S5, endrin at site M7, and dieldrin was determined only in soil samples (average concentration 70 µg kg^{-1}). Aldrin is very easily metabolized into dieldrin, as the concentrations of dieldrin in soil samples are higher, the detected concentrations of aldrin in the samples may indicate their earlier application.

The OCPs such as HCHs and DDTs were extensively used in agriculture and forestry.[24,25] The concentrations of $\sum_4$HCH in soil and sediment samples are presented in Fig. 1.

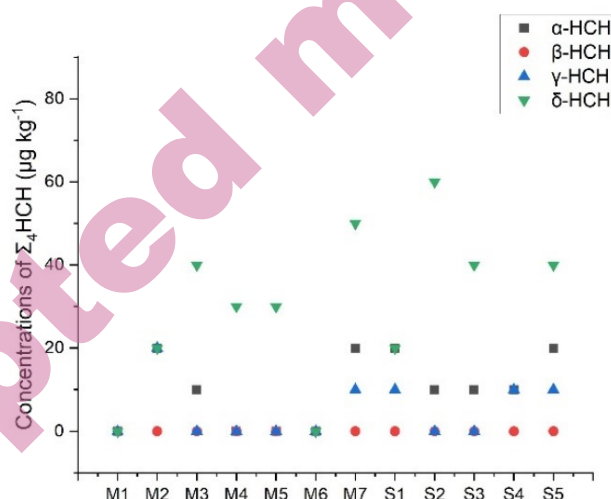Fig. 1. The concentrations of $\sum_4$HCH (µg kg^{-1}) in sediment samples from the Sava River (S1 – S5) and soil samples that are flooded at high Kolubara River groundwater levels (M1 – M7).

In the soil samples, the concentration of $\sum_4$HCH ranged from n.d. to the highest levels found at the sites M6 100 µg kg^{-1}. Sediment samples showed lower $\sum_4$HCH concentrations (n.d. – 60 µg kg^{-1}). Among the HCH isomers, δ-HCH makes up the largest share, while β-HCH was n.d. in the samples (Fig. 2). The residues of δ-HCH could be used as indicators of the historical usage of HCHs.[26] The absence of β-HCH in samples could potentially be explained by the fact that it didn't happen isomerization of γ-to α- and then α-to β-HCH.[27,28] Lindane and technical HCH are two formulations of the pesticide HCHs that are commercially

available. The α-/γ-HCH isomer ratio can be used to distinguish the source of HCHs. The α-/γ-HCH isomer ratio < 3 indicates that HCHs mainly originate from the input of lindane. The α-/γ-HCH isomer ratio > 7 indicates that HCHs probably originated from industrial HCH and the contaminants have been degraded over a long period. In this study, the isomeric HCH composition indicates that the main source of HCHs is lindane (α-/γ-HCH ratio < 3).

In the soil samples concentration of $\sum_3$DDT ranges between n.d. to 70 µg kg^{-1} (highest level at site M3), and sediment samples between 10 µg kg^{-1} to 50 µg kg^{-1} (highest level at site S1). The 4,4′-DDT was the predominant compound in soil samples, followed by 4,4′-DDE, while 4,4′-DDD was n.d. In sediment samples, 4,4′-DDE and 4,4′-DDD were n.d. not in any sample. Lower concentrations of DDE and DDD and the high concentration of DDT in the samples indicate recent use of this pesticide.[29,30,31]The ratio $\sum$DDE + $\sum$DDD)/$\sum$DDTs > 0.5 suggests that accumulated DDT has undergone long-term degradation; whereas a lower ratio indicates recent DDT input. In this study, the ratio between the transformation products ($\sum$DDE +$\sum$DDD) and $\sum$DDTs also indicate recent DDT input. This most likely happened due to the illegal use of DDT for agricultural purposes and for controlling vector-borne diseases in the region. In the OZ region, DDT was not approved for further use in agriculture in the period 1971 – 1973, and in 1989 DDT was banned in forestry, until 1994 it was still used in public health.

Industrial endosulfan contains two main components α- and β-endosulfan in a ratio of 7:3. Since α-endosulfan was determined only in soil samples at site M7, β-endosulfan was detected in soil samples at sites M4, M6, and M7, and endosulfan sulfate was detected in soil with an average concentration of 32 µg kg^{-1} it is suggested that there is no new input of endosulfan in the region, and detected concentrations mainly originates from the historical use of endosulfan that may have been degraded to endosulfan sulfate. The main source of trans and cis chlordane in the environment is industrial chlordane. Its main components include 11 % cis chlordane, 13 % trans chlordane, 5 % heptachlor, and 5 % heptachlor-epoxide. In this study, there is no recent or historical use of chlordane since chlordane and metabolites were n.d. In the soil samples, methoxychlor concentrations ranged between n.d. to 140 µg kg^{-1}, and in sediment samples concentrations ranged between n.d. to 10 µg kg^{-1}. Methoxychlor is an OCP that has been used as a replacement for DDT.

To assess ecotoxicological risks associated with OCP contamination, determined concentrations were compared with national soil and sediment quality guidelines.[32,33] The detected concentrations of OCPs are above the threshold maximum values for soil, and the prescribed target values for sediments. Due to the existence of larger areas under crops near the OZ, it is to be expected that increased use and spreading of herbicides, pesticides, and other protective chemical agents. Beetles and bats of OZ, as carnivores of the first order consumers,

are particularly sensitive to chemical measures in agriculture and the use of insecticides. Accumulation of chemicals in the body of consumers can have a lethal effect, which is transmitted through trophic chains to higher-order consumers.

Polychlorinated biphenyls in soil and sediments

The CV of PCBs in soil and sediment samples was 141.42 %, which indicates that there is considerable variation in the content of PCBs in the OZ region and a high degree of their local enrichment in soil samples (sites M4 and M7). The $\sum_6$PCB in soil samples was in the range between n.d. and 340 µg kg^{-1}, peaking at site M4. The results demonstrated the presence of lower PCB congeners (PCB-28 and PCB-52). Higher concentrations of lower PCB congeners are probably the result of atmospheric deposition rates.[34,35,36] Since they are more volatile, PCB congeners with lower chlorine content can be transported through the atmosphere and deposited at long distances from the emission source.[37]

Although earlier research has shown that river sediment acts as a sink for PCBs[38] in this study, PCBs were n.d. in the sediment samples. The reason for not determining PCBs in sediments from the Sava River can be caused by changes in river flow rate (small movement), depth, direction, breadth, and other morphodynamical factors in the investigated area.[39,40]

Considering that PCBs were n.d. in the sediment samples the national soil quality guideline[33] was used to estimate the contaminants in the OZ region. The $\sum_6$PCB in soil samples are above the threshold maximum values for soil (20 µg kg^{-1}).

To estimate the ecological risk posed by PCBs Hakanson's potential ecological risk index (Er^i) was used.[41,42] The Er^i was calculated normalized concentration using PCB background concentration (10 µg kg^{-1}) and using a toxicity factor of 40.[42] Samples with $Er^i < 40$ have low potential ecological risk, $40 \leq Er^i < 80$ moderate potential ecological risk, $80 \leq Er^i < 160$ considerable potential ecological risk; $160 \leq Er^i < 320$ high potential ecological risk, and with $Er^i \geq 320$ have very high ecological risk. In the OZ region, PCBs pose a very high ecological risk.

Polybrominated diphenyl ethers in soil and sediments

The CV of PBDEs in soil and sediment samples was 94.28 %, which indicates that there is considerable variation in the content of PBDEs in the OZ region and a high degree of their local enrichment in soil samples (sites M4 and M7).

The concentrations of the $\sum_8$PBDE in soil samples ranged from 60 µg kg^{-1} to 170 µg kg^{-1}, and in sediment samples from 10 µg kg^{-1} to 20 µg kg^{-1}. The PBDE-209 was the predominant congener in the soil and sediment samples. This congener is normally detected in high concentrations in soil in e-waste sites.[3] Environmentally unsound management of e-waste results in soil contamination and could lead to the diffusion of PBDEs from the point pollution source to

contaminate the surrounding environment about 5 km from the dumpsites.[43] The possibility of PBDEs from the e-waste recycling area diffusing into the ambient regions could result in a halo pattern of PBDEs contamination to at least 74 km radius.[44] The influence of point pollution sources on the surrounding environment has been termed the "halo effect".[44] The presence of PBDEs in soils from the territory of OZ is probably the consequence of the uncontrolled disposal of e-waste.

National soil and sediment quality guidelines[32,33] do not prescribe threshold maximum values for soils and the prescribed target values for sediments.

Polycyclic aromatic hydrocarbons in soil and sediments

Sixteen target PAHs were detected in all the samples, suggesting the wide distribution of PAHs in the urban stream. The CV of PAHs in soil and sediment samples was 55.19 %, which indicates that there is no considerable variation in the content of PAHs in the OZ region. The $\sum_{16}$PAH in soil samples ranged from 850 µg kg^{-1} to 8880 µg kg^{-1} (mean = 44740 µg kg^{-1}, median = 3910 µg kg^{-1}), and in sediment samples from 7860 µg kg^{-1} to 14620 µg kg^{-1} (mean = 10202 µg kg^{-1}, median = 8780 µg kg^{-1}). The sum of 7 probable human carcinogenic PAHs ($\sum_7$CPAH: BaA, CHR, BbF, BkF, BaP, IND, and dBahA)[45] varied from 100 µg kg^{-1} to 570 µg kg^{-1} (mean = 418 µg kg^{-1}, median = 445 µg kg^{-1}) indicating moderate contamination ($\sum_7$CPAH ranging from 100 µg kg^{-1} to 1000 µg kg^{-1}).[46]

PAHs are primarily released into the environment from petrogenic, pyrogenic, and biogenic sources.[47] To investigate the potential sources of PAHs diagnostic ratios methods have been widely used.[48] Commonly used diagnostic ratios include ANT/(ANT+PHE), IND/(IND+BghiP), BaA/(BaA+CHR) and FLT/(FLT+PYR).[49] In this study, the ratios of IND/(IND+BghiP) were in the range of 0.5 – 1 (combustion), the ratios of ANT/(ANT+PHE) were above 0.5 (combustion), the ratios of BaA/(BaA+CHR) were above 0.6 (combustion), and the ratios of FLT/(FLT+PYR) were above 0.6 (biomass/coal combustion) (Fig. 2).

In the OZ region according to the results, PAHs in soil and sediments mainly come from pyrogenic sources. In the wider surroundings of the observed area, there is a high number of pollution sources. Here, above all, we mean the thermal power plant, which is located about 500 m southeast of OZ and the center of the urban area. Since most sources of PAHs are located in, or near urban centers, PAHs are usually found in high concentrations in aquatic sediments[50,51], which is also the case in this research.

To assess ecotoxicological risks associated with PAHs contamination, determined concentrations were compared with national soil and sediment quality guidelines.[32,33] The detected concentrations of PAHs are above the threshold maximum values for soils, and the prescribed target values for sediments (1000 µg kg^{-1}).
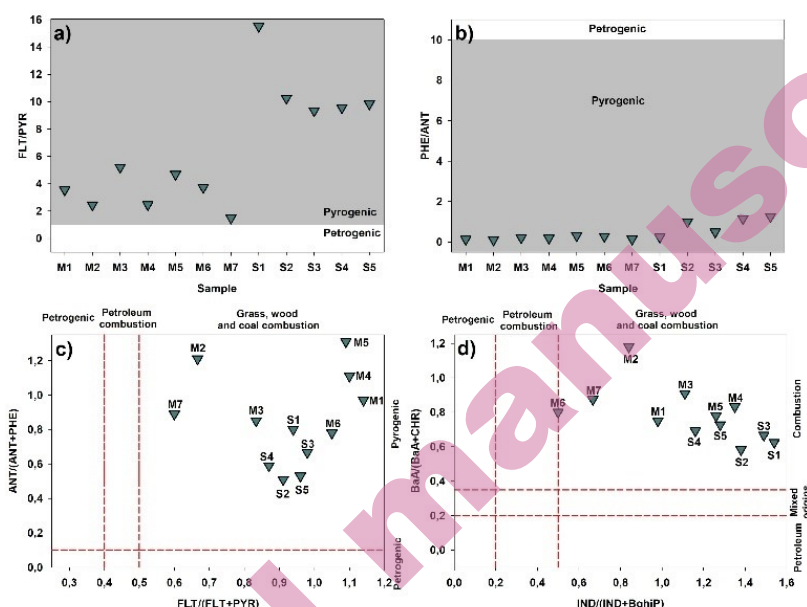
Fig. 2. Molecular relations used for identifying sources of PAH emissions in sediment samples from the Sava River (S1 – S5) and soil samples that are flooded at high Kolubara River groundwater levels (M1 – M7).

Health risk induced by the presence of PAH congeners in the soils can be estimated by calculation of incremental lifetime cancer risk (ILCR) associated with three pathways of exposure: oral ingestion – ILCRing, dermal contact – ILCRderm, and inhalation – ILCRinh[52,53,54]: All the parameters used for ILCRs calculation are given in Table S-I.

Table S-II presents ILCRs and total cancer risks (TCR$_{PAH}$) for children and adults. TCR$_{PAH}$ in soils ranged from 6.1×10^{-4} to 2.9×10^{-3} for adults and from 6.9×10^{-4} to 3.3×10^{-3} for children. The ILCR values can be interpreted as follows: ILCRs $\leq 10^{-6}$ indicate negligible risk, ILCRs in the range of $10^{-6} – 10^{-4}$ are treated as low risk, ILCRs from 10^{-4} to 10^{-3} are considered moderate, and the values between 10^{-3} and 10^{-1} indicate a high health risk to the population.[54] The presence of 16 priority PAHs in analyzed soils and sediments poses moderate to high cancer risk to the population (Table S-II).

Total Hg in soil and sediments

Total Hg concentrations ranged from 0.29 mg kg^{-1} to 3.20 mg kg^{-1} (mean 2.20 mg kg^{-1}, median 2.26 mg kg^{-1}) in soil samples, and from 2.78 mg kg^{-1} to 3.24 mg kg^{-1} (mean 3.05 mg kg^{-1}, median 3.12 mg kg^{-1}) in sediment samples. Results demonstrated a relatively high Hg concentration in the study area. However, the distribution of Hg in sediments of the Sava River was studied in more detail. The

elevated Hg concentration is partly the consequence of a geological anomaly, that is, a natural Hg enrichment of the upstream Slovenian drainage basins of the Sava River.[60] Earlier research found a 100-fold Hg enrichment in deep overbank sediments, as compared to the surface sediment, and attributed this to an even higher Hg input from the Slovenian catchment area in the past. As the number of samples taken during this screening is limited, definite conclusions on Hg contamination levels will have to wait for more detailed research.

Health risks induced by Hg in soils were estimated by applying the model proposed by the United States Environmental Protection Agency (US EPA).[61] Three possible mechanisms of exposure were considered (ingestion, inhalation, and dermal contact) to assess carcinogenic and non-carcinogenic risks from Hg. The methodology of risk determination was described in detail in a previous publication.[62]

Non-carcinogenic risk was estimated through hazard quotients (HQ) for ingestion (HQing), inhalation (HQinh), and dermal exposure (HQder). Descriptive statistics of these quotients are shown in Table S-III for both children and adults.

The effect of soil Hg pollution intake through inhalation is negligible compared to ingestion and dermal exposure. Summing up HQs from all three exposure pathways' hazard indexes HI were obtained. A hazard index higher than 1 implies an increased possibility of incidence of non-carcinogenic harmful health effects.[61] Hg in the analyzed soil poses a considerable health risk to children who are generally more sensitive to environmental pollution than adults.

To assess ecotoxicological risks associated with Hg contamination, determined concentrations were compared with national soil and sediment quality guidelines.[31,33] The detected Hg concentrations are above the threshold maximum values for soils, and the prescribed target values for sediments (0.3 mg kg^{-1}).

Differences between studied sites

Cluster analysis engaged the complete linkage algorithm and the City block (Manhattan) distances to estimate the proximity of the samples (Fig. S-2). The linkage distance, between the main clusters was substantial, approximately 8500. Samples M4 and M5 were the most similar, as the samples M6 and M7. Furthermore, the height of the dendrogram indicates the order in which the clusters were joined. The dendrogram shows the big difference between the cluster of soil (M1 – M7) and sediment (S1 – S5) samples, indicating that the two groups of samples differ in chemical properties, particularly different POP concentrations.

The parting within samples can be seen from the PCA analysis (Fig. 3 A, B, C, and D). Samples M4 and M7 are separated according to the highest concentrations of OCPs. Predominant congener PCB-52 and PBDE-209 were in soil sample M4. Sediment samples were differentiated by PAH concentrations.
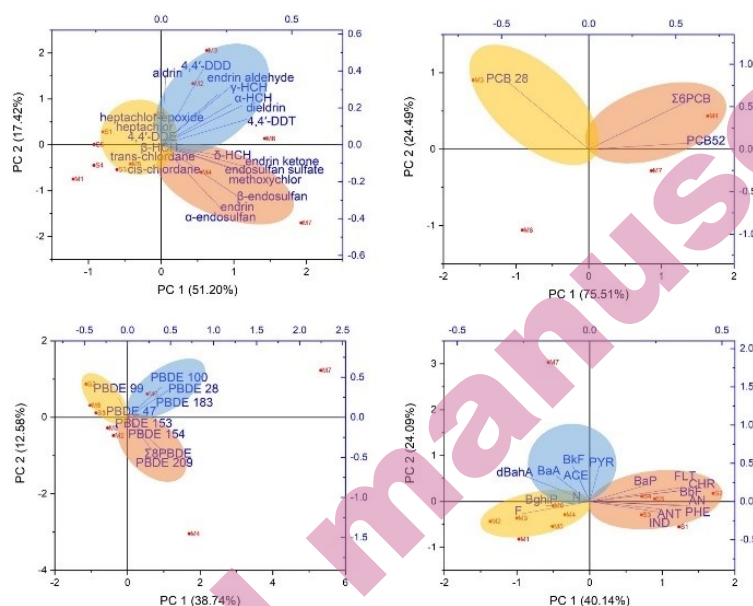
Fig. 3 The PCA biplot diagram describes the relations between the contents of POPs, Hg, soil and sediment properties in sediment samples from the Sava River (S1 – S5) and soil samples that are flooded at high Kolubara River groundwater levels (M1 – M7).

CONCLUSION

Based on the results, the detected concentrations of OCPs, PCBs, PAHs, and Hg are above the threshold maximum values for soils, and the prescribed target values for sediments. In the OZ region, PCBs pose a very high ecological risk. The presence of 16 priority PAHs in analyzed soils and sediments poses a moderate to high cancer risk to the population, and Hg poses a considerable health risk to children who are generally more sensitive to environmental pollution than adults. Based on the results, protected areas in urban environments should receive special attention and should be evaluated regarding their environmental, eco-geochemical, economic, and socio-cultural dimension. One of the reasons for this is that protected area are particularly affected by human action most often due to inferior decision making. Management strategies that incorporate socio-economic activities and the protection of urban protected areas are obligatory for future demands. This should primarily include the valuation of ecosystem services that protected areas provide and the assessment of the pollution status. Urbanization and pollution in general can influence the ability of ecosystems to support the human population. The connection to management, planning, policy, and overall urban green spaces policy represents a new future innovation in the cities.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13034, or from the corresponding author on request.

И З В О Д

УТИЦАЈ ДУГОТРАЈНИХ ОРГАНСКИХ ЗАГАЂУЈУЋИХ СУПСТАНЦИ И ЖИВЕ НА ЗАШТИЋЕНО ПОДРУЧЈЕ „ОБРЕНОВАЧКИ ЗАБРАН"

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Ова студија има за циљ да процени и прати стање урбаног заштићеног подручја анализом нивоа дуготрајних органских загађујућих супстанци (POPs) и живе (Hg) у земљишту и седиментима. На основу резултата, детектоване концентрације органохлорних пестицида (OCP), полихлорованих бифенила (PCB), полицикличних ароматичних угљоводоника (PAH) и Hg су изнад граничних максималних вредности за земљиште и прописаних циљних вредности за седименте. У истраживаном подручју концентрације PCB представљају веома висок еколошки ризик. Укупна концентрације 16 приоритетних PAH-ова у анализираном земљишту и седиментима представља умерен до висок ризик од рака, а концентрације Hg представљају значајан здравствени ризик за децу. Истраживање је показало да је очување урбаних заштићених подручја кључно за одрживост животне средине. У урбаним срединама ове области треба вредновати у смислу њихових еколошких, еко-геохемијских, економских и социо-културних димензија. Вредност постојања ове природне оазе је у њеном естетском и хидролошком утицају, локалној регулацији климе, стамбеној изолованости и значајном уметничко-архитектонском и хортикултурном обликовању. Веза између еко-геохемијских и управљачких пракси, планирања и политике урбаних зелених површина требало би да постане усвојена иновација у градовима у будућности.

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