

Organic and inorganic priority substances in sediments of Ludaš Lake, a cross-border natural resource on the Ramsar list

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Abstract For the first time, long-term monitoring (from 2002 to 2014) was carried out of surface sediments in Ludaš Lake, a Ramsar site in northern Serbia. Organic (16 EPA PAHs, mineral oils, selected pesticides and polychlorinated biphenyls (PCBs)) and inorganic substances (eight heavy metals: Ni, Zn, Cd, Cr, Cu, Pb, As and Hg) were continually investigated. Dibenzo[*a,h*]anthracene (DahA) and fluorene (Flo) were found at levels indicative of causing adverse effects to biota. Diagnostic ratios of specific PAHs were dominated by high molecular weight components, particularly DahA, which contributed 81.78 % of the total high carcinogens, benzo[*b*]fluoranthene (BbF) and Flo. Potential ecological risk factors (ERi) and the high relative standard deviations (RSD) obtained (up to 245 %) for the parameters monitored confirm the high periodical anthropogenic impact from industry, municipal wastewater and agriculture. The highest concentration of inorganic pollution found was for Cd (440–831 mg/kg) at all sites, Cu (439 mg/kg) in the eastern part of the lake and Cu (388 mg/kg) and Hg (771 mg/kg) in the northern part of the lake. Based on factor analysis of principal component analysis (PCA/FA), As and phenanthrene (Phe) had significant loadings (0.808 and 0.907, respectively). This association of As with organic anthropogenic sources was also confirmed with

the sum of PAHs, pyrene (Pyr) and mineral oil by 3D factor plot, corroborating the theory of As mobilization from metal-reducing microbes as organic (methylated) forms, accelerated by phenanthrene. According to EU national and regional data results, this research suggests that Cu, As, dibenzo[*a,h*]anthracene and Flo should be added to the list of priority pollutants within the context of applying the European Water Framework Directive (WFD).

Keywords Sediment monitoring · Priority substance identification · Toxicity indices

Introduction

The Serbian National Strategy on Environmental Protection in the field of water and sediment management is based on the Water Framework Directive (WFD, 2000/60/EC (EC 2000)) which was transposed and adapted into national legislation (RS 50/2012). European sediment studies (Fleit and Lakatos 2003; Rippey et al. 2008; Panagos et al. 2013) and local data (Škrbić et al. 2005; Prica et al. 2008; Dalmacija et al. 2008, 2010; Savić et al. 2013; Sakan et al. 2013; Štrbac 2014) have confirmed the need for continual monitoring of related priority substances in sediment: 8 heavy metals (Ni, Zn, Cd, Cr, Cu, Pb, As and Hg) and the 10 EPA PAHs, in accordance with the recommendations in the Serbian legislation (RS 50/2012).

The nature and rate of sedimentation in local lake environments depend on interactions between the groundwater, the continental climate and geogenic and intense anthropogenic influences. The changing conditions result in large fluctuations in the mass fractions of organic and inorganic parameters, as shown in previous studies carried out in the Pannonian Basin (Golobočanin et al. 2004; Krčmar et al. 2013; Sakan et al. 2013; Grba et al. 2015).

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Research into sediment pollution has focused on distinguishing between natural and anthropogenic pollutant sources. For metals, the geoaccumulation index (I_{geo}) was developed by Müller (1979) and categorizes pollution into seven different classes. The potential ecological risk factor (ERi) and ecological risk index (RI) of heavy metals are also used for sediment classification (Hakanson 1980). Diagnostic ratios of specific PAH congeners allow further classification of anthropogenic pollution. Petrogenic sources include PAHs with low molecular weights (LMWs) containing two to three benzene rings, while pyrogenic resources mostly include PAHs with high molecular weight (HMW), containing four to six benzene rings (Rocher et al. 2004; Wang et al. 2006; Yunker et al. 2002; Zhang et al. 2004; Kanzari et al. 2014). The carcinogenicity of sediment pollution may also be analysed, using toxic equivalency factor (TEF) methodology (US EPA 1993), which estimates the total carcinogenicity of seven carcinogenic, probable or possible carcinogen PAHs (Fu et al. 2011).

This paper focuses on a monitoring program at Ludaš Lake, a Ramsar site in northern Serbia. A cross-border initiative with Hungary has recently been proposed to increase the protection of this nature reserve via its inclusion in the Kiskörös basin. In order to apply the WFD and provide the most appropriate environmental impact assessment for sediments in the Pannonian Basin, the monitoring and evaluation programme was run from 2002 to 2014. This programme is used to define specific priority substances for this unique region, on the basis of results from multiple indicators, supported by chemometric analysis. By using this approach, anthropogenic, geological and ecological hazards in the wider region of Ludaš Lake are analysed and systemized.

Materials and methods

Sampling sites and sample collection

Ludaš Lake covers an area of 3.17 km² with a length of 4 km from north to south and a depth of up to 2 m (average 0.9 m) (Rudić et al. 2015). The lake lies about 12 km north-east from the city of Subotica. It is a shallow lake in northern Serbia between the Danube and Tisa rivers, next to the Hungarian border and adjacent to the National Park of Kiskunság Keckskemét. This lake is highly variable in terms of its physico-chemical characteristics: source water, lake size, morphology, water chemistry and trophic status.

This study focused primarily on loess sediments from the Ludaš Lake Ramsar site and includes three sediment profiles S1 to S3, selected due to their significant proximity to various anthropogenic and natural influences (Fig. 1, Table 1).

A total of 42 surface sediment samples were taken from 0 to 0.50 m as composite samples, in order to assess the

horizontal pollution profiles (water depth ranges from 1.0 to 1.2 m). Fourteen surface sediment samples (0 to 0.50 m) were collected from each site (S1, S2 and S3): two samples per year (spring and autumn), during 2002, 2003, 2004, 2005, 2008, 2010 and 2014. In order to determine the source and level of pollution, natural background analyte values were taken from sampling site (S_{back}) from 25 to 50-cm depth, located 10 km east of Ludaš Lake (near the Tisa at Martonoš village), as shown in Fig. 1.

Fresh sediment was collected by Eijkelkamp core sampler from the middle of the sediment reach at Ludaš Lake, according to standard method for sediment sampling ISO 5667-12:1995. All samples were split and immediately placed into sealed plastic acid-rinsed boxes (15 × 15 cm and 20-cm deep). The samples were stored at 4 °C and transported to the laboratory for further analysis. All materials used for sampling, treatment and storage of samples and solutions were carefully chosen and acid-cleaned (EPA 2004) to minimize contamination.

Physico-chemical analyses

Reagents and standards

Deionized water used for the physico-chemical analyses was obtained by Labconco system (resistivity at 25 °C 18 MΩ cm). For metal analysis, standard solutions were prepared from analytical grade Suprapure quality reagents (Merck or J.T. Baker). For digestion of the sediment samples, a combination of HNO₃ and HCl Suprapure acids was used (Merck).

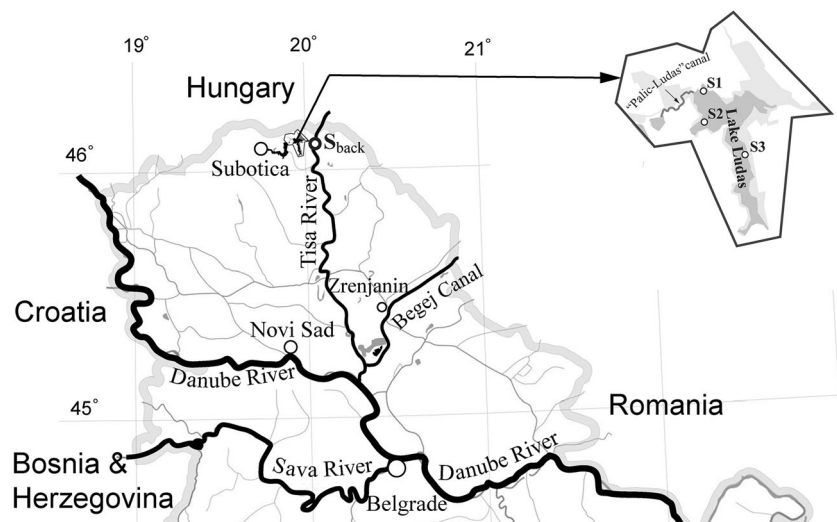
PAH standards were purchased from Dr. Ehrenstorfer (PAH-Mix 64 in benzene/dichloromethane = 50/50 at a concentration of 2000 mg/L for each compound). Phenanthrene-d10 was used as internal standard and was purchased from Supelco (Cat. No. 48094, 2000 µg/mL in methanol solution).

Mineral oil was determined with a standard mixture of mineral oils of different boiling points: type A (diesel oil without additives) and type B (lubricating oils free of additives) and *n*-decane (C₁₀H₂₂), *n*-eicosan (C₂₀H₄₂) and tetracontane (C₄₀H₈₂) purchased from Dr. Ehrenstorfer. All organic solvents used were for organic residue analysis purchased from J.T. Baker and Pestanal. Florisil with granulation of 150 to 250 µm (60 to 100 mesh) was purchased from Sigma-Aldrich.

Characterization of sediment samples

The sediment samples were prepared in the laboratory in accordance with ISO Standard 11464:2006 and thereafter passed through a 250-µm sieve. Chemical characterization was performed as follows: pH (ISO 10390:2005), oxidation-reduction potential (modified APHA AWA WEF 2580 protocol (Rice et al. 2012), dry matter (EN 12879:2000), organic matter

Fig. 1 Map of North Serbia and sampling locations (S1 to S3) in Ludaš Lake, near Serbia-Hungary border



(OM) expressed as loss on ignition according to EN 12879:2000, clay content, fraction $<2 \mu\text{m}$, according to ISO 11277:2009, chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) according to the EPA protocols (EPA 1986).

The chemical extraction for determination of pseudo-total metal content in sediment was performed in accordance with EPA method 3051A (2007b). Sediment extracts were analysed for Ni, Zn, Cd, Cr, Cu and Pb by flame atomic absorption spectrometry (FAAS) (PerkinElmer, AAnalyst 700) in accordance with EPA method 7000b (2007c). Arsenic in the extracts was measured by graphite furnace atomic absorption spectrometry (GFAAS) according to EPA method 7010 (2007d). Hg in the extracts was measured by cold vapour atomic absorption spectrometry by modified EN 1483:2007 method.

For heavy metals and PAHs, detection limits (MDLs) and practical quantitation levels (PQLs) were determined during method validation by analysis of six replicate samples with low analyte contents. The MDL was calculated as $3 \times \text{STD}$ (standard deviation), while PQL was calculated as $5 \times \text{MDL}$. Precision of the metal analysis was determined by repeat analysis of certified reference material CRM016-50g (Trace Metals-Fresh Water Sediment) and for the PAHs analysis by

CNS391-50g (PAHs, PCBs and Pesticides in Freshwater Sediment, Fluka).

MDL and PQL values for the analytical methods applied, and the precisions expressed as the relative standard deviation (RSD), are given in Tables 2 and 3. For all 42 samples, extractions were performed in triplicate, and the results expressed as the mean.

The index of hydrocarbons in the sediment was measured by gas chromatography-flame ionization detection (GC-FID; Agilent Technologies 6890) according to ISO/TR 11046:1994 method. MDL and PQL values for hydrocarbons were 50 and 125 mg/kg, respectively. Recoveries were from 72 to 113 % and the RSD in the range 17.6 to 30 %.

The 16 US EPA priority PAHs were determined: naphthalene (Nap), anthracene (Ant), phenanthrene (Phe), fluoranthene (Flur), fluorene (Flo), acenaphthene (Ace), acenaphthylene (Acy), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*g,h,i*]-perylene (BghiP), indeno[1,2,3-*cd*]pyrene (InP) and dibenzo[*a,h*]anthracene (DahA). Nap, Ant, Flur, BbF, BkF, BaP, InP and BghiP are listed as priority substances by the WFD. Ten PAHs (Nap, Ant, Phe, Flur, BaA, Chr, BkF, BaP, BghiP and InP) are specifically recommended for monitoring by Serbian legislation

Table 1 Brief description of sample site locations in Ludaš Lake

Sites	Latitude	Longitude	Altitude range (m)	Description of area
S1	46° 6' 19.53"	19° 48' 48.02"	94	The most northern point of Ludaš Lake
S2	46° 5' 52.63"	19° 48' 52.72"	94	Eastern part of the lake
S3	46° 5' 16.72"	19° 49' 47.04"	93	The most southern point of the lake
S_{back}	46° 6' 0.64"	20° 2' 25.27"	77	Located 10 km east from Ludaš Lake (near the Tisa River at Martonoš village)

Table 2 MDL, PQL, recovery and RSD values for the heavy metal methods applied

Parameter	Method	MDL (mg/kg)	PQL (mg/kg)	Recovery (%)	Precision RSD (%)
Heavy metals					
Nickel	EPA 7000b	9.30	19.0	95	10
Zink	EPA 7000b	0.57	1.20	84.6	7.69
Cadmium	EPA 7000b	0.71	1.45	94.8	7.12
Chrome	EPA 7000b	1.11	2.25	91.8	13.02
Copper	EPA 7000b	1.06	2.15	97.6	3.44
Lead	EPA 7000b	12.5	25.0	98.5	9.35
Arsenic	EPA 7010	0.064	0.130	104.6	16.5
Mercury	EN 1483:2007	5.2	25	103	13.3

(RS 50/2012). Nevertheless, this study monitored all 16 US EPA PAHs in the period 2002–2014 with the same frequency as the other parameters.

PAHs were analysed by gas chromatography with mass detection (Agilent Technologies 7890A GC System/5975C VL MSD) with Agilent J&W Scientific DB-5MS column according to EPA methods 8270C (EPA 2008), 3660B (EPA 1996b), 3630C (EPA 1996a) and 3550b (EPA 2007a). For all PAHs, the MDLs and PQLs are presented in Table 3.

Synthetic sediment multiparameter indicators

Significant fluctuations in the levels of metals were observed in the investigated area (Tables 4 and 5). Major synthetic multiparameter indicators were thus calculated: geoaccumulation

index (I_{geo}) (Müller 1979) and potential ecological risk index (RI) (Hakanson 1980).

PAH and metal mass fractions were correlated by statistical analysis, and the origin of the organic pollution, particularly PAHs, was analysed by using several synthetic indicators. Ratios of fluoranthene to the sum of fluoranthene and pyrene, expressed as $Flur/(Flur + Pyr)$, classify pollution as pyrogenic (>0.4) or petrogenic (<0.4) in origin, with values ranging from 0.4 to 0.5 suggesting fuel combustion and values >0.5 suggesting the combustion of grass, coal or wood (Yunker et al. 2002). Other diagnostic combinations of PAH isomers investigated include $InP/(InP + BghiP)$, $Ant/(Ant + Phe)$, $BaA/(BaA + Chr)$, BaA/Chr and $InP/BghiP$ (Kanzari et al. 2014).

TEF methodology was used to quantify the carcinogenicity of seven PAHs which are carcinogenic, probable or possible carcinogens (CANPAHs) relative to

Table 3 MDL, PQL, recovery and RSD values for the PAHs and mineral oil analyses in sediment

Parameter	Method	MDL (µg/kg)	PQL (µg/kg)	Recovery (%)	Precision RSD (%)
PAHs	Methods for all PAHs				
Naphthalene		4.2	9.7	77.3	26.2
Anthracene		4.31	10.8	115.5	18.0
Phenanthrene		3.70	9.26	85.6	19.8
Fluoranthene		3.92	9.80	103.8	14.2
Fluorene	EPA 8270C	3.91	9.78	88.9	34.5
Acenaphthene		3.89	9.77	72.3	20.2
Acenaphthylene	EPA 3660B	3.93	9.81	70.5	18.5
Pyrene		3.97	9.92	84.4	18.6
Benzo(a)anthracene	EPA 3630C	4.43	11.1	77.4	10.7
Chrysene		3.95	9.88	99.6	17.0
Benzo(k)fluoranthene	EPA 3550b	3.69	9.23	106.4	15.9
Benzo(a)pyrene		4.45	11.1	75.5	16.3
Benzo(b)fluoranthene		4.38	11.08	106.4	15.9
Benzo(g,h,i)perylene		4.77	11.9	78.2	19.2
Indeno(1,2,3-cd)pyrene		4.19	10.3	95.5	20.9
Dibenzo(a,h)anthracene		4.21	10.5	95.5	20.9
Mineral oil	ISO/TR 11046:1994	50.0	125.0	85.1	25.2

Table 4 Maximum, minimum, mean and RSD values of heavy metals and other sediment quality parameters in sediments (from 0 to 50-cm depth) of all sites studied in Lake Ludaš ($n = 42$ samples, 14 per site)

Sites	Ni (mg/ kg)	Zn (mg/ kg)	Cd (mg/ kg)	Cr (mg/ kg)	Cu (mg/ kg)	Pb (mg/ kg)	As (mg/ kg)	Hg (mg/ kg)	PAH ₁₆ (μ g/kg)	Min. oil (mg/kg)	Clay (%)	OM (%)	COD (g O ₂ /kg)	BOD ₅ (g O ₂ /kg)	
S1	Max	330	1010	23.0	1830	2300	280	130	2.70	483	1800	51.2	46.0	310	458
	Min	10.0	29.8	0.07	28.6	11.8	9.29	45.0	0.01	32.8	42.0	11.2	11.0	130	33.2
	Mean	124	393	7.69	493	348.4	79.6	57.3	0.79	189	735	31.5	29.1	209	152
	RSD	95.5	101	94.5	133	179	126	57.5	107	92.9	77.2	41.01	41.5	31.7	78.8
S2	Max	320	600	23.0	450	2600	182	92.1	0.42	244	1240	42.7	80.0	810	299
	Min	25.0	51.0	0.24	10.0	22.6	10.4	25.6	0.01	41.8	1.00	16.5	21.0	198	25.0
	Mean	92.9	209	7.47	135	251	55.7	39.4	0.21	133.1	400	28.3	35.5	360	111
	RSD	87.2	79.3	109.7	93.5	270	108	61.5	65.5	62.7	91.3	31.8	43.3	54.1	71.7
S3	Max	730	160	12.2	140	430	170	49.4	1.70	152.9	982	48.7	45.0	470	280
	Min	8.00	14.0	0.06	9.91	11.3	7.39	36.0	0.01	29.1	10.0	16.9	18.8	83.7	21.5
	Mean	84.1	59.5	4.10	28.3	59.1	38.3	42.5	0.29	74.6	238	34.2	29.6	265	136
	RSD	224	78.9	98.7	124.6	187	129	9.93	159	46.0	126.5	30.4	28.8	57.6	64.7

benzo[*a*]pyrene and to estimate the total benzo[*a*]pyrene equivalent concentration ($B[a]P_{eq}$), calculated as $Total\ B[a]P_{eq} = \sum Ci \times TEFi$, where Ci is the concentration of individual CANPAHs (BaA, Chr, BkF, BaP, BbF, InP and DahA) and $TEFi$ is the corresponding toxic equivalency factor for BaA, BaP, BbF, BkF, InP, DahA and Chr as follows: 0.1, 1, 0.1, 0.01, 0.1, 1 and 0.001 (US EPA 1993). Of these PAHs, benzo[*a*]pyrene is classified as carcinogenic to humans, chrysene, indeno[1,2,3-*cd*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]anthracene are possibly carcinogenic to humans and dibenzo[*a,h*]anthracene is probably

carcinogenic to humans, according to the International Agency for Research on Cancer (2016).

Statistical analysis

All statistical data processing was carried out by using STATISTICA (Statsoft Inc., USA; version 12.0 for Windows). Principal component analysis/factor analysis (PCA/FA) and Pearson's correlation coefficient analysis identified the relationships among contaminants in the surface (from 0 to 50-cm depth) sediments and their probable sources.

Table 5 Comparison between heavy metal concentrations (mg/kg), mineral oil (mg/kg) and sum of PAH₁₀ (μ g/kg) of all sampling sites (S1–S3) from Lake Ludaš ($n = 42$ samples, 14 per site) from 0 to 50-cm depth, with relevant natural upper continental crust (UCC) values for loess sediment, background analyte values (S_{back}) and national and different international regulation values

	Values from investigated sediments (S1–S3)				Relevant comparison data									
	Minimum	Maximum	Mean	RSD	Natural, local and legislation values					Sediment quality guidelines (SQGs)				
					S_{back}	UCC	Northern Serbia	RS 50/2012	ÖNORM S 2088-2	ERL	ERM	TEL	PEL	
Ni	8.00	730	100	134	36.6	44	36.8	44	60	20.9	51.6	18.0	36.0	
Zn	14.0	1010	220	127	152.9	71	76.3	430	300	150	410	123	315	
Cd	0.06	23	6.42	106	0.83	0.098	2.85	6.4	1	1.20	9.60	0.60	3.50	
Cr	9.91	1830	212	196	23.87	85	41.0	240	100	81.0	370	37.3	90.0	
Cu	11.3	2600	219	245	29.63	25	28.9	110	100	24.0	270	35.7	197	
Pb	7.39	280	57.9	127	12.46	17	17	310	100	46.7	218	35.0	91.3	
As	0.08	130	46.4	52.7	22.4	5.1	–	42	20	8.20	70.0	5.90	17.0	
Hg	0.004	2.700	0.43	140.5	0.14	0.05	–	0.3	1.0	0.20	0.70	0.20	0.50	
Min. oil	1.00	1801	458	101.8	–	–	–	3000	–	–	–	–	–	
Σ PAH ₁₀	0.07	177	43.9	91.3	–	–	–	10,000	–	–	–	–	–	

Analysis of variance (ANOVA) was performed to analyse the significant spatial and temporal differences ($p < 0.05$).

The distribution of analysed parameters in the studied environment was performed by factor analysis of principal component analysis on the average heavy metal and PAH data sets, characterizing the collected sediment samples. All analyses were performed on a normalized data set (z -scale transformation) to avoid misclassification due to the wide differences in data dimensionality, and Ward's method was used with squared Euclidean distances, as a measure of similarity to assess the interrelationships among the sampling sites. As Henry et al. (1984) suggested that the minimum number of samples (n) for FA should be such that $N > 30 + (V + 3) / 2$, where V represents the number of variables, after removing outliers, 16 variables and 42 samples were considered for factor analysis.

In order to reduce the number of dimensions and extract the most important synthetic information to select the key variables of interest by particular sources, PCA/FA were applied as the most common multivariate statistical methods used in environmental studies (Zhiyuan et al. 2011), apportioning them to natural, geochemistry processes vs. anthropogenic influences. PCA/FA, with the Varimax normalized method of standardized component loadings, was conducted to maximize the variation among the variables under each factor, and those varimax factors (VFs) with eigenvalues >1 were retained by Kaiser's criteria (Kaiser 1960). In this research, the Pearson correlation coefficient was used to measure the strength of relationships between pairs of contaminants within samples (positively or negatively related with statistical significance set at $p < 0.05$ or $p < 0.01$).

Results and discussion

Results of sediment characterization

This paper presents results from a large-scale monitoring programme at three sampling sites (S1–S3) from Ludaš Lake surface sediments (from 0 to 0.5 m). All 16 EPA PAHs were monitored, which includes 7 of the 20 recommended priority substances for long-term trend monitoring in biota and/or sediments (Directive 2013/39/EU). Heavy metals Ni, Cd, Pb and Hg have priority substance status and were also monitored, as were the cyclodiene pesticides (aldrin, dieldrin and endrin). Furthermore, in accordance with Serbian legislation (RS 50/2012), four more metals (Zn, Cr, Cu and As), mineral oils, pesticides (α -HCH, β -HCH, γ -HCH (lindane), heptachlorepoxyde, heptachlor, δ -HCH, endosulfan I, DDT and its metabolites) and the sum of six proposed PCB congeners (28, 52, 101, 118, 138, 153 and 180) were also measured continually.

In almost all cases, the results for the pesticides and the sum of PCB analysis were below the limits of detection, and they were therefore excluded from the analysis in this paper.

Organic and inorganic sediment parameters

The minimum, maximum and average values of heavy metals, sum of PAH₁₆ and mineral oil (OIL_{min}), clay, OM, COD and BOD₅ parameters for the surface sediments at the three investigated sites (S1–S3) are summarized in Table 4. The average content of organic matter (OM) expressed as loss on ignition ranged from 29.12 to 35.51 %. Based on these results, it can be concluded that most of the sediment samples represent sediments with medium organic carbon contents. The average BOD₅/COD ratios at each sampling locations range from 0.21 to 0.41, indicating a low to moderate contribution of biodegradable organic matter in the total organic matter budget. It is important to note the uneven distribution of the average amount of organic matter, COD values, BOD₅ values, mineral oil and almost all heavy metals except Cd, between the selected locations (S1, S2 and S3). The high RSD values (from 92 % for PAHs and up to 245 % for Cu, Tables 4 and 5) confirm this observation. Generally, the mean values of metals decrease from S1 to S3, but the organic parameters do not follow this pattern. In addition, the pH of all the investigated sediments was about 6.7 to 8.8. The redox values for all the sediment samples have high negatively values ranging from -309 to -287.4 mV.

Heavy metal concentration in the surface sediments of Ludaš Lake is listed in Table 4, and their summarized ranges are given in Table 5. During the investigation period, all heavy metals showed significant spatial variations (ANOVA, $p < 0.05$). The concentration of heavy metals in the surface sediments corresponds with the industry, municipal wastewater and traffic pollution from the city of Subotica and agriculture in this region and may also be a consequence of periodical seasonal water fluctuations.

The maximum mass fractions of Zn, Cr, Pb, As, Hg, PAH₁₆, mineral oil and clay were found at sampling site S1, which had the highest mean heavy metal values. Taking into account the position of the city of Subotica and also the higher altitude of the terrain compared to Ludaš Lake (Fig. 1, Table 1), the largest contamination loading comes from the "Palić-Ludas" canal direction, which carries a mixture of atmospheric water collected by open-canal network, wastewater and water from Lake Palić, which represents an important water source for Ludaš Lake (Rudić et al. 2015). The following industries are also active nearby: food, textiles, metal, chemical and others, which all influence the pollution of the shallow lake aquatic system.

Except for As, site S3 had the lowest values for all investigated heavy metals, COD and BOD₅ values, whereas S2 had lower levels of As (Tables 4 and 5) but the highest levels of Cd

and Cu. The minimum and maximum levels of Ni (8–730 mg/kg) were also observed at S3. The high variation in Ni values is due to its geological origin and periodical oscillations in subterranean water levels, whereas the situation with Cd (0.07–23.0 mg/kg), Cr (28.6–1830 mg/kg) and Cu (11.8–2300 mg/kg), which at location S1 have significantly higher RSD values of 94.5, 133 and 179 %, respectively (Table 4), is probably related to strong anthropogenic factors. A striking rebound is evident also for Cu at S2 sampling site (Tables 4 and 5). Similarities between heavy metal and PAH₁₆ in high amplitudes values were observed. S1 has the highest range and maximum (33–483 µg/kg), while the S3 site had the lowest minimum values of PAH₁₆ (29 µg/kg). The mean value following this pattern as it was observed for the selected PAH₁₀ (relevant to Serbian legislation (RS 50/2012) does not take into account Pyr, BbF and DahA during the monitoring program.

Observing the mean mass fractions of metals (with somewhat lower values of As and Hg at S2 than S3 site) and PAH distribution in the surface sediment, the following general graduation can be set: site 1 > site 2 > site 3. The high negative redox value at all sites indicates the occurrence of anoxia, which favours the binding of metal sulphides in bio-unavailable forms during their resuspension implying a high level of metals at all locations. The area near the Ludaš Lake near the city of Subotica is mainly agriculture and farmland, but the city itself is an important industrial and transportation centre of Serbia. The unusually large fluctuations of Zn (29.8–1010 mg/kg), Cr (28.6–1830 mg/kg) and Cu (11.8–2300 mg/kg) at S1 and Cu (22.6–2600 mg/kg) at S2 site all followed the mineral oil pattern (Tables 4 and 5), showing the direct periodical influence of anthropogenic activities mostly by industry (chemical fertilizer factory, rail wagon factory, export industry, windmill factory, milk producer, producer of strong alcohol drinks, etc.) situated to the east, in the central and south-east areas of the city of Subotica (the seventh largest city in Serbia with round 106,000 inhabitants), which is located 10 km from the border of Serbia and Hungary.

Inorganic sediment contamination and ecological indices

As a standard procedure in the identification of sources and levels of pollution, the geoaccumulation index (I_{geo}) was calculated in order to understand the geogenic versus anthropogenic hazards (Müller 1979). The potential ecological risk factor (ERi) and ecological risk index (RI) of heavy metals (Hakanson 1980) for sediments at all sites in Ludaš Lake were also evaluated (classification of these indices are given in Table 1, and the formulas are described in detailed in the Supplementary information).

In terms of diverse impact on the investigative area, this study focuses on values above 1, classified as moderately

polluted (class 2) or worse, due to possible periodical variations in heavy metal concentration.

The values for I_{geo} index (Fig. 1a in the Supplementary information) ranged from -4.4 to 5.9. High I_{geo} levels (above 1) were obtained at all sites. At S1 I_{geo} (Cu) = 5.69, I_{geo} (Cr) = 5.68, I_{geo} (Cd) = 4.21, I_{geo} (Pb) = 3.91, I_{geo} (Hg) = 3.68, I_{geo} (Ni) = 2.59, I_{geo} (Zn) = 2.14 and I_{geo} (As) = 1.95. The I_{geo} values at site S2 are similar for Cu, Cd, Ni, As and Pb and somewhat smaller for Cr, Zn and Hg. At site S3, I_{geo} values for Hg and Pb are in the same categorization as those at site S1. However, the other metals at site S3 reveal an interesting divergence. Zn contamination at S3 has an I_{geo} below zero (-0.52), with As at a similar level (0.56). Cd is one class less and Ni one class higher than at sites S1 and S2. The lowest values for Cu and Cr by location are at S3 for Cu and at S2 for Cr.

Analysis for each metal of the mean values over the entire duration of the study reveals a different situation. Only S1 site has mean I_{geo} values higher than 1, for Cd (1.01), Cu (1.12) and Cr (2.33). In this respect, these metals could be permanent sources of pollution in this area, while the temporary nature of the other metals indicates dual origin, but dominantly geogenic.

In terms of maximum I_{geo} values, S1 and S2 are strongly polluted by Cu, S1 is strongly polluted by Cr, S1 and S2 are strongly to very strongly polluted by Cd, S1 and S3 are strongly polluted by Hg and S1–S3 are strongly polluted by Pb and S3 by Ni. The moderately polluted sites are S3 by Cr and S2 by Zn and Hg, and the Ni and Zn values at S1 and Ni at S2 suggest that they are moderately to strongly polluted. Based on I_{geo} , the degree of pollution of the surface sediments of Ludaš Lake is lowest at S3 and highest at site S1.

From the conclusions above, based on high maximums and higher mean values of I_{geo} and ERi indicators (Fig. 1a, b, respectively, in the Supplementary information), Cd, Cu, Cr, Pb and Hg are parameters which should be more frequently monitored. Based on the RI mean values, site S1 has a high potential for ecological risk (RI = 679.26), S2 (RI = 435.51) has considerable and site S3 has moderate ecological risk (RI = 289.00), according to the Hakanson (1980) categorization (Table 1 in the Supplementary information). Considering these spatial distributions of pollutants at Ludaš Lake, the ecological risk decreases from north to south.

The minimum levels of both I_{geo} and ERi were observed in 2014. During 2002, 2003, 2004 and 2008, the sediment was moderately to strongly polluted by Cd at all sites. Cr was moderately to strongly polluting at S2 and S3 from 2002 to 2004. Before 2010, the ecological risk factor (ERi) also shows that this pollution poses an ecological threat, with Cd (from 415 to 570) and Hg (from 170 to 614) levels at site S1 ranging from the high to very high risk categories. Interestingly, the risk from Hg at site S1 dropped quickly from 2002 to 2004, as did the risk from Pb. The ERi at sites S2 and S3 were

somewhat different, due to the hydrogeological characteristics of the terrain, frequent periodic floods and droughts and the uneven pace of industrial and agricultural activities in the Ludaš Lake area. It can however be concluded that as of 2010, the ERI at these sites is again dropping with time.

Organic sediment toxicity indices, based on selected PAHs

Concentration of PAHs were far below the legally prescribed value for total concentration of carcinogenic, probable or possibly carcinogenic PAHs (Σ CANPAHs), with all the sediments from Ludaš Lake varying from 9.94 to 262.0 $\mu\text{g}/\text{kg}$ (dry wt.), with an average of 36.39 to 84.17 $\mu\text{g}/\text{kg}$ (dry wt.) and accounting for 41–47 % of total PAHs (defined as Σ CANPAHs/ Σ PAH₁₆ ratio), as given in Table 6. The Σ CANPAHs has a maximum at S1 in 2008, while over the course of this investigation, a generally increasing trend was observed from 2003 to 2014 at all locations (Fig. 3 in the Supplementary information).

The maximum and highest average levels of Σ CANPAHs and B[a]P_{eq} are found at S1 (Table 6). Particularly high total and mean values of most carcinogenic PAHs were found at the northern S1 site, except for BkF, BaP and InP which have higher mean concentration at site S2. Among the different PAHs at location S1, the contribution to the total B[a]P_{eq} decreased in the order: DahA (81.78 %) > BaP (8.53 %) > BbF (7.50 %) > Inp (1.13 %) > BaA (0.94 %) > BkF (0.11 %) > Chr (0.02 %).

Generally, sites S1 and S2 had similar distributions of all carcinogenic PAHs related to B[a]P_{eq}, whereas S3 has lower concentration but similar distributions. The very high contribution of DahA to the Σ BaP_{eq} observed during the period of study suggests that this compound should be more frequently monitored regarding human and ecological risk from exposure to this specific PAH. All other carcinogenic PAHs related to B[a]P_{eq} have very low concentration, especially BkF and Chr.

The characteristic PAH molecular diagnostic ratios for the surface sediments at locations S1 to S3 in Ludaš Lake were investigated. The mean Flur/(Flur + Pyr) ratios <0.4 (ranged from 0.30 to 0.34, Table 7) indicate the petrogenic origin of the PAHs, but the maximum values are higher than 4, indicating periodical pyrogenic influences probably of biomass burning from agriculture nearby area and coal combustion from industry and surrounding settlements. The ratios of low molecular weight PAHs (LMW with two to three rings) to high molecular weight PAHs (HMW with four to six rings) were below 1, with a maximum value of 0.56 at sampling site S3 (Table 7), which also implies that the majority of PAHs in these alluvial sediments originate from pyrogenic sources. This assumption was also confirmed by the InP/(InP + BghiP) ratio, where all mean values are higher than 0.5. The pyrogenic sources of sediment pollution are also established

by several other formulas from Table 7. It can be concluded that sources were mixed but that dominantly pyrogenic sources from grass and coal combustion were responsible for the fluctuations in the PAH concentration observed in the Σ CANPAHs parameter (Fig. 3 in the Supplementary information). It should be noted that the PAHs could also originate from fertilizer (Nam et al. 2003) with loss mechanisms in the soil, such as volatilization, abiotic degradation, biodegradation, transboundary transfer and via crops (Moreda et al. 1998).

Monitoring of this coterminous location should be continued even if these values are far below the limits, as their cumulative effect could be carcinogenic. Also, most PAHs can be used as markers of pollution in correlation with other metals and organic parameters, and as such, they should be continued to be monitored. However, based on the current status of contamination, none of the surface sediments are in need of remediation.

Concentrations of heavy metals in the Ludaš Lake region compared to sediment quality guidelines

As many factors influenced the content of heavy metals in the sediment especially fluvial, its specificities are taken into account and experimental result were compared with national legislation values (RS 50/12) and average natural northern Serbia values (Kostić 2001). From geochemical aspects, this northern part of Vojvodina belongs to thick sequences of interstratified loess-paleosol and provides one of the most complete and most sensitive European terrestrial records of climatic and environmental changes during the Middle and Late Pleistocene (Markovic et al. 2009). In order to complete the picture, data were compared with natural concentration from upper continental crust (UCC) for loess sediment (Rudnick and Gao 2004) as well as the related Austrian regulative (ÖNORM S 2088-2 2000).

Evaluation of potential ecological toxic effects were done comparing the level of heavy metals from Ludaš Lake to several other sediment or soil quality guidelines from around the world, such as international sediment quality guidelines (SQGs) taken from Long et al. (1995) and Macdonald et al. (1996), with related levels as threshold effect level (TEL) and probable effect level (PEL) determined by Smith et al. (1996), effects range low (ERL) and the effects range median (ERM) given by Long et al. (1995). At the low-range values (i.e. ERLs or TELs), adverse effects upon sediment-dwelling fauna would only be expected infrequently, whereas above the higher ERM and PEL concentrations, adverse effects are likely to occur.

In order to estimate the level of contamination, we compared the mean values of all heavy metals from S1 to S3 sampling sites to reference data. All investigated data significantly exceed the background values, average natural northern

Table 6 Concentrations in surface sediments (from 0 to 50-cm depth) from S1 to S3 (*n* = 42 samples, 14 per site) in Lake Ludaš and related risk assessment guideline values for PAHs (µg/kg dry weight)

PAHs	Aromatic ring	Investigated sediment concentrations of PAHs (µg/kg dry weight)						Risk assessment guideline values			
		Concentration range			Concentration mean			SQG (µg/kg)			
		S1	S2	S3	S1	S2	S3	ERL	ERM	TEL	PEL
Nap	2	0.005–1.42	0.001–3.54	0.001–6.94	1.06	1.20	3.19	160	2100	34.6	391
Ant	3	0.01–5.00	0.001–12.0	0.001–3.54	1.87	2.45	1.51	85.3	1100	46.9	245
Phe	3	0.04–43.4	0.03–38.0	0.03–8.90	12.7	8.20	4.37	240	1500	86.7	544
Flur	3	0.02–39.3	0.02–55.0	0.01–12.0	10.5	12.2	5.14	600	5100	113	149
Flo	3	1.42–178	1.42–28.5	1.42–18.3	30.7	12.3	5.62	19	540	21.20	144
Ace	3	0.06–10.2	0.05–2.75	0.04–3.54	3.21	1.96	1.33	44	640	5.87	128
Acy	3	0.06–4.74	0.05–3.54	0.04–3.54	2.30	1.71	2.03	16	500	6.71	88.9
Pyr	4	3.54–95.7	3.54–52.0	3.54–33.3	37.9	21.3	13.0	665	2600	153	1398
BaA ^b	4	0.05–10.5	0.01–9.90	0.004–6.20	3.73	3.30	2.81	261	1600	74.8	693
Chr ^b	4	0.01–21.3	0.01–8.80	0.003–3.54	5.99	3.24	2.30	384	2800	108	846
BkF ^b	5	0.01–16.7	0.01–13.1	0.004–4.33	4.47	4.96	2.81	280	1620	na	na
BaP ^a	5	0.01–9.65	0.001–8.24	0.001–6.50	3.38	3.93	2.85	430	1600	88.8	763
BbF ^b	5	1.42–170	1.42–42.8	1.42–27.44	29.7	16.8	9.34	320	1800	na	na
BghiP	6	0.01–15.8	0.01–15.9	0.003–3.56	4.17	4.80	2.02	430	1600	na	na
InP ^b	6	0.01–15.9	0.01–17.7	0.003–5.80	4.47	5.70	2.50	na	na	na	na
DahA ^b	6	1.42–178	1.42–125	1.42–80.4	32.4	28.9	13.78	63.4	260	6.22	135
∑PAH ₁₆	32.76–483	41.80–244	29.08–153	189	133	74.64	–	–	–	–	–
∑PAH ₁₀	0.16–179	0.09–182	0.06–61.3	52.3	49.9	29.51	–	–	–	–	–
∑CANPAHs	9.94–262	18.42–169	9.94–108	84.2	66.9	36.39	–	–	–	–	–
∑CANPAHs/∑PAH ₁₆	0.23–0.61	0.25–0.71	0.34–0.71	0.41	0.47	0.46	–	–	–	–	–
∑B[a]P _{eq}	3.28–182	4.13–130	3.28–83.3	39.6	35.5	18.12	–	–	–	–	–

Classified by the IARC as follows:

^a Carcinogenic to humans (group 1)

^b Possibly cancerogenic to humans (group 2B)

^c Probably carcinogenic to humans (group 2A)

Serbia values (Kostić 2001) and UCC values for loess sediment (Table 5). The level of Cr (9.9–1830), Cu (11.3–2600) and Cd (0.06–23.0) has large range and from seven to nine

times higher values than natural background. Mean values of Ni and Cu are higher compared with national norm (RS 50/2012) values. Zn, Pb and Hg have lower values compared

Table 7 Characteristic PAH molecular diagnostic ratios for surface sediments (from 0 to 50-cm depth) from sites S1 to S3 (*n* = 42 samples, 14 per site) in Lake Ludaš

Molecular diagnostic ratio	Ratio range			Ratio mean			Source parameter classification			
	S1	S2	S3	S1	S2	S3	Petrogenic	Pyrogenic	Fuel combustion	Grass/coal/wood combustion
LMW/HMW	0.001–1.06	0.001–1.04	0.001–0.56	0.38	0.34	0.29	>1	<1		
Flur/(Flur + Pyr)	0.001–0.50	0.001–0.63	0.001–0.62	0.30	0.34	0.33	<0.4	>0.4	0.4–0.5	>0.5
InP/(InP + BghiP)	0.427–0.71	0.481–0.71	0.481–0.72	0.52	0.54	0.56	<0.2	>0.5	0.2–0.5	>0.5
Ant/(Ant + Phe)	0.063–0.50	0.013–0.89	0.020–0.50	0.18	0.28	0.23	<0.1	>0.1		
BaA/(BaA + Chr)	0.261–0.79	0.287–0.87	0.350–0.69	0.47	0.50	0.52	<0.2	>0.35		
BaA/Chr	0.354–3.85	0.402–6.97	0.538–2.21	1.16	1.63	1.17	<0.4	>0.4		
InP/BghiP	0.744–2.49	0.927–2.49	0.927–2.60	1.19	1.25	1.38	<0.2	>0.2		

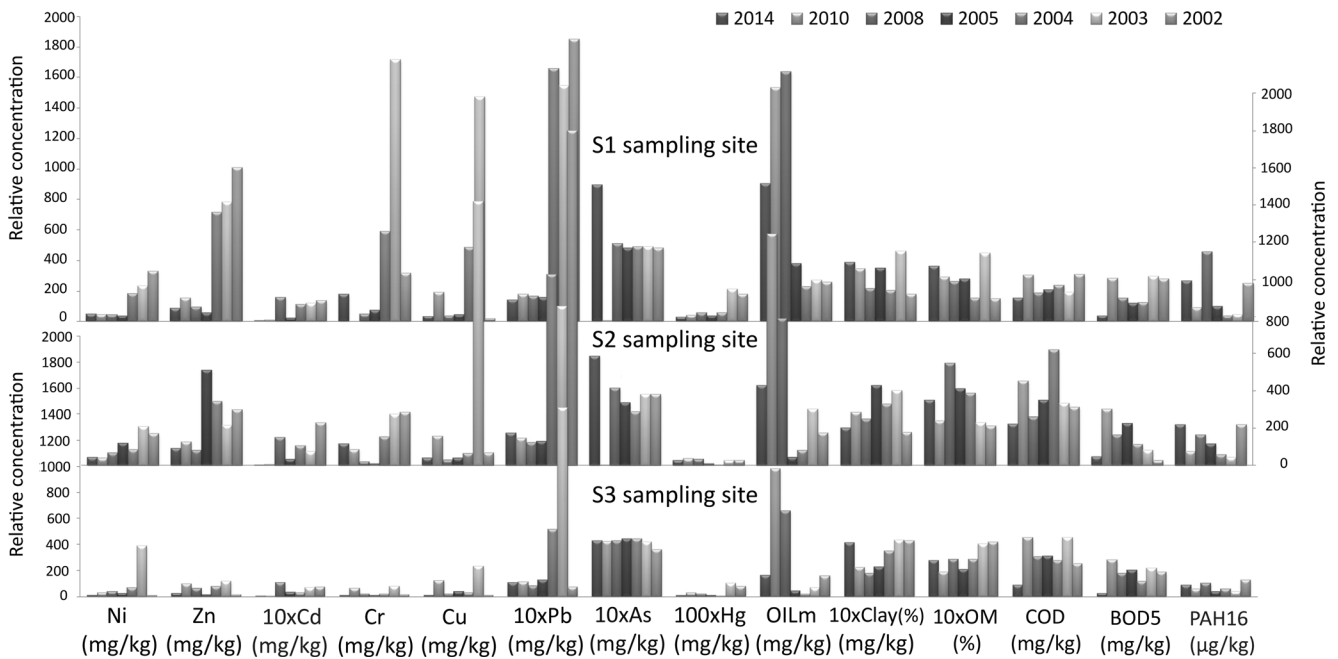


Fig. 2 Timeline plot of relative mass fractions of Ni, Zn, Cd, Cr, Cu, Pb, As, Hg, mineral oils, clay, organic matters, COD, BOD₅ and sum of 16 EPA PAHs from the surface sediment data set (from 0 to 50-cm depth). The average results are presented for each year (from 2002 to 2014), with

the averages from the most recent years on the left and the oldest samples on the right. In order to aid comparison of parameters with different levels of contamination, where indicated in the figure, some parameters were multiplied by factors of 10 or 100

to ÖNORM S 2088-2. Mean mass fractions of metals are higher than ERL values. Except Ni (100.3 mg/kg), all

heavy metals have means value lower than ERM, but maximum particularly higher like Zn (1010 mg/kg), Cr (1830 mg/kg), Cu (2600 mg/kg) and Hg (2.7 mg/kg) indicating that they are harmful to biota. The high dissimilarity of all metals from natural and legislation values are implying dominantly anthropogenic sources of contamination. Zn, Pb and Hg have lower mean value than PEL as given in Table 5. The mean values of As (46.4 mg/kg) from all sites are higher than those prescribed by the all natural, legislation values and SQGs except ERM values (Table 5), indicating dominantly complex origin from natural sources such as the underlying bedrock or transported parent alluvium material as it have been previously observed (Dalmacija 1998). Pb has lower values compared to RS 50/2012 but much higher than natural values (Table 5) that affiliate these metals to frequently monitoring metal group (Cu, Cr, Zn, Hg and Ni).

Table 8 Loadings of experimental variables (14) on significant principal components for the Lake Ludaš data set based on values from 42 samples (14 per site) from 0 to 50-cm depth

Variable	VF1	VF2	VF3	VF4
Ni	0.741	0.164	-0.036	0.102
Zn	0.796	0.097	0.008	0.109
Cd	<i>0.642</i>	-0.231	-0.345	-0.333
Cr	0.789	0.022	0.401	0.046
Cu	0.487	0.080	<i>0.635</i>	-0.290
Pb	0.873	0.241	-0.020	-0.092
As	0.062	-0.247	0.130	0.808
Hg	0.822	-0.136	0.196	0.007
OILm	-0.140	-0.902	0.096	-0.121
Clay	-0.035	0.448	0.351	-0.015
OM	-0.013	0.044	0.026	0.029
COD	-0.072	0.016	0.821	0.382
BOD ₅	0.100	-0.042	0.899	0.105
Phe	0.030	-0.054	0.123	0.907
Pyr	-0.055	-0.801	-0.053	0.481
PAH ₁₆	-0.100	-0.763	-0.066	0.464
Eigenvalue	4.30	3.21	2.43	1.32
% Total variance	26.89	20.07	15.19	8.26
Cumulative % variance	26.89	46.96	62.16	70.41

Bold and italic values indicate strong and moderate loadings, respectively

PAHs and mineral oil sediment quality guidelines

Total concentrations of the 10 priority PAHs (Nap, Ant, Phe, Flur, BaA, Chr, BkF, BaP, BghiP and InP) ranged from 0.06 to 182.2 µg/kg, with mean values from 29.51 to 52.32 µg/kg at S3 and S1, respectively (Table 6). Compared to the RS 50/2012 value for the sum of related PAH₁₀ (10,000 µg/kg), these levels should have a minor effect on biota. The sum of PAH₁₆ has something higher values than PAH₁₀ but bears a similar low risk level with a similar distribution in each sampling site.

Table 9 Pearson correlation matrix of heavy metals and other sediment quality parameters, from sites S1 to S3 in Lake Ludaš for surface sediment based on values from 42 samples (14 per site) from 0 to 50-cm depth

Variable	Ni	Zn	Cd	Cr	Cu	Pb	As	Hg	OILm	Clay	OM	COD	BOD ₅	Phe	Pyr	PAH ₁₆
Ni	1.000															
Zn	0.496*	1.000														
Cd	0.382**	0.419*	1.000													
Cr	0.403**	0.652*	0.341**	1.000												
Cu	0.218	0.325**	0.177	0.573*	1.000											
Pb	0.671*	0.628*	0.506*	0.623*	0.529*	1.000										
As	0.054	-0.002	-0.148	0.137	-0.058	-0.045	1.000									
Hg	0.592**	0.523*	0.348**	0.777*	0.454*	0.637*	0.082	1.000								
OILm	-0.220	-0.199	0.036	-0.080	-0.062	-0.314**	0.119	0.038	1.000							
Clay	0.040	-0.088	-0.151	0.171	0.236	0.050	-0.157	0.077	-0.283	1.000						
OM	-0.037	-0.167	0.159	0.099	0.013	-0.088	-0.006	0.084	-0.070	0.291	1.000					
COD	-0.000	-0.058	-0.363**	0.283	0.285	-0.068	0.421*	0.065	-0.010	0.246	0.180	1.000				
BOD ₅	0.162	0.145	-0.171	0.382**	0.494*	-0.033	0.173	0.214	0.043	0.237	0.089	0.797*	1.000			
Phe	0.022	0.174	-0.325**	0.141	-0.097	-0.091	0.660*	0.050	-0.004	0.064	0.076	0.366**	0.190	1.000		
Pyr	-0.102	-0.055	0.012	-0.128	-0.265	-0.243	0.535*	0.055	0.650*	-0.294	-0.091	0.143	0.029	0.458*	1.000	
PAH ₁₆	-0.141	-0.072	-0.053	-0.119	-0.260	-0.299	0.471*	-0.007	0.577*	-0.356**	-0.154	0.075	0.017	0.450*	0.823*	1.000

*Significance at the 0.01 probability level (two-tailed)

**Significance at the 0.05 probability level (two-tailed)

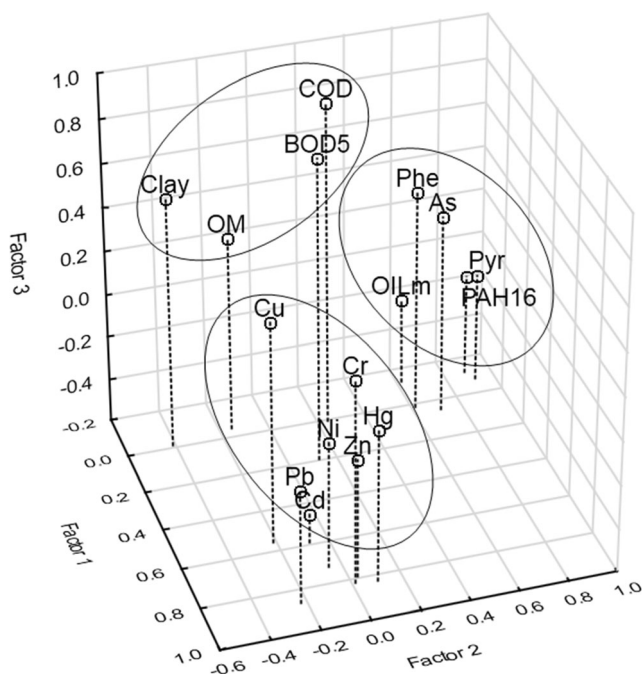


Fig. 3 Three-dimensional plot of loading from three VFs of organic and inorganic parameters assembled in three groups from the surface sediment data set (from 0 to 50-cm depth)

According to respective SQGs accepting Flo compared to ERL and TEL and DahA compared to TEL values at location S1, all other PAHs at all sites have lower values (Table 6). This suggests that adverse biological effects might occasionally occur at location S1. Likewise, it is good to note that the mean level of the total concentrations of the seven probably carcinogenic PAHs at S1 site has higher values than at locations S2 and S3 (Table 6).

Mineral oils from all sampling sites have wide range from 1.00 to 1801.53 mg/kg, with the mean gradient S1 > S2 > S3 (Table 4) but much lower than the values given in RS 50/2012 (Table 5). The proximity of the Tisa River and industry were probably the source of these elevated mineral oil concentration. In order to determinate the sources of this organic contaminant, the further statistical analysis were done with regard to the common origin of the PAHs.

Changes in sediment contamination over time (2002–2014)

In order to provide an insight into how the pollution at Ludaš Lake has changed over time, Fig. 2 summarizes the analytical results for each parameter of interest.

Ludaš Lake is fed by the Palić-Ludaš canal (Fig. 1) and drains from north to south into the Tisa River. As can be seen in Fig. 2, location S1, the site closest to the city of Subotica, therefore has the most anthropogenic pollution, and S3 the least. The trends observed for the heavy metals, whereby with the exception of As, mean mass fractions have generally declined in recent years, are consistent with the I_{geo} results presented above: As had the lowest I_{geo} value all the heavy metals, and its mass fractions

remain largely constant, suggesting natural origin. For the other metals (which showed higher I_{geo} values), anthropogenic pollution events occurred in the early years of this study but then stopped, presumably due to the global financial crisis, resulting in a steady decline in the heavy metal mass fractions in the lake sediments as time goes by. On the other hand, PAH₁₆, mineral oils and the other organic parameters show somewhat opposite trends, starting at low mass fractions and steadily increasing during the study. This suggests that they are the result of different anthropogenic activities, such as agriculture and combustion.

Due to the nature of the pollutants and hydrogeological aspects, the spatial groundwater influences in this region and the trends observed in Fig. 2, the statistical approaches utilized in the further investigations were performed on normalized data, to avoid the negative consequences of large oscillations in the values of all parameters within the investigated period.

Multivariate statistical analyses

Principal component analysis/factor analysis and other synthetic parameters

The complex nature of associations among the metals and PAHs were elaborated by multivariate analysis based on PCA/FA performed on the normalized data. The results are shown in the Tables 8 and 9 and Fig. 3. VFs of the entire data set (Table 8) revealed four VFs (VF1, VF2, VF3 and VF4) with eigenvalues >1. Special emphasis was given values with significant loading >0.70 that were considered as significant (strong). For investigated surface sediments, VFs explained 71.12 % of the total variance in the sediment quality data set.

The first and most important component, the VF1 accounting for 26.89 % of the total variance, was significantly correlated with Pb, Hg, Zn, Cr, Ni and moderated Cd. This feature generally reflects the local influence of active hydrothermal circulation, and it is dominantly due to geological (natural) origin of these metals from the parent Pannonian sediment. The minimum values which are very below the natural values confirm their dominantly geochemical status (Table 5). Hg and Cr have higher correlation factor ($r = 0.777, p < 0.01$, Table 9), and their release into the environment is mostly due to human activity mostly as leaching from agricultural soil after fertilization or from landfills (Qian et al. 2016). The unusually increase of the concentration of investigated heavy metals is caused by the periodic flooding in this part of the Pannonian Basin and human activities that cause sediment and water pollution.

The second component (VF2) accounting for 20.07 % of the total variance and negative significant loading of mineral oil, Pyr and PAH₁₆ (Table 8) and molecular diagnostic ratio of Pyr and Flur that have maximum values at all three sites more than 0.4 classified all sites as pyrogenic periodically contaminated. Low correlation of Pyr and mineral oil was observed in

Table 9 ($r = 0.66$, $p < 0.01$) confirming the given assumption indicating variations in pollution intensity possibly from metal processing industry and industrial wastewater from the city of Subotica but predominantly from water transport in the nearby Tisa River.

Organic parameters (COD and BOD₅) and Cu have high and moderate at VF3 loading, respectively (Table 9) confirming the binding of this metal with organic matter fraction in sediment, because this area receives sewage from the city, which carries a large load of organic matter. Although, improved system for waste and water utility of the city of Subotica has not yet been optimized at an acceptable level (Petričević et al. 2012).

The moderate correlation of As and Phe was observed ($r = 0.66$, $p < 0.01$, Table 9) and confirmed by significant loadings as 0.808 and 0.907, respectively, of fourth VF that accounts for 8.26 % of total variance. The dual origin of arsenic (anthropogenic and mineral) can be used to explain this correlation. The association of As with organic anthropogenic source is partly from the process of enhancing As mobilization from metal-reducing microbes (Barringer and Reilly 2013) as organic (methylated) forms, which are generally considered the least toxic (Cudić et al. 2007). Study from Cebon et al. (2014) confirmed that the presence of phenanthrene accelerates microbial degradation of organic matter which can subsequently react with As. Therefore, increasing the mass fractions of phenanthrene in water-sediment matrix implies an increase in microbial substrate and therefore arsenic dominantly methylated forms.

In order to perceive the wider dependence of organic and inorganic parameters, the grouping to the case of multiple variables was carried out on the three factor components. This was illustrated by three-dimensional scatter plot (Fig. 3). Compared to loading in the factor analysis (Table 8) in Fig. 3, the parameters assembled in three groups have slightly different arrangements most in relation to the organic parameters. It is interesting that COD, BOD₅, clay and OM in the third group differ from VF3 showing a lack of moderate linkage of these general organic parameters to Cu that is clustered in the first major group with other metals explaining their primary geogenic origin (Fig. 3). As, Phe, Pyr, PAHs and OILm are clustered in the second major group, indicating their similar distribution patterns and sources. This pattern also confirmed the binding of As with organic sources from human activity. After a given analysis, it can be noted the significant correlations of As among organic pollutants and complex grouping of inorganic contaminants by mostly geochemical origin and periodical influencing by human activity. Arsenic is the most abounded toxic metal in freshwater system in Vojvodina region posing a serious threat to human health (Dalmacija 1998). The further studies should explain the geochemistry behaviour and toxic origin of As in this complex sediment-water system in order to do hot spot mapping of

these particular metals and establish the possible solutions for its reduction to the level of acceptance for living organisms especially in aquatic ecosystems and freshwater quality requirements.

Conclusion

The systematic long-term investigation detailed in this work revealed many environmental factors which can influence the chemistry and monitoring concept of priority substances in significant wetland areas such as Ludaš Lake.

Based on the analysis given, both dibenzo[*a,h*]anthracene and fluorine should be added to the list of priority substances, due to their abundance, carcinogenicity and ecotoxicity. A specific relation between As and organic pollutants was observed, particularly phenanthrene, which supports further intensive monitoring and investigation to define the nature of this link. Cd, Cr, Cu, Pb and Hg were also highlighted as elements in need of further study due to their dual geochemical and anthropogenic origins and their intense impact on benthic processes. There is a need to identify their specific loadings from industry, municipal wastewater and agriculture and define their transport mechanisms and eventual fate.

Although the temporal trends observed in this paper show an overall reduction in the levels of pollution in Ludaš Lake, the historical pollution at this Ramsar site shows the importance of taking care in the design of future monitoring programs. As the regional economic output improves, coverage of current and new organic and heavy metal pollutants from diverse and actual sources should be ensured by establishing a strategy and freshwater and sediment quality monitoring network focusing on the environmental hazards identified.

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