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 analysing 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 analysed 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 interconnection 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

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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. The monitoring of polluting substances can contribute to the 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 the 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 universal 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.[9–11] The 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] The 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] 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 analysing 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 of Supplementary material to this paper), 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. CHROMABOND QuEChERS Mix I, Extraction, EN 15662, 6.5 g were added to the suspension. 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 analysed by GS with an electron capture detector (GC–ECD). The analysis of PCBs was performed by GC with a mass spectrometry detector (GC–MS). The PAHs were analysed 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, the samples were analysed 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 the 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 ($\approx$ 70 %), silt ($\approx$ 20 %) and clay ($\approx$ 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 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 the total concentrations of $\sum_{20}$OCP, endrin aldehyde, and endrin ketone accounted for the largest share. The Endrin aldehyde and the endrin ketone were found in concentrations of n.d. to 190 µg kg^{-1} and n.d. to 120 µg kg^{-1} in

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115   soil, and of 40 to 180 µg kg^{-1} and n.d. to 70 µg kg^{-1} in sediment samples. The
116   endrin aldehyde and the endrin ketone were never commercial products but
117   occurred as impurities of endrin or as degradation products.[22] In 1951, endrin
118   was first used as a rodenticide, insecticide, and avicide to control voles, cut-
119   worms, grasshoppers and other pests on tobacco, cotton, sugarcane, grain and
120   apple orchards.[23] However, endrin has never been used for termite proofing or
121   other applications in urban areas, unlike aldrin/dieldrin.[23] The main reason for
122   discontinuing its use is endrin's toxicity to non-target populations of raptors
123   (birds of prey) and migratory birds. The detected concentrations of endrin in the
124   samples may indicate their earlier application.[22] Aldrin was determined on sites
125   M3 and S5, endrin at site M7, and dieldrin was determined only in soil samples
126   (average concentration 70 µg kg^{-1}). Aldrin is very easily metabolized into dield-
127   rin, as the concentrations of dieldrin in soil samples are higher, the detected con-
128   centrations of aldrin in the samples may indicate their earlier application.
129   The OCPs such as HCHs and DDTs were extensively used in agriculture and
130   forestry.[24,25] The concentrations of $\sum_4$HCH in soil and sediment samples are
131   presented in Fig. 1.
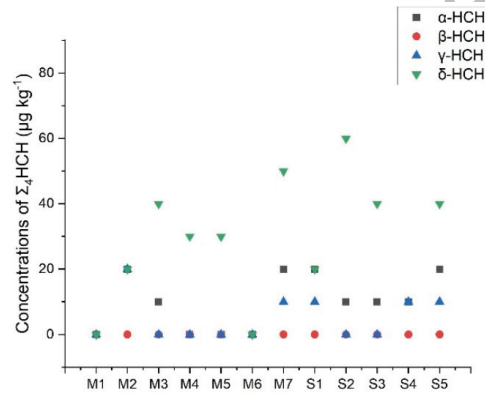
132
133   Fig. 1. The concentrations of $\sum_4$HCH (µg kg^{-1}) in sediment samples from the Sava River
134   (S1–S5) and soil samples that are flooded at high Kolubara River groundwater levels (M1–M7).

135   In the soil samples, the concentration of $\sum_4$HCH ranged from n.d. to the
136   highest levels found at the sites M6 100 µg kg^{-1}. The sediment samples showed
137   lower $\sum_4$HCH concentrations (n.d. – 60 µg kg^{-1}). Among the HCH isomers,
138   δ-HCH makes up the largest share, while β-HCH was n.d. in the samples (Fig. 2).
139   The residues of δ-HCH could be used as indicators of the historical usage of
140   HCHs.[26] The absence of β-HCH in the samples could potentially be explained by

141 the fact that the isomerization of γ- to α- and then α- to β-HCH didn't hap-
142 pen.[27,28] Lindane and technical HCH are two formulations of the pesticide HCHs
143 that are commercially available. The α-/γ-HCH isomer ratio can be used to dis-
144 tinguish the source of HCHs. The α-/γ-HCH isomer ratio < 3 indicates that HCHs
145 mainly originate from the input of lindane. The α-/γ-HCH isomer ratio > 7 indi-
146 cates that HCHs probably originated from industrial HCH and the contaminants
147 have been degraded over a long period. In this study, the isomeric HCH compo-
148 sition indicates that the main source of HCHs is lindane (α-/γ-HCH ratio < 3).
149   In the soil samples concentration of $\sum_3$DDT ranges between n.d. to 70 µg
150 kg^{-1} (highest level at site M3), and sediment samples between 10 to 50 µg kg^{-1}
151 (highest level at site S1). The 4,4′-DDT was the predominant compound in soil
152 samples, followed by 4,4′-DDE, while 4,4′-DDD was n.d. In sediment samples,
153 4,4′-DDE and 4,4′-DDD were n.d. not in any sample. Lower concentrations of
154 DDE and DDD and the high concentration of DDT in the samples indicate recent
155 use of this pesticide.[29–31]The ratio $\sum$DDE + $\sum$DDD)/$\sum$DDTs > 0.5 suggests that
156 accumulated DDT has undergone long-term degradation; whereas a lower ratio
157 indicates recent DDT input. In this study, the ratio between the transformation
158 products ($\sum$DDE +$\sum$DDD) and $\sum$DDTs also indicate recent DDT input. This
159 most likely happened due to the illegal use of DDT for agricultural purposes and
160 for controlling vector-borne diseases in the region. In the OZ region, DDT was
161 not approved for further use in agriculture in the period 1971–1973, and in 1989
162 DDT was banned in forestry, until 1994 it was still used in public health.
163   Industrial endosulfan contains two main components α- and β-endosulfan in
164 a ratio of 7:3. Since α-endosulfan was determined only in soil samples at site M7,
165 β-endosulfan was detected in soil samples at sites M4, M6, and M7, and endo-
166 sulfan sulphate was detected in soil with an average concentration of 32 µg kg^{-1}
167 it is suggested that there is no new input of endosulfan in the region, and that the
168 detected concentrations mainly originates from the historical use of endosulfan
169 that may have been degraded to endosulfan sulphate. The main source of trans
170 and cis chlordane in the environment is industrial chlordane. Its main compo-
171 nents include 11 % cis chlordane, 13 % trans chlordane, 5 % heptachlor and 5 %
172 heptachlor-epoxide. In this study, there is no recent or historical use of chlordane
173 since chlordane and metabolites were n.d. In the soil samples, the methoxychlor
174 concentrations ranged between n.d. to 140 µg kg^{-1}, and in the sediment samples
175 concentrations ranged between n.d. to 10 µg kg^{-1}. Methoxychlor is an OCP that
176 has been used as a replacement for DDT.
177   To assess ecotoxicological risks associated with OCP contamination, deter-
178 mined concentrations were compared with national soil and sediment quality
179 guidelines.[32,33] The detected concentrations of OCPs are above the threshold the
180 maximum values for soil, and the prescribed target values for sediments. Due to
181 the existence of larger areas under crops near the OZ, it is to be expected that the

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182 increased use and the spreading of herbicides, pesticides, and other protective
183 chemical agents would occur. Beetles and bats of OZ, as carnivores of the first
184 order consumers, are particularly sensitive to chemical measures in agriculture
185 and the use of insecticides. The accumulation of chemicals in the body of con-
186 sumers can have a lethal effect, which is transmitted through trophic chains to
187 higher-order consumers.

188 *Polychlorinated biphenyls in soil and sediments*

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

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

203 Considering that PCBs were n.d. in the sediment samples the national soil
204 quality guideline[33] was used to estimate the contaminants in the OZ region. The
205 $\sum_6$PCB in soil samples are above the threshold maximum values for soil (20 μg
206 kg^{-1}).

207 To estimate the ecological risk posed by PCBs Hakanson's potential ecolog-
208 ical risk index (Er^i) was used.[41,42] The Er^i was calculated normalized concen-
209 tration using PCB background concentration (10 μg kg^{-1}) and using a toxicity
210 factor of 40.[42] Samples with $Er^i < 40$ have low potential ecological risk, $40 \leq Er^i$
211 < 80 moderate potential ecological risk, $80 \leq Er^i < 160$ considerable potential
212 ecological risk; $160 \leq Er^i < 320$ high potential ecological risk, and with $Er^i \geq 320$
213 have very high ecological risk. In the OZ region, PCBs pose a very high eco-
214 logical risk.

215 *Polybrominated diphenyl ethers in soil and sediments*

216 The CV of PBDEs in soil and sediment samples was 94.28 %, which indi-
217 cates that there is considerable variation in the content of PBDEs in the OZ reg-
218 ion and a high degree of their local enrichment in soil samples (sites M4 and
219 M7).

220 The concentrations of the $\sum_8$PBDE in soil samples ranged from 60 to 170 μg
221 kg^{-1}, and in sediment samples from 10 to 20 μg kg^{-1}. The PBDE-209 was the
222 predominant congener in the soil and sediment samples. This congener is norm-
223 ally detected in high concentrations in soil in e-waste sites.[3] Environmentally
224 unsound management of e-waste results in soil contamination and could lead to
225 the diffusion of PBDEs from the point pollution source to contaminate the sur-
226 rounding environment about 5 km from the dumpsites.[43] The possibility of PBDEs
227 from the e-waste recycling area diffusing into the ambient regions could result in
228 a halo pattern of PBDEs contamination to at least 74 km radius.[44] The influence
229 of point pollution sources on the surrounding environment has been termed the
230 "halo effect".[44] The presence of PBDEs in soils from the territory of OZ is pro-
231 bably the consequence of the uncontrolled disposal of e-waste.
232 National soil and sediment quality guidelines[32,33] do not prescribe threshold
233 maximum values for soils and the prescribed target values for sediments.

234 *Polycyclic aromatic hydrocarbons in soil and sediments*

235 Sixteen target PAHs were detected in all the samples, suggesting the wide
236 distribution of PAHs in the urban stream. The CV of PAHs in soil and sediment
237 samples was 55.19 %, which indicates that there is no considerable variation in
238 the content of PAHs in the OZ region. The $\sum_{16}$PAH in soil samples ranged from
239 850 to 8880 μg kg^{-1} (mean = 44740 μg kg^{-1}, median = 3910 μg kg^{-1}), and in
240 sediment samples from 7860 to 14620 μg kg^{-1} (mean = 10202 μg kg^{-1}, median =
241 8780 μg kg^{-1}). The sum of 7 probable human carcinogenic PAHs ($\sum_7$CPAH:
242 BaA, CHR, BbF, BkF, BaP, IND and dBahA)[45] varied from 100 to 570 μg kg^{-1}
243 (mean = 418 μg kg^{-1}, median = 445 μg kg^{-1}) indicating moderate contamination
244 ($\sum_7$CPAH ranging from 100 to 1000 μg kg^{-1}).[46]
245 PAHs are primarily released into the environment from petrogenic, pyro-
246 genic and biogenic sources.[47] To investigate the potential sources of PAHs diag-
247 nostic ratios methods have been widely used.[48] Commonly used diagnostic ratios
248 include ANT/(ANT+PHE), IND/(IND+BghiP), BaA/(BaA+CHR) and FLT/
249 /(FLT+PYR).[49] In this study, the ratios of IND/(IND+BghiP) were in the range
250 of 0.5–1 (combustion), the ratios of ANT/(ANT+PHE) were above 0.5 (combust-
251 ion), the ratios of BaA/(BaA+CHR) were above 0.6 (combustion), and the ratios
252 of FLT/(FLT+PYR) were above 0.6 (biomass/coal combustion) (Fig. 2).
253 In the OZ region according to the results, PAHs in soil and sediments mainly
254 come from pyrogenic sources. In the wider surroundings of the observed area,
255 there is a high number of pollution sources. Here, above all, we mean the thermal
256 power plant, which is located about 500 m southeast of OZ and the centre of the
257 urban area. Since most sources of PAHs are located in, or near urban centres,
258 PAHs are usually found in high concentrations in aquatic sediments[50,51], which
259 is also the case in this research.
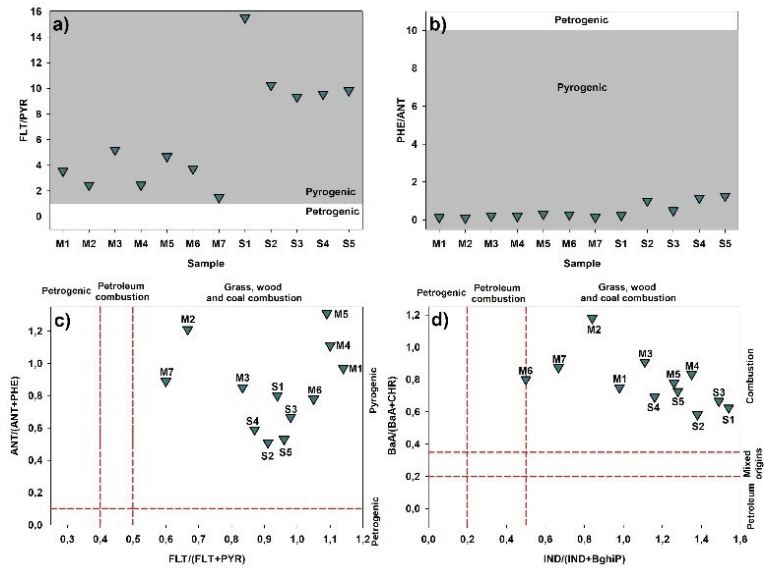
Fig. 2. Molecular relations used for identifying sources of PAH emissions in sediment samples from the Sava River (S1–S5) and soil samples that are flooded at high Kolubara River groundwater levels (M1–M7).

To assess ecotoxicological risks associated with PAHs contamination, the determined concentrations were compared with the 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 ($1000\ \mu g\ kg^{-1}$).

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 – *ILCR*ing, dermal contact – *ILCR*derm and inhalation – *ILCR*inh.[52–54] All the parameters used for *ILCR*s calculation are given in Table S-I.

Table S-II presents *ILCR*s 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: *ILCR*s $\leq 10^{-6}$ indicate negligible risk, *ILCR*s in the range of 10^{-6}–10^{-4} are treated as low risk, *ILCR*s 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

280 presence of 16 priority PAHs in analysed soils and sediments poses moderate to
281 high cancer risk to the population (Table S-II).

282 *Total Hg in soil and sediments*

283 Total Hg concentrations ranged from 0.29 to 3.20 mg kg^{-1} (mean 2.20 mg
284 kg^{-1}, median 2.26 mg kg^{-1}) in soil samples, and from 2.78 to 3.24 mg kg^{-1}
285 (mean 3.05 mg kg^{-1}, median 3.12 mg kg^{-1}) in sediment samples. The results
286 demonstrated a relatively high Hg concentration in the study area. However, the
287 distribution of Hg in sediments of the Sava River was studied in more detail. The
288 elevated Hg concentration is partly the consequence of a geological anomaly, that
289 is, a natural Hg enrichment of the upstream Slovenian drainage basins of the
290 Sava River.[60] Earlier research found a 100-fold Hg enrichment in deep overbank
291 sediments, as compared to the surface sediment, and attributed this to an even
292 higher Hg input from the Slovenian catchment area in the past. As the number of
293 samples taken during this screening is limited, definite conclusions on Hg con-
294 tamination levels will have to wait for more detailed research.

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

301 Non-carcinogenic risk was estimated through hazard quotients (*HQ*) for ing-
302 estion (*HQ*ing), inhalation (*HQ*inh) and dermal exposure (*HQ*der). The descript-
303 ive statistics of these quotients are shown in Table S-III for both children and
304 adults.

305 The effect of soil Hg pollution intake through inhalation is negligible com-
306 pared to ingestion and dermal exposure. Summing up *HQ*s from all three expo-
307 sure pathways' hazard indexes *HI* were obtained. A hazard index higher than 1
308 implies an increased possibility of incidence of non-carcinogenic harmful health
309 effects.[61] Hg in the analysed soil poses a considerable health risk to children who
310 are generally more sensitive to environmental pollution than adults.

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

315 *Differences between studied sites*

316 The cluster analysis engaged the complete linkage algorithm and the City
317 block (Manhattan) distances to estimate the proximity of the samples (Fig. S-2 of
318 the Supplementary material). The linkage distance, between the main clusters

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319   was substantial, approximately 8500. Samples M4 and M5 were the most similar,
320   as the samples M6 and M7. Furthermore, the height of the dendrogram indicates
321   the order in which the clusters were joined. The dendrogram shows the big differ-
322   ence between the cluster of soil (M1–M7) and sediment (S1–S5) samples, indi-
323   cating that the two groups of samples differ in chemical properties, particularly
324   different POP concentrations.
325   The parting within samples can be seen from the PCA analysis (Fig. 3A–D).
326   Samples M4 and M7 are separated according to the highest concentrations of
327   OCPs. Predominant congener PCB-52 and PBDE-209 were in soil sample M4.
328   The sediment samples were differentiated by PAH concentrations.
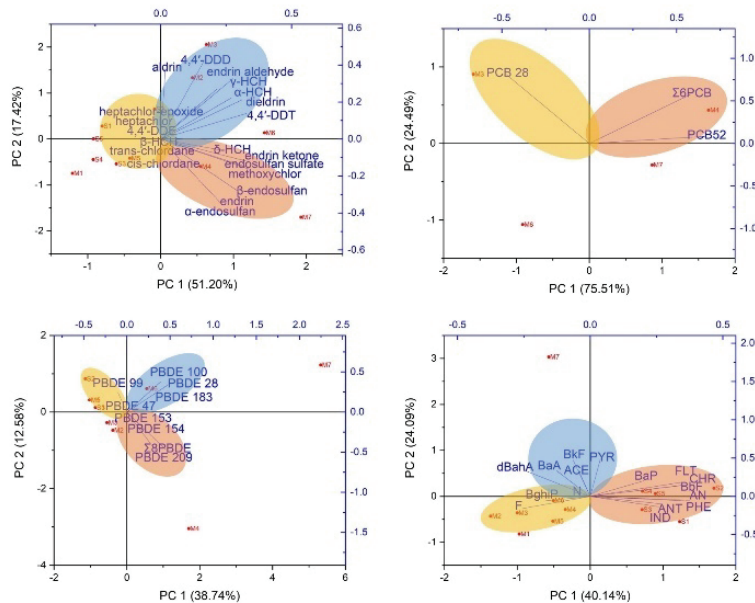
329
330   Fig. 3. The PCA biplot diagram describes the relations between the contents of POPs, Hg, soil
331   and sediment properties in sediment samples from the Sava River (S1–S5) and soil samples
332   that are flooded at high Kolubara River groundwater levels (M1–M7).

333   CONCLUSION

334   Based on the results, the detected concentrations of OCPs, PCBs, PAHs and
335   Hg are above the threshold maximum values and the prescribed target values for
336   sediments for the soils analysed in this reseach. In the OZ region, PCBs pose a
337   very high ecological risk. The presence of 16 priority PAHs in analysed soils and

338 sediments poses a moderate to high cancer risk to the population, and Hg poses a
339 considerable health risk to children who are generally more sensitive to environ-
340 mental pollution than adults. Based on the results, the protected areas in urban
341 environments should receive special attention and should be evaluated regarding
342 their environmental, eco-geochemical, economic and socio-cultural dimension.
343 One of the reasons for this is that the protected area is particularly affected by
344 human action most often due to inferior decision making. The management strat-
345 egies that incorporate socio-economic activities and the protection of urban pro-
346 tected areas are required for future demands. This should primarily include the
347 valuation of ecosystem services that protected areas provide and the assessment
348 of the pollution status. Urbanization and pollution in general can influence the
349 ability of ecosystems to support the human population. The interconnection
350 between management, planning, policy and overall urban green spaces policy
351 represents a new future innovation in the cities.

352 ## SUPPLEMENTARY MATERIAL

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

361 ИЗВОД
362 УТИЦАЈ ДУГОТРАЈНИХ ОРГАНСКИХ ЗАГАЂУЈУЋИХ СУПСТАНЦИ И ЖИВЕ НА
363 ЗАШТИЋЕНО ПОДРУЧЈЕ „ОБРЕНОВАЧКИ ЗАБРАН"

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369 Ова студија има за циљ да процени и прати стање урбаног заштићеног подручја
370 анализом нивоа дуготрајних органских загађујућих супстанци (POPs) и живе (Hg) у
371 земљишту и седиментима. На основу резултата, детектоване концентрације органохлор-
372 них пестицида (OCP), полихлорованих бифенила (PCB), полицикличних ароматичних
373 угљоводоника (PAH) и Hg су изнад граничних максималних вредности за земљиште и
374 прописаних циљних вредности за седименте. У истраживаном подручју концентрације
375 PCB представљају веома висок еколошки ризик. Укупна концентрација 16 приоритетних
376 PAH у анализираном земљишту и седиментима представља умерен до висок ризик од
377 рака, а концентрације Hg представљају значајан здравствени ризик за децу. Истра-
378 живање је показало да је очување урбаних заштићених подручја кључно за одрживост
379 животне средине. У урбаним срединама ове области треба вредновати у смислу њихових
380 еколошких, еко-геохемијских, економских и социо-културних димензија. Вредност

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381 постојања ове природне оазе је у њеном естетском и хидролошком утицају, локалној
382 регулацији климе, стамбеној изолованости и значајном уметничко-архитектонском и
383 хортикултурном обликовању. Повезаност између еко-геохемијских и управљачких
384 пракси, планирања и политике урбаних зелених површина требало би да постане усво-
385 јена иновација у градовима у будућности.

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

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STUDY AREA

The protected area „Obrenovački zabran" (OZ) is located between the Sava and Kolubara Rivers in northwest Serbia (Fig. S-1). More precisely, with its extreme north-eastern border, OZ reaches the right bank of the Sava River, and in the south and east, it almost abuts the left bank of the Kolubara River. The OZ is located 1.5 km east of the city of Obrenovac and 12 km southwest of the suburbs of the city of Belgrade (the capital of Serbia). The total protected area is 47,77.18 ha. The whole location is specific by its hydrological, morphological, and geological characteristics. The protected area belongs to the plain terrain, i.e., the alluvial plains of the Sava and Kolubara Rivers above, which is a river terrace Lower Pliocene age, marly clay are dark gray to gray, and underlying river terrace sediments. Due to the meandering of the Sava and Kolubara Rivers during the Holocene, the formated terrace represents a common terrace for both Rivers. Five sediment samples (S1 – S5) and 7 soil samples (M1 – M7) were taken from the protected area OZ. The surface sediments and the soil were taken at a depth of 0 – 10 cm. The sediment samples were taken from the Sava River and soil samples were taken from the area that is flooded at high Kolubara River groundwater levels. The collected samples were immediately transferred into dark glass bottles and transported to the laboratory.

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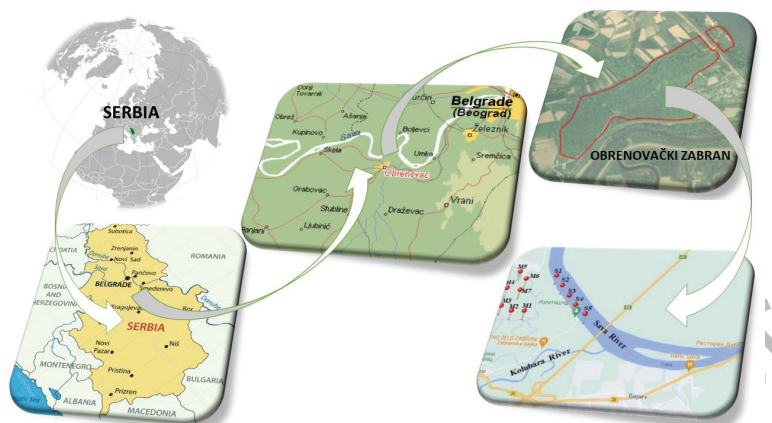
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557 Fig. S-1. Study area of „Obrenovački zabran" with sampling locations (S1 – S5 are sediment
558 samples, M1 – M7 soil samples).

559 TABLE S-I. Parameters used for incremental lifetime cancer risk (ILCR) calculation

Parameter	Description	Unit	Adults	Children	Reference
CSF_{ing}	Ingestion carcinogenic slope factor	$kg\ d\ mg^{-1}$	7.3	7.3	56
IR_{ing}	Ingestion rate	$mg\ d^{-1}$	100	200	57
EF	Exposure frequency	$d\ y^{-1}$	350	350	57
ED	Exposure duration	y	24	6	58
BW	Body weight	kg	70	15	59
AT	Average life span	d	25550	25550	58
CSF_{derm}	Dermal carcinogenic slope factor	$kg\ d\ mg^{-1}$	25	25	56
SA	Dermal surface exposure	$cm^2\ d^{-1}$	5700	2800	57
AF	Dermal adherence factor	$mg\ cm^{-2}$	0.07	0.2	57
ABS	Dermal adsorption fraction	Unitless	0.13	0.13	57
CSF_{inh}	Inhalation carcinogenic slope factor	$kg\ d\ mg^{-1}$	3.85	3.85	56
IR_{inh}	Inhalation rate	$m^3\ d^{-1}$	20	10	56
PEF	Particle emission factor	$m^3\ kg^{-1}$	1.36×10^9	1.36×10^9	57

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562   TABLE S-II. Incremental lifetime cancer risk (ILCR) and total cancer risk (TCR_{PAH}) from
563   PAHs

Samples	ADULTS				CHILDREN			
	ILCRing	ILCRder	ILCRinh	TCR_{PAH}	ILCRing	ILCRder	ILCRinh	TCR_{PAH}
M1	2.2E-04	3.9E-04	1.7E-08	6.1E-04	3.1E-04	3.8E-04	5.9E-09	6.9E-04
M2	4.7E-04	8.3E-04	3.6E-08	1.3E-03	6.6E-04	8.2E-04	1.3E-08	1.5E-03
M3	5.9E-04	1.0E-03	4.6E-08	1.6E-03	8.2E-04	1.0E-03	1.6E-08	1.8E-03
M4	3.5E-04	6.3E-04	2.8E-08	9.9E-04	5.0E-04	6.2E-04	9.6E-09	1.1E-03
M5	5.1E-04	9.0E-04	3.9E-08	1.4E-03	7.1E-04	8.8E-04	1.4E-08	1.6E-03
M6	2.2E-04	3.9E-04	1.7E-08	6.1E-04	3.0E-04	3.8E-04	5.9E-09	6.9E-04
M7	1.0E-03	1.9E-03	8.1E-08	2.9E-03	1.5E-03	1.8E-03	2.8E-08	3.3E-03
S1	3.1E-04	5.5E-04	2.4E-08	8.6E-04	4.3E-04	5.4E-04	8.4E-09	9.7E-04
S2	4.1E-04	7.2E-04	3.2E-08	1.1E-03	5.7E-04	7.1E-04	1.1E-08	1.3E-03
S3	3.3E-04	5.8E-04	2.5E-08	9.0E-04	4.5E-04	5.7E-04	8.8E-09	1.0E-03
S4	5.7E-04	1.0E-03	4.4E-08	1.6E-03	8.0E-04	1.0E-03	1.5E-08	1.8E-03
S5	6.4E-04	1.1E-03	5.0E-08	1.8E-03	9.0E-04	1.1E-03	1.7E-08	2.0E-03
Soil Min	2.2E-04	3.9E-04	1.7E-08	6.1E-04	3.0E-04	3.8E-04	5.9E-09	6.9E-04
Soil MAX	1.0E-03	1.9E-03	8.1E-08	2.9E-03	1.5E-03	1.8E-03	2.8E-08	3.3E-03
Soil Average	4.9E-04	8.6E-04	3.8E-08	1.3E-03	6.8E-04	8.5E-04	1.3E-08	1.5E-03
Soil SD	2.8E-04	5.0E-04	2.2E-08	7.9E-04	4.0E-04	4.9E-04	7.7E-09	8.9E-04
Soil Median	4.7E-04	8.3E-04	3.6E-08	1.3E-03	6.6E-04	8.2E-04	1.3E-08	1.5E-03
Sediment Min	3.1E-04	5.5E-04	2.4E-08	8.6E-04	4.3E-04	5.4E-04	8.4E-09	9.7E-04
Sediment MAX	6.4E-04	1.1E-03	5.0E-08	1.8E-03	9.0E-04	1.1E-03	1.7E-08	2.0E-03
Sediment Average	4.5E-04	8.0E-04	3.5E-08	1.3E-03	6.3E-04	7.9E-04	1.2E-08	1.4E-03
Sediment SD	1.5E-04	2.7E-04	1.2E-08	4.2E-04	2.1E-04	2.6E-04	4.0E-09	4.7E-04
Sediment Median	4.1E-04	7.2E-04	3.2E-08	1.1E-03	5.7E-04	7.1E-04	1.1E-08	1.3E-03

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566   TABLE S-III. Non-cancer and cancer health risks from Hg in soil (samples M1 – M7)

		NON-CANCER RISK							
		HQing		HQinh		HQder		HI	
		Child	Adult	Child	Adult	Child	Adult	Child	Adult
Hg	Mean	9.4E-02	1.0E-02	9.2E-06	2.7E-05	5.8E-02	7.7E-03	1.5E-01	1.8E-02
	Min	1.2E-02	1.3E-03	1.2E-06	2.3E-05	7.6E-03	1.0E-03	2.0E-02	2.4E-03
	Max	1.4E-01	1.5E-02	1.3E-05	3.3E-05	8.4E-02	1.1E-02	2.2E-01	2.6E-02
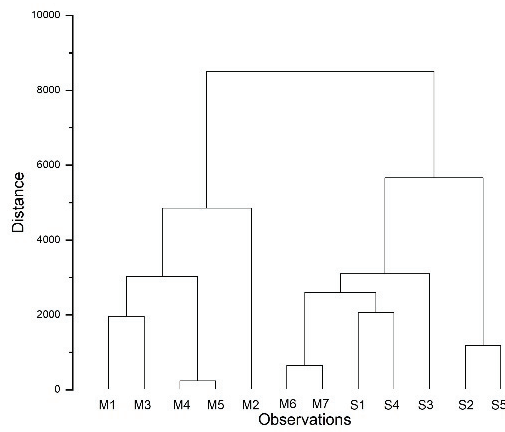
567
568   Fig. S-2. Cluster analysis of observed sediment samples from the Sava River (S1 – S5) and
569   soil samples (M1 – M7) that are flooded at high Kolubara River groundwater levels.