



Geochronological investigation of the Danube Djerdap Lake sediments (Serbia): sedimentology and inorganic composition

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Abstract The objective of this study is geochronological investigation of sedimentological and inorganic composition, in the Danube Djerdap Lake sediments in order to obtain reliable information about former pollution. Eleven samples were taken from the 135-cm-deep sediment core drilled at the Orlova location. Since the core represents sediments deposited during 1972–2016, the sedimentation rate of $\sim 3 \text{ cm year}^{-1}$ was estimated. Grain size, mineralogical and geochemical composition was determined. Sediments are sandy silts and clayey silts, and only the

deepest and shallowest layers contain $> 30\%$ of sand-size fraction. The highest concentrations of minor elements are found in the oldest sediment (1972–1977) as a consequence of the high flux of the material from variable sources. During the sedimentation period (1975–1990), the concentrations of analyzed elements are generally decreasing until the beginning of 1990s. After this period, there are two distinct decreases and two distinct increases in concentrations of elements. The fluctuations in minor element concentrations are a consequence of both natural and anthropogenic sources. Granitic rocks situated south are source of minerals that carry minor elements. Enrichment Factor, Geoaccumulation Index, Contamination Factor and Pollution Load Index indicate that concentrations of certain minor elements at specific depositional periods have anthropogenic source.

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Introduction

Rivers, which approximately deliver 20 billion metric tons of transported sediment to oceans every year, play a key role in Earth surface processes, marine sedimentation and biogeochemical cycles in oceans (Shao

et al. 2012). Minor elements have a tendency to accumulate in sediments. The capacity of sediment to adsorb and retain contaminants depends of their characteristics such as surface area and surface properties of the particles (Filgueiras et al. 2004). The main sources of minor elements in drainage basins are weathering of rocks (Chetelat et al. 2013) and anthropogenic activities. The main anthropogenic source of minor elements is mining and smelting, disposal of effluents containing minor elements, industrial waste and haphazard use of fertilizers and pesticides that contain minor elements (Varol and Şen 2012). The concentrations of minor elements are affected by sediment mineralogy, grain size and distribution. Content of organic matter and clay-sized fraction and surface area control the minor element mobility (Lapwortha et al. 2012). Minor elements are adsorbed by organic substances and Fe and Mn oxides with the adsorption capacity increasing with the particle size decreasing. Adsorbed minor elements can be released again in the environment by processes dependant on pH and redox potential (Filgueiras et al. 2004).

Danube River is the second largest river in Europe and the most international river in the world (Salewicz 1991). The total length of the Danube River is 2875 km, its annual water flow is $110\text{--}220 \times 10^9 \text{ m}^3$, and from the catchment area of about 817,000 km², a considerable quantity of sediment, 7–30 million tons, is annually transported (Literathy and Laszlo 1995; Babić Mladenović et al. 2013). The hydropower dam Djerdap 1 was constructed during 1972 on Danube at the Serbia-Romania border, at 943 km from the mouth. Building of the dam resulted in the formation of the Djerdap Lake, with a volume of about 3500 million m³. This was an increase of about 2100 million m³ compared to the volume of the Danube's natural channel. Before the dam was built, it was estimated that 50% (i.e., 20,000–30,000 kt year⁻¹) of the suspended sediments entering the Djerdap 1 Reservoir would be retained; however, it is now estimated that the total suspended load (8900 kt year⁻¹) is much lower than the above postulated load. Nevertheless, construction of the dam disturbed the natural equilibrium of Danube flow along that stretch and induced impacts both in the backwater zone and downstream of the dam.

The Danube River is not only a large, highly varying and international river basin, but also it

receives correspondingly an enormous pollution load of a high variety of emission sources in terms of quantity and quality. Consequently, in the last 15 years many initiatives have been started to obtain detailed information about the state of pollution throughout the total river system and as a result the current information about the quality and quantity of contamination as well as about major emission sources is very detailed. Voitke et al. (2003) studied the quality of sediments along the whole Danube flow and found that the pollution was relatively low in the Austrian and Hungarian parts. Same authors determined an increase in concentration of minor elements at the Djerdap Lake, and then a constant level or a slight decrease was found down to the Danube Delta. However, due to various reasons (political situation, improving analytical methods, continuous identification of new and emerging pollutants etc.) the knowledge about former pollution and its sources is much more restricted. One possibility to get retrospective information is appointed to geochronological analyses of appropriate sediment archives. Although this approach has also its limitations, pollution histories can be obtained with a high environmental relevance.

For geochronological studies in the Danube river system, the Djerdap Lake represents a very favorable sediment archive. Water and sediment from the entire upstream portion of the Danube River basin, shared by many countries with a total population of about 80 million, concentrate at the Serbian sector of the Danube, especially in the Djerdap Lake (Babić Mladenović et al. 2013).

The tributaries flowing into the Danube River greatly affect the sediment regime bringing large volumes of sediment (Babić Mladenović et al. 2013) which increases the heavy metal concentrations in sediments (Pajević et al. 2008). Heavy metal content in sediments of the Danube River and its tributaries have been studied by numerous of authors; however, no relevant methods have been established for quantification of minor elements in the water–sediment system (Vuković et al. 2014). Milenković et al. (2005) found that concentration of certain metals (Fe, Mn, Ni, Zn, Cu, Cr and Cd) increased on average 46.6% for Zn up to 156.2% for Ni in the period since early 1980s until 2005. On the contrary, during the same time span a decrease of 8.2% of Pb concentration and 269% of Hg was observed.

Vuković et al. (2014) analyzed heavy metal concentration in Danube sediments on four locations from Belgrade to Djerdap Lake and found that heavy metal concentration slightly increased downstream. Furthermore, these authors found that concentration of minor elements displayed seasonal variations and was higher in autumn up to 20% than in spring.

The research in this study includes geochronological investigation of sedimentological, inorganic and organic composition in the Djerdap Lake. According to Heim and Schwarzbauer (2013), there are three main prerequisites that a sediment archive should fulfill in order to be suitable for reconstruction of load histories: an undisturbed sedimentation of fine-grained particles, sufficiently long sedimentation interval, between 10 and 100 years, and knowledge of specific input sources, pathways and transport processes. The Djerdap Lake sediment archive accomplishes all of them. The main objective of this study is geochronological investigation of inorganic and organic anthropogenic pollutants in the Djerdap Lake sediments, as indicators for different emission sources. Given the scope of the research, the results are presented in two papers. The investigation of sedimentological and inorganic composition, specifically of minor elements, in the Djerdap Lake sediments is given in this paper.

Study area

The sediment core was sampled at the location Orlova in the Djerdap Lake (N 7562863 E 4946016, 84 m above sea level) in March 2016 (Fig. 1). According to the division of Serbian reach of Danube given by Babić Mladenović et al. (2013), the sampling location belongs to the Djerdap Danube section, which is the middle of the Serbian part of Danube and covers the reach from Golubac to Kladovo (1042–931 km).

The Orlova location was selected due to two main reasons. The first reason is that the deposition of lake sediments in this area commenced on the flooded agricultural land, which facilitates determination of the relative age of sediments. The second reason is that it has uniform geological setting represented by the Lower Carboniferous granitoids.

Sedimentation rate in the Djerdap Lake varies with the distance from the dam. In previous studies, it was estimated that the sedimentation rate in the Djerdap reservoir is $\sim 4.9 \text{ cm year}^{-1}$ while in the upper

Danube stretch it reaches $23.3 \text{ cm year}^{-1}$ (Teodoru and Wehrli 2005). Vuković et al. (2014) estimated that the sedimentation rate near Veliko Gradište, which is about 30 km upstream from Orlova, is $3 \pm 1 \text{ cm year}^{-1}$. Similar sedimentation rate can be estimated from the Orlova drill-hole analyzed in this study.

Drilled core had a total depth of 135 cm of river sediments before the soil was reached, indicating that the deepest part of the core sediments was deposited immediately after the lake was formed (Fig. 1). Since core of 135 cm depth represents sediments deposited during the time span of 44 years (1972–2016), the sedimentation rate of $\sim 3 \text{ cm year}^{-1}$ can be estimated. According to this sedimentation rate and the time of deposition, samples can roughly be assigned a specific age (Fig. 1).

The drill-hole was divided into 11 samples, the top 5 samples are of 15 cm each, and the following 6 samples are 10 cm each. Since the core was excavated in March 2016, the first interval of 15 cm is marked as 5-year period 2011–2016.

Climate conditions of the area of the Djerdap Lake

Climate in the area of the Djerdap Lake is typical continental with average temperature of $11.6 \text{ }^\circ\text{C}$ (RHMZ 2018). Mean precipitation for the period 1991–2006 was 672 mm with distinct annual alternations (Fig. 2). During the same period prevailing winds, with average velocity of 2.11 ms^{-1} , were mainly coming from North and South, while East and West winds had lower velocity and lower frequency (Fig. 3). Dominant winds in the study area were NW (264 days), SW (254 days) and N (253 days), with average annual velocity of 1.88, 3.73 and 2.82 ms^{-1} , respectively (RHMZ 2018; Fig. 3).

Water level of the Djerdap Lake

Water level at the Veliko Gradište, as the nearest measuring station to the Orlova, was mainly around 700 cm during the period 1991–2016 (Fig. 4). During 2006 maximal water level of 960 cm was measured, while minimal water levels were measured at distinct times: 1995 (640 cm), 1996 (575 cm), 2000 (500 cm), 2001 (440 cm) and 2015 (588 cm).

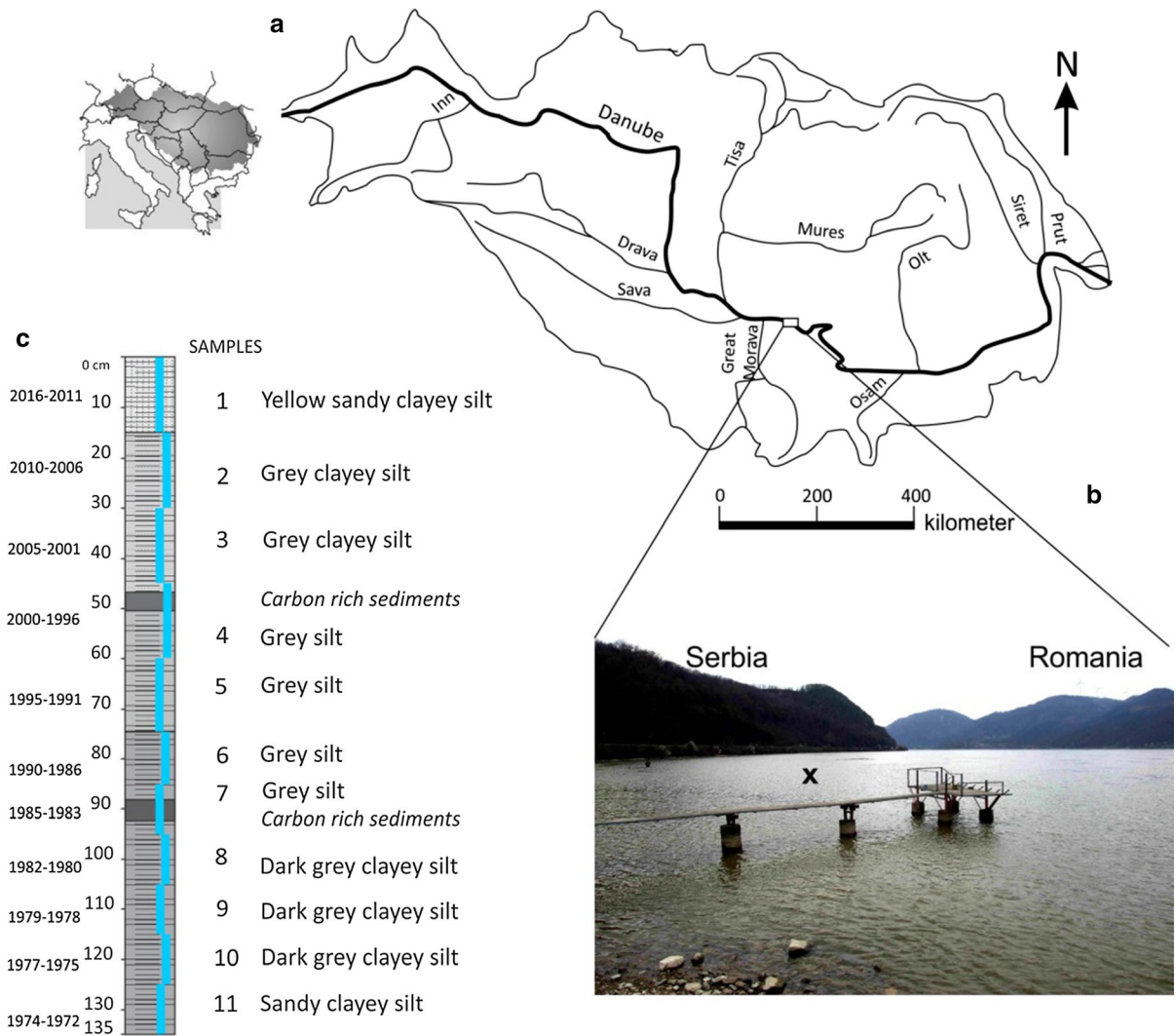


Fig. 1 a Map of the Danube basin, b photograph of the Orlova sampling location (X—exact drilling location) and c lithostratigraphic column of the sediment core

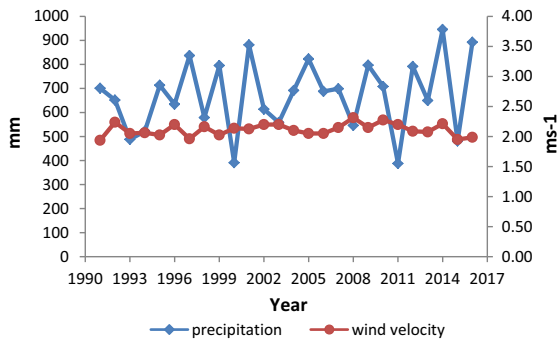


Fig. 2 Average precipitation and wind velocity at the Djerdap Lake (1991–2016)

Methodology

Particle size analyses

Grain size analysis was performed according to a standard wet sieving procedure (Dane and Topp 2002) using the following sieve sizes: 1, 0.5, 0.25, 0.125 and 0.063 mm. The sieved material was dried in an oven and weighed. The size of fractions of the material < 0.063 mm was analyzed using standard pipet method.

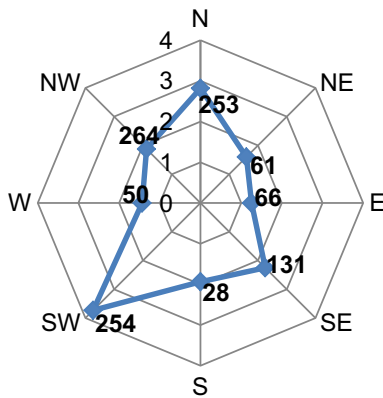
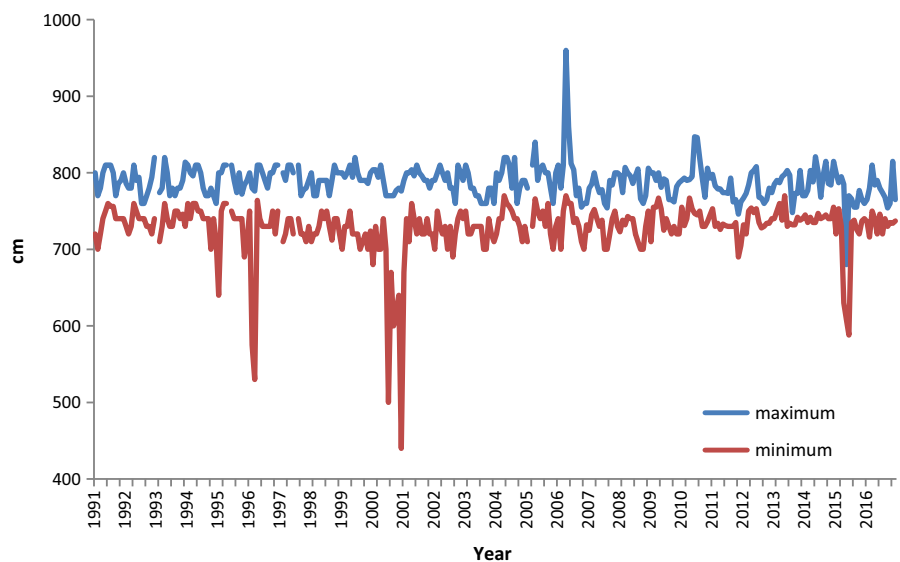


Fig. 3 Wind rose for the Djerdap Lake area (1991–2016) with average daily frequency

Mineralogical analyses

Mineralogical analysis was carried out using the X-ray powder diffraction (XRPD). It was performed on a Philips PW 1710 powder diffractometer with $\text{CuK}\alpha_{1,2} = 1.54178 \text{ \AA}$ radiation and a 40 kV, 30 mA. The XRD (X-ray diffraction) pattern was recorded over a 2θ interval of $4^\circ\text{--}70^\circ$, with a step size of 0.02° and the fixed counting time of 1 s per step. X-ray diffractogram of sample was subjected to quantitative mineralogical analysis using FullProf computer program (Rodríguez-Carvajal 1993) based on the principles for diffractogram profiling set out by Rietveld (1969). Quantification of amorphous and sulfide phase was not done.

Fig. 4 Water level change at the Djerdap Lake (1991–2006)



Concentrations of major elements

Concentrations of major elements were determined using the X-ray fluorescence (XRF). After drying until constant mass at 105°C , samples were prepared as pressed pellets by mixing coal and tableting aid wax (Hoechst wax C micro powder produced by Merck (Lot number-K36429014636) in ratio 85:15, respectively. Pressure of 25t in Retsch PP25 hydraulic press was applied during 5 min to the mixture in order to produce stable pellets which were 32 mm in diameter and around 3 mm high. Semi-quantitative and qualitative analysis was performed with ARL PERFORM'X Sequential X-Ray Fluorescence Spectrometer (Thermo Fisher Scientific, Switzerland). The spectrometer was equipped with 4200 W Rh X-ray tube, goniometer containing seven optical crystals (AX16C, AX09, AX03, GE111, PET, LiF200, LiF220) and two detectors (flow proportional counter—FPC and scintillation detector—SC). Instrument is able to detect all elements from C to Am, but for semi-quantitative analysis only measurements of Na and heavier elements were considered (O and C concentrations were obtained calculating from the lost on ignition). Semi-quantitative analysis was performed with ARL software UniQuant specialized for the standardless analysis. Results of qualitative analysis were used to eliminate any doubts regarding measurements of the elements close to the detection limit and possible interferences emerged as consequence of line overlaps.

Concentrations of minor elements

Concentrations of minor elements were determined using the inductively coupled plasma (ICP). All solutions were prepared using analytical grade reagents and deionized water with resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$ obtained from a Milli-Q system (Millipore, Bedford, USA).

The digestion of sediment samples (0.5 g) was performed by adding 9 ml HNO_3 (65% v/v), 3 ml HF (48% v/v) and 2 ml HCl (37% v/v) in PFA vessels according standard procedure for microwave-assisted acid digestion of siliceous and organically based matrices (EPA Method 3052) with an CEM MARS5 system (CEM Corp., Matthews, NC). After digestion, cooled samples were filtrated through membrane filter ($0.45 \mu\text{m}$) and diluted with deionized water to a total volume of 50 ml.

The blank analytical solutions were performed with same procedure as quality control of the reagents. All procedures were performed in triplicate, including the blank analytical solutions.

Basic calibration was performed by the measurement of 5 calibration solutions with concentrations ranging from 0.01 to 2.0 mg l^{-1} . The linear correlation coefficients were typically > 0.99 . The limits of detection (LODs) were determined as the concentration corresponding to three times the standard deviation of 10 blank samples.

The quality of data was checked through recovery experiments by certificated reference material Sewage Sludge 2 (CRM 029-50G, Fluka Analytical).

For minor element determination, inductively coupled plasma optical emission spectrometer with axial view (Thermo scientific iCAP 6000 series ICP-Spectrometer, USA) was used. Argon gas with a minimum purity of 99.999% was used to purge the optics and plasma generation. Operating optimal parameters were: RF frequency 27.12 MHz; operating power 1.15 kW; pump rate 50 rpm; plasma argon flow rate 0.5 l min^{-1} ; auxiliary argon flow rate 0.5 l min^{-1} ; sample flow rate 0.02 ml min^{-1} .

The emission wavelengths (nm) for determination were as follows: Zn 206.200, Cu 327.393, Ni 231.604, As 189.042, Pb 216.997, Cr 267.716, Cd 214.480 and Co 228.616.

Results and discussion

Mineralogical and grain size composition

Sediment samples from Djerdap Lake core have similar mineralogical composition. They consist of quartz, mica, chlorite, calcite, dolomite, feldspar and smectite clay minerals.

Grain size composition is similar for most sediment samples, except for the deepest and the shallowest layers which both contain $> 30\%$ of sand-size fraction (Fig. 5). Sand-size fraction is mostly built of granite fragments (Fig. 6).

The deepest sediment samples represent the initial lake stage after the dam was built in 1972. During this period, material from various parts of the surrounding environment, disturbed during building of the dam, was deposited in the Djerdap Lake. Therefore, the exact origin of material deposited during the initial time interval (1972–1977) cannot be precisely determined. After this period, the environment around the Djerdap Lake reached new equilibrium and adjusted to the imposed anthropogenic changes to the landscape. The sediments deposited during the period 1975–2010 (15–130 cm) contain sand fraction between 6.48 and 21.92%. According to Shepard (1954), these sediments are classified as sandy silts and clayey silts. The shallowest sediments (0–15 cm) deposited during the period 2011–2016 have highest sand contents relative to other samples, which is most probably a consequence of prevailing winds (Fig. 3) and low water level (Fig. 4).

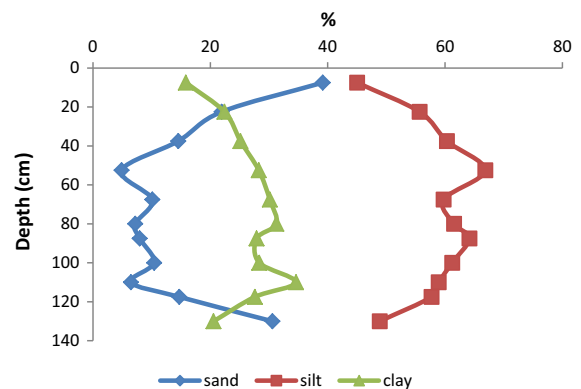


Fig. 5 Grain size composition of the Djerdap Lake drill-hole sediments

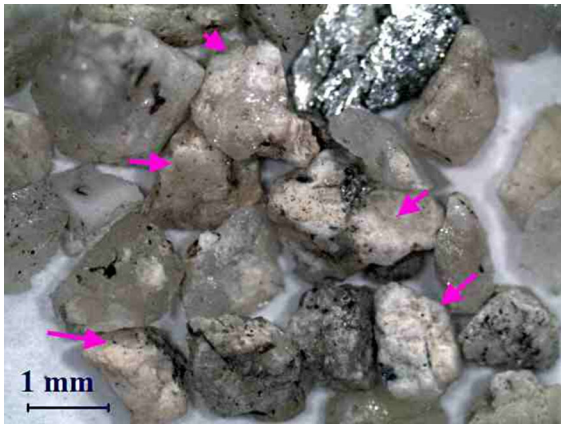


Fig. 6 Granite fragments in the sand fraction of the Djerdap Lake sediments

Major element variation in sediments

The concentrations of major elements in sediments from the Djerdap Lake are in accordance with their mineralogical composition (Fig. 7).

Generally, contents of Ca and Mg are slightly increasing from the bottom to top sediments indicating the increasing content of carbonate minerals. K and Fe

show less variation in the lower part of the drill-hole, while the opposite trend is obvious for content of Si. Contents of Na, Al and Mn are varying throughout the drill-hole without an easily detectable trend.

Minor element variation in sediments

Besides the contents of major elements, the concentrations of Cu, Zn, Pb, As, Cd, Cr, Ni and Co were determined in the Djerdap Lake sediments at the Orlova location. The highest concentrations of all tested elements are found in the oldest sediment layers below 120 cm depth, corresponding to the deposition period 1972–1977 (Fig. 8). This result is a consequence of the high flux of the material from variable sources which transport was initiated during dam building and lake formation, which corresponds to the grain size composition (Fig. 5). Therefore, minor element concentrations in these samples are not entirely representative result of the Danube River sediment composition but are a characteristic of the disturbed environment during dam building that occurred this time period.

During the subsequent sedimentation stage (1975–1990, 75–130 cm), the concentrations of tested

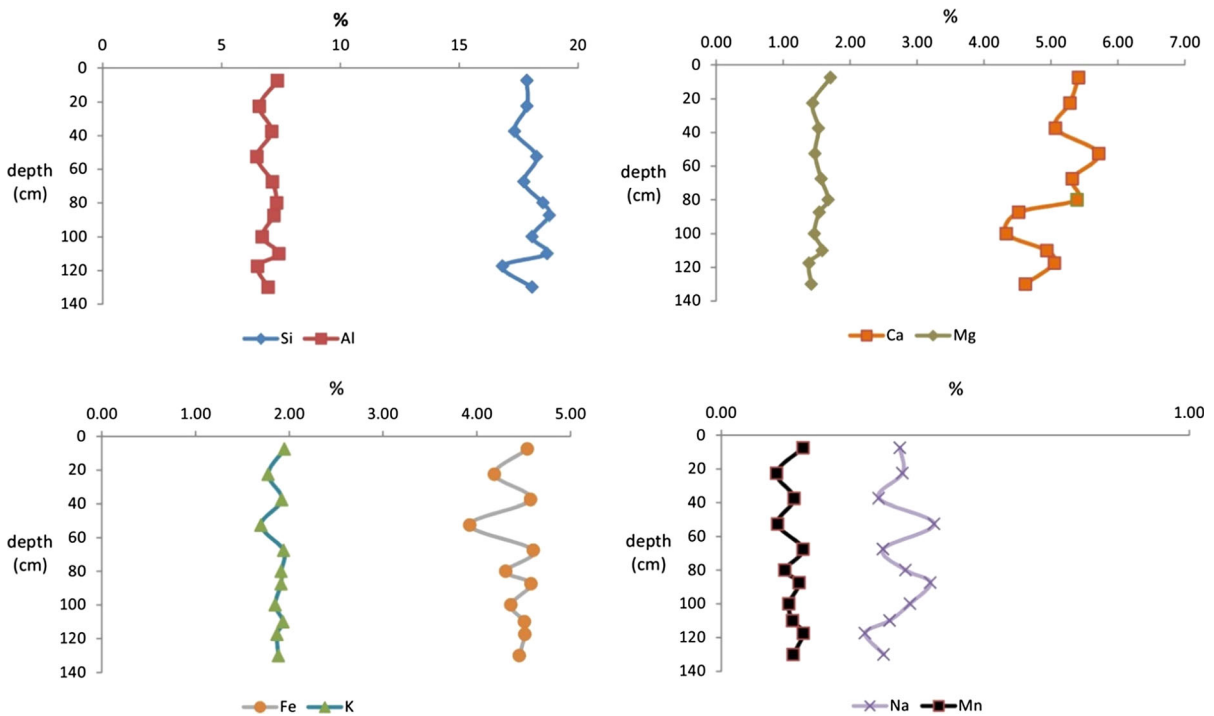


Fig. 7 Concentrations of major elements in sediments from the Djerdap Lake drill-hole (%)

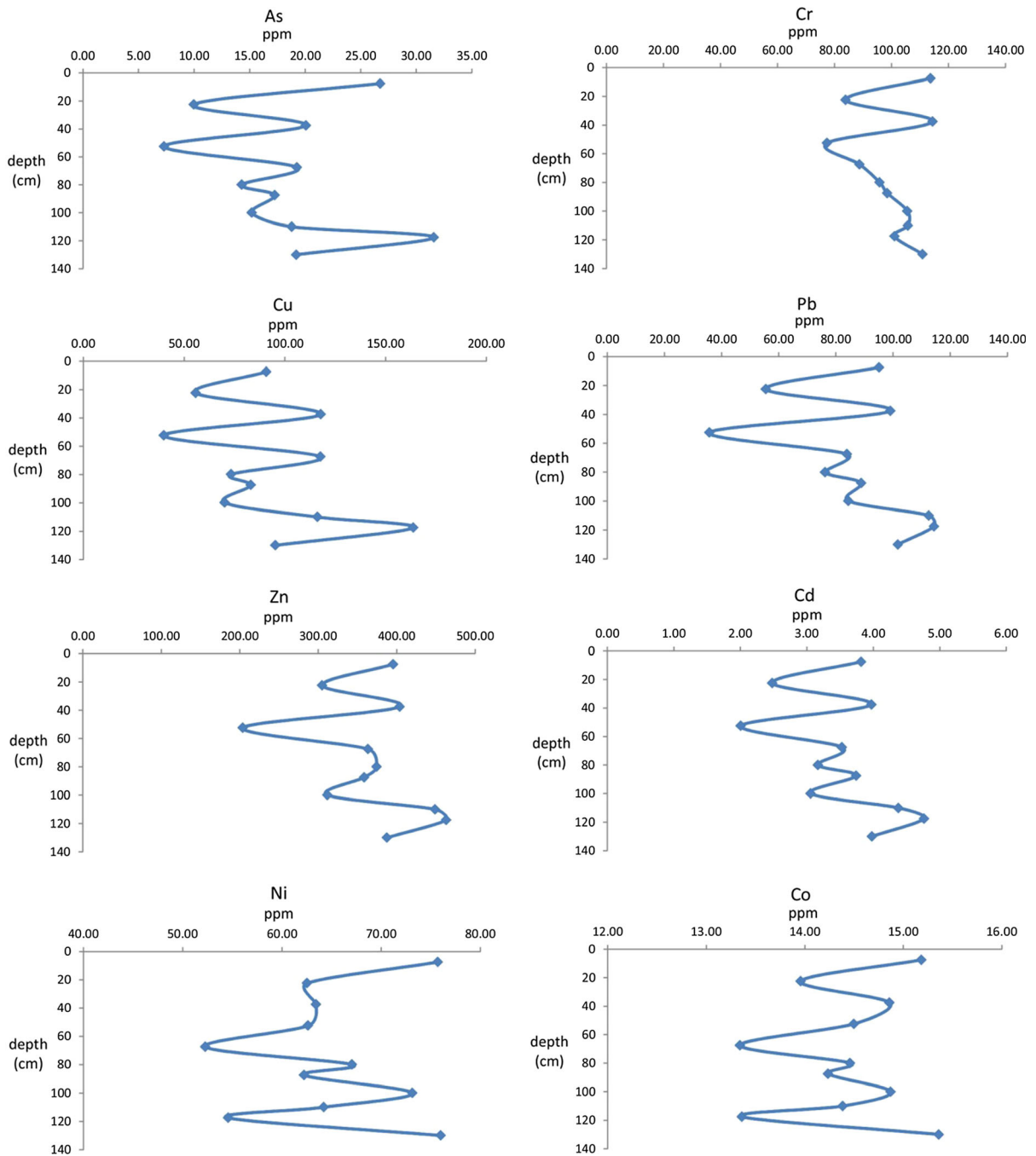


Fig. 8 Concentrations of minor elements in sediments from the Djerdap Lake drill-hole

elements are showing variations, but concentrations are generally decreasing until the beginning of 1990s (90 cm; Fig. 8). After this period, the variations in concentrations of analyzed elements are showing notable fluctuations. There are two distinct decreases

and two distinct increases in concentrations of analyzed elements. First decrease corresponds to the period 1996–2000 (45–60 cm) and the second to the period 2006–2010 (15–30 cm), while the periods of increased concentrations are 2001–2005 (30–45 cm),

and the last period of observation 2011–2016 (0–15 cm).

Elements Zn, Pb, Cd, As and Cr are mutually well correlated, while Cu is correlated with all of these elements beside Cr in the analyzed sediments (Table 1). These elements are also well correlated with Fe and Mn, indicating that they are probably bound to Fe–Mn oxides in sediments. Ni and Co show high mutual correlation, but they are not correlated to any other element. This confirms that these two elements have the same source probably different than other elements.

Temporal change of contents of elements and grain size fractions

As shown above, the obtained results show that the concentration of minor elements in Djerdap Lake sediments shows substantial fluctuations during the entire analyzed period 1972–2016. After the initial deposition stage (1972–1979, 120–135 cm) characterized by high concentration of minor elements (Fig. 8), sedimentation continued through the longest stable period of deposition in the Djerdap Lake (1980–1990, 75–110 cm). For the subsequent sedimentation period, a notable fluctuation in concentrations of elements was characteristic. Generally, the concentrations were low during 1991–2001 and 2007–2010 and high during 2002–2006 and 2011–2016. In order to determine to rate of increase between this stable stage of sedimentation (1977–1990, 75–130 cm) and other depositional stages, the rate of increase was calculated using the following formula:

$$\text{Increase} = \text{observation value} - \text{original value}$$

$$\% \text{Increase} = \text{increase} \div \text{original value} \times 100.$$

Obtained results of rate of increase for major elements and grain size fractions are given in Table 2 and for minor elements in Table 3. Sand fractions decreased for 75% in sediments since the Djerdap Lake was formed (1972–1979) compared to the following period 1980–1990 for the reason explained in the previous discussion. During the same period, concentrations of As and Cu increased for > 50%, Cd 21.87% and Pb for 19.37%, Zn for 13.32% and Cr 4.51%. The concentration of Ni and Co decreased from the initial Lake stage compared to the following

Table 1 Correlations between concentrations of major and minor elements in Djerdap lake sediments

	Ni	Cu	Pb	Zn	Cd	As	Cr	Si	Na	Mg	Al	K	Ca	Mn	Fe
Co	0.931**	-0.379	0.047	-0.106	-0.074	-0.12	0.568	0.097	0.224	0.228	0.268	0.069	-0.24	-0.161	-0.074
Ni		-0.406	0.063	-0.075	-0.081	-0.071	0.534	0.196	0.22	0.227	0.224	0.076	-0.305	-0.156	-0.085
Cu			0.846**	0.867**	0.907**	0.867**	0.486	-0.421	-0.846**	-0.117	0.178	0.597	-0.177	0.776**	0.749**
Pb				0.942**	0.976**	0.834**	0.813**	-0.133	-0.704*	0.051	0.451	0.785**	-0.506	0.769**	0.856**
Zn					0.954**	0.828**	0.692*	-0.099	-0.767**	0.158	0.498	0.793**	-0.272	0.701*	0.812**
Cd						0.877**	0.722*	-0.173	-0.717*	0.027	0.411	0.747**	-0.386	0.804**	0.840**
As							0.645*	-0.405	-0.701*	0.069	0.229	0.638*	-0.166	0.871**	0.746**
Cr								-0.176	-0.47	0.208	0.496	0.698*	-0.509	0.564	0.695*
Si									0.558	0.502	0.54	0.179	-0.113	-0.192	-0.073
Na										0.189	-0.073	-0.465	0.056	-0.499	-0.569
Mg											0.824**	0.565	0.34	0.209	0.243
Al												0.840**	-0.06	0.426	0.605*
K													-0.289	0.771**	0.912**
Ca														-0.266	-0.446
Mn															0.884**

**Correlation is significant at the 0.01 level (2-tailed), *correlation is significant at the 0.05 level (2-tailed)

Table 2 Percent of increase of major elements and grain size fractions between given periods and period (1977–1990)

Period	Si	Al	Na	K	Ca	Mg	Fe	Mn	Sand	Silt	Clay
2016–2011	– 1.72	4.76	1.44	2.90	12.58	12.87	1.89	12.88	203.64	– 23.36	– 44.21
2010–2007	– 1.72	– 6.07	2.90	– 6.33	9.88	– 4.62	– 5.97	– 23.67	69.97	– 5.21	– 21.02
2006–2002	4.56	– 1.34	10.51	– 1.32	– 5.41	– 0.99	– 2.67	– 0.59	– 12.74	– 2.71	11.40
1991–2001	– 0.95	– 2.93	6.35	– 3.96	14.71	0.66	– 4.28	– 4.74	– 41.85	7.78	2.91
1972–1979	– 3.96	– 4.00	– 13.03	– 0.92	0.57	– 7.10	0.65	6.25	75.63	– 9.28	– 15.17

Table 3 Percent of increase of minor elements between given periods and period 1977–1990

Period	Co	Ni	Cu	Pb	Zn	Cd	As	Cr
2016–2011	4.79	13.57	5.94	5.12	5.92	6.40	63.21	12.14
2010–2007	– 3.66	– 6.21	– 34.94	– 38.66	– 18.31	– 30.79	– 39.16	– 17.24
2006–2002	2.56	– 4.85	37.49	9.51	8.15	10.74	22.42	12.85
1991–2001	– 3.92	– 13.81	– 8.04	– 33.92	– 24.01	– 22.84	– 18.99	– 18.05
1972–1979	– 0.88	– 2.06	51.09	19.37	13.92	21.87	54.92	4.51

period additionally proving a different source of these elements.

During the three following periods (1991–2001, 2002–2006 and 2007–2010), the concentration of Na and Ca slightly increased as a consequence of variable flux of material from granitoides and carbonate rocks. During the last analyzed period (2011–2016), content of sand fraction and concentrations of all tested elements, besides Si, as well as content of sand fraction, substantially increased (Fig. 2, 7, 8).

Concentrations of minor elements during the period 1990–2001 decreased in high range: from 3.93% for Co, up to 33.92% for Zn. During the subsequent period 2002–2006, the concentrations of all minor elements, except Ni, increased. Similar results were obtained in previous study done by Milenković et al. (2005). These authors compared concentrations of heavy elements in Djerdap Lake sediments with the data obtained by Vasiljević and Tomašević (1985). Both studies were conducted at the same location, and results showed that concentrations of Fe, Mn, Ni, Zn, Cu, Cr and Cd increased over the entire gorge, while concentrations of Hg and Pb decreased during the 20-year time span.

The percent of decrease during the period 2007–2010 compared to the period 1980–1990 is substantial for all elements except Ni and Co. These results are probably showing a transitional period in economy, implementation of environmental laws and

usage of unleaded gasoline. The percent of increase rises again very high in the last period of investigation 2011–2016. Ni and Co are following trends of other elements due to large amount of sediments mobilized and transported through the entire watershed due to 100-year occurrence floods that devastated the West Balkan region in May 2014.

Pollution indices

Best way to determine more precisely whether the source of minor elements in river sediments has geogenic or anthropogenic origin is to calculate the pollution indices (e.g., Li et al. 2018; Looi et al. 2018; Barbieri 2016; Çevik et al. 2009). The obtained values of pollution indices heavily depend on the used background values, and recent study indicates that natural background values are most suitable, and whenever it is possible should be used (Štrbac et al. 2017). Establishing background values that are representative for the large watersheds such as Danube is not an easy task. One way to overcome this problem is to use background values from certain river reaches. However, in the case of the Djerdap Lake, where water and sediment from the entire upstream part of the Danube River watershed, shared by a many countries with an entire population of above 80 million people, this is not feasible.

Table 4 Enrichment factor for the Djerdap Lake sediments

Depth (cm)	Time period	Ni	Cu	Pb	Zn	Cd	As	Cr
0–15	2016–2011	0.69	0.63	0.93	0.96	1.44	0.69	0.80
15–30	2010–2006	0.64	0.43	0.61	0.82	1.05	0.29	0.66
30–45	2005–2001	0.60	0.84	1.00	1.01	1.55	0.53	0.84
45–60	2000–1996	0.65	0.31	0.40	0.56	0.86	0.21	0.62
60–75	1995–1991	0.49	0.84	0.84	0.91	1.37	0.51	0.65
75–90	1990–1987	0.62	0.51	0.75	0.91	1.20	0.37	0.68
90–100	1986–1984	0.58	0.59	0.89	0.89	1.44	0.45	0.71
100–110	1983–1981	0.73	0.53	0.90	0.83	1.27	0.43	0.82
110–120	1980–1978	0.58	0.79	1.09	1.08	1.64	0.48	0.74
120–130	1977–1975	0.56	1.27	1.26	1.27	2.03	0.92	0.81
130–135	1974–1972	0.73	0.69	1.05	0.99	1.59	0.52	0.83

Woitke et al. (2003) is one of the rare studies in which sediment composition was analyzed along the whole Danube River. These authors analyzed sediment samples at 74 locations along Danube from Neu-Ulm, Germany (km 2589) down to Danube Delta in Romania and 24 samples from the tributaries. For the purpose of this study, the following average concentrations of minor elements obtained by Woitke et al. (2003) were used as background values: Al 33,300 ppm, Ni 49.6 ppm, Cu 65.7 ppm, Pb 46.3 ppm, Zn 187 ppm, Cd 1.20 ppm, As 17.6 ppm, Cr 64 ppm. These authors have not analyzed concentrations of Co, so the pollution status of this element could not be estimated.

Enrichment factor (Ef) is used to determine the degree of anthropogenic heavy metal pollution (Ergin et al. 1991). It is calculated from the ratio of the found concentrations of an analyzed metal normalized with the concentrations of Al and the concentrations of the same metal normalized with the concentration of Al in the background sample:

$$Ef = Cx/CAI_{(sample)} \times Bx/BAI_{(background\ value)}$$

The Ef classes are: Ef < 1 no enrichment; Ef 1–3 minor enrichment; Ef 3–5 moderate enrichment; Ef 5–10 moderately severe enrichment; Ef 10–25 severe enrichment; Ef 25–50 extremely severe enrichment (Birch and Olmos 2008).

The values of Ef are given in Table 4. Cadmium has minor enrichment in all samples except in the 45–60 cm interval (1996–2001), copper has minor enrichment in sample at 120–30 cm depth (1975–1977), lead and zinc in the lower part of the core at 110–135 cm depth (1972–1980) and in the

interval 30–45 cm (2001–2005). Ef for Ni, As, and Cr in all samples shows no enrichment.

The Geoaccumulation Index I_{geo} , introduced by Muller (1979), is calculated using the following equation:

$$I_{geo} = \log_2(Cx/1.5 \times Bx)$$

Cx is the measured concentration of the element and Bx parameter is the geochemical background value. The constant 1.5 allows analyses of the natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences. I_{geo} classes suggested by Yaqin et al. (2008) are < 0 unpolluted; 0–1 unpolluted to moderately polluted; 1–2 moderately polluted; 2–3 moderately to highly polluted; 3–4 highly polluted; 4–5 highly to very highly polluted; and 5–6 very highly polluted.

The calculated values for I_{geo} are shown in Table 5. The I_{geo} index for Cd shows moderately polluted class 2 for 110–135 cm (1972–1980), 90–100 cm (1984–1986), 30–45 cm (2001–2005) and 0–15 cm (2011–2016) intervals. Calculated I_{geo} values show moderately polluted class 2 for Cu and As in the period 45–60 cm (1996–2000) and As for 15–30 cm (2006–2010). Analyzed sediments are uncontaminated to moderately contaminated (class 0 and 1) for all other elements in all investigated periods.

Contamination factor C_f^i is the ratio obtained by dividing the concentration of metal (C) in the sediment by the background value (C_0 ; Hakanson 1980):

$$C_f^i = C_o^i/C_n^i$$

Table 5 Geoaccumulation index for sediments from the Djerdap Lake

Depth (cm)	Time period	Ni	Cu	Pb	Zn	Cd	As	Cr
0–15	2016–2011	0.03	– 0.12	0.45	0.50	1.08	0.02	0.24
15–30	2010–2006	– 0.25	– 0.82	– 0.32	0.12	0.46	– 1.40	– 0.19
30–45	2005–2001	– 0.23	0.26	0.51	0.53	1.14	– 0.40	0.25
45–60	2000–1996	– 0.25	– 1.30	– 0.96	– 0.46	0.16	– 1.86	– 0.31
60–75	1995–1991	– 0.51	0.26	0.27	0.37	0.97	– 0.46	– 0.11
75–90	1990–1987	– 0.15	– 0.43	0.13	0.42	0.82	– 0.88	0.00
90–100	1986–1984	– 0.26	– 0.24	0.36	0.36	1.06	– 0.61	0.04
100–110	1983–1981	– 0.02	– 0.49	0.28	0.15	0.77	– 0.80	0.14
110–120	1980–1978	– 0.21	0.24	0.70	0.68	1.28	– 0.49	0.14
120–130	1977–1975	– 0.45	0.73	0.72	0.72	1.40	0.26	0.07
130–135	1974–1972	0.03	– 0.05	0.55	0.47	1.15	– 0.46	0.21

Table 6 Contamination factor and Pollution Load Index (PLI) for the Djerdap Lake sediments

Depth (cm)	Time period	Ni	Cu	Pb	Zn	Cd	As	Cr	PLI
0–15	2016–2011	1.34	1.01	1.66	1.40	3.35	0.83	1.34	1.87
15–30	2010–2006	1.06	0.31	0.89	1.02	2.73	– 0.59	0.90	1.18
30–45	2005–2001	1.08	1.39	1.72	1.43	3.41	0.42	1.35	1.84
45–60	2000–1996	1.06	– 0.17	0.25	0.44	2.42	– 1.04	0.78	0.92
60–75	1995–1991	0.80	1.39	1.48	1.28	3.23	0.36	0.98	1.62
75–90	1990–1987	1.16	0.71	1.35	1.32	3.08	– 0.07	1.09	1.49
90–100	1986–1984	1.05	0.89	1.57	1.26	3.32	0.20	1.13	1.61
100–110	1983–1981	1.29	0.64	1.49	1.06	3.03	0.02	1.23	1.50
110–120	1980–1978	1.10	1.37	1.91	1.58	3.55	0.33	1.23	1.89
120–130	1977–1975	0.86	1.86	1.93	1.63	3.67	1.07	1.17	2.11
130–135	1974–1972	1.34	1.08	1.76	1.37	3.41	0.36	1.30	1.81

where C_f^i is contamination factor for a certain minor elements, which can reflect the pollution character of the investigated region but cannot reveal the ecological effects and hazards, C_o^i is the concentration of minor elements in sediment, and C_n^i is a reference value for minor elements. C_f^i classes suggested by Hakanson (1980) were: < 1 low contamination factor; $1 \leq C_f^i < 3$ moderate contamination factor; $3 > C_f^i < 6$ considerable contamination factor; > 6 very high contamination factors.

The calculated values for C_f^i are shown in Table 6. The C_f^i index for As shows moderate contamination factor, except for the sample from 120 to 130 cm of depth where it shows considerable contamination factor. Concentrations of Ni, Cu, Pb, Zn and Cr show from moderate to considerable contamination factor. Only for Cd C_f^i has very high contamination.

The Pollution Load Index (PLI) for a particular site is evaluated following the method proposed by Tomilson et al. (1980). It is calculated using the following equation:

$$PLI = (Cf_1^i, Cf_2^i, Cf_3^i \times Cf_n^i)$$

where Cf^i is the contamination factor of each heavy metal. The PLI classifies the excess heavy metal concentration as the ratio of sample concentrations to background values. The PLI classes suggested by Tomilson et al. (1980) are: < 1 is no polluted condition and > 1 polluted condition. The values of calculated PLI are given in Table 6. Calculated PLI values indicated that sediments were polluted throughout all deposition time except in the 45–60 cm interval (2001–2006).

Possible sources of minor elements in the Djerdap Lake sediments

Obtained results indicate a combination of natural and anthropogenic sources of minor elements. There is no unique cause of fluctuations of element concentration both regarding decreases and increases, but rather a combination of geological and human-induced factors.

Granitic rocks which are situated south of the Orlova are mainly built of quartz and feldspars and also contain sulfide minerals that carry minor elements. Weathered material from these rocks is brought to the Djerdap Lake environment most often by SE winds, which have highest velocity and very high frequency (Fig. 3).

Besides local geological setting, as it has been shown in previous studies, the material that rivers Sava, Tisa and Danube itself are transporting has elevated concentrations of minor elements due to geological composition of the Danube watershed (Štrbac et al. 2014; Vasić and Kašanin-Grubin 2015). Even though the precise anthropogenic sources of minor elements in Serbia have not been identified, minor elements in the Djerdap Lake sediment have anthropogenic origin despite the relatively low concentrations of minor elements in the Danube water and sediment during the last 10 years (Vuković et al. 2014).

The decrease in concentration of minor elements during the second half of 1990s (45–60 cm) is probably a consequence of the economic sanctions against the FR Yugoslavia. The sanctions had a major impact on the Yugoslav economy and society and a devastating impact on the industry. Second decrease was during the period when application of environmental laws in Serbia, and more importantly, countries upstream from Serbia, as a positive result of more control in industry as a source of pollution.

Two increases in concentrations of tested elements are occurring in the period 2001–2005 (30–45 cm) and 2011–2016 (0–15 cm; Fig. 7). There are several possible reasons that could help in understanding elevated element concentrations during 2001–2005. The first is probably the Baia Mare cyanide spill in Romania in 2000. During this incident, 20,000 m³ of zinc, lead and copper-contaminated water made its way into the Tisza and then the Danube killing large number of fish in Hungary and Romania. Second

reason might be the NATO bombing against the FR Yugoslavia during spring 1999. Popović et al. (2009) found that the significant amounts of Pb and Cd in the mobile phase of sediments in Fruška Gora National Park, Deliblatska Peščara and Zasavica Protected Areas which all lie in the immediate vicinity of the Danube. These authors found that the elevated concentrations of Cd and Pb originate from airborne sources when the Pančevo Oil Refinery was targeted. The third possible reason is the influence of ore processing and concentration mills in the area of Moldova Noua in Romanian part of Djerdap Lake. Oaie et al. (2005) indicate that this location is a source of increased concentrations in Cu, Zn and Pb in the Djerdap Lake.

Conclusions

The Djerdap Lake has proven to be a very promising sediment archive for geochronological studies in the Danube river system. Sedimentation rate of $\sim 3 \text{ cm year}^{-1}$ was determined based on the drill-hole depth and total deposition period 1972–2016. Samples taken at specific depth intervals were assigned approximate time period of deposition. Geochronological investigation of persistent organic compounds is presented in part B, while in this part (Part A) inorganic and mineralogical data are discussed.

Mineralogical data indicate that analyzed sediments are mostly sandy silts and clayey silts and only the deepest and the shallowest layers contain $> 30\%$ of sand-size fraction. All sediments are composed of quartz, mica, chlorite, calcite, dolomite, feldspar and smectite clay minerals. Major element content shows certain variations with depth but is in accordance with the mineralogical composition. Content of minor elements exhibits more variations during the whole period of deposition. The highest concentrations of all tested elements are found in the oldest sediment (1972–1979) as a consequence of the high flux of the material from variable sources. Transport of this material was initiated during dam building and lake formation. During the following sedimentation period (1980–1991), the concentrations of analyzed elements are generally decreasing until the beginning of 1990s. After this period there are two distinct decreases and two distinct increases in concentrations of analyzed

elements. First decrease corresponds to the period 1996–2000 and the second to the period 2007–2011, while the periods of increased concentrations are 2002–2006, and the last period of observation 2012–2016.

The fluctuations in minor metal concentrations are a consequence of both natural and anthropogenic sources. Granitic rocks situated south of the sampling location are source of minerals that carry minor elements. Weathered material is brought to the Djerdap Lake environment most often by SE winds, which have highest velocity and very high frequency. Pollution indices indicate that concentrations of minor elements at certain depositional periods have anthropogenic source. At this point, it is hard to identify the exact pollution source, but there are several possible events in the past that could cause this element status. Further studies which would include sampling at more location will allow a more detail geochronological assessment of the Djerdap Lake.

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