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Study of potential harmful elements (arsenic, mercury and selenium) in surface sediments from Serbian rivers and artificial lakes

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Abstract

This investigation examines surface sediment samples from rivers and artificial lakes (Serbia) to quantify levels of potentially harmful elements (As, Hg, and Se) and several ancillary elements (Al, Fe, Mn, Ca, Mg, C, H, N, and S). These data provide the first global analysis of Hg, As and Se levels in a well-studied system. Combination of different methods was applied for estimation of the environmental status of sediments and to determine the potential risk of

ecological damage: digestion with aqua regia and determination of element content, determination of elements mobile forms by ammonium-acetate extraction, calculation of contamination indexes - index of geoaccumulation and enrichment factor, comparison with sediment quality guidelines and other literature data, and use of statistical methods. Results indicate that the sediments are slightly enriched with As and Hg, but not with Se. Fact that values for Se contents was less than the international threshold levels, suggesting the very probable absence of risk of contamination over the catchment with this element. The average pollution levels in Serbian river and artificial lakes expressed in terms of geoaccumulation indexes of As and Hg indicate that the environment is uncontaminated to moderately contaminated. All values of EF for Hg were below 2, indicating deficiency to minimal enrichment with Hg on studied localities. The EF values of As indicate deficiency to moderate enrichment (EF ranged from 0.11 to 3.54). According to the comparison to quality standard, the As in sediments of the studied area have potential risk. High content of arsenic in river and lake sediments indicate that arsenic pollution problem that lasts longer period of time.

Key words: arsenic, mercury, selenium, sediment, river, Se:Hg ratio, S:Se ratio

1. Introduction

In a natural environment, As, Hg, and Se are considered potential harmful elements (PHEs) when their concentrations exceed certain levels. They can also be categorized as atmophile elements, because their mass transport through the atmosphere is often greater than via streams (Li et al. 2016). In recent years, much attention has been focused on the geochemical behaviour of these elements (Rezende et al., 2011; Zhang, 2014; Jagtap et al., 2015; Jiang et al., 2015; Chen et al., 2016; Tepanosyan et al., 2016).

Arsenic is a toxic, ubiquitous element with metalloid properties, is almost often present in environmental samples. It is found in nature in metal ore deposits, mainly as arsenides of Cu, Ni and Fe. Arsenic compounds are used mainly in agriculture and forestry as pesticides and herbicides; and in smaller amounts, as additive in the glass and ceramic industries as feed additives (Patel et al., 2005). Although it is classified as a metalloid, it is also referred to as a metal, and in the context of toxicology as a heavy metal. Sediments are important sinks of inorganic arsenic in natural systems. However, inorganic arsenic is not permanently fixed, since pH, temperature or redox potential changes and presence of organic matter or ionic exchange processes can mobilise arsenic compounds from the sediment (Raposo et al., 2004).

Selenium in the environment is a significant research area as environmental selenium provides a source for biological uptake. Selenium is generally widely distributed and is cycled through environmental compartments via both natural and anthropogenic processes. Approximately, 40% of total Se emissions result from anthropogenic activities (Savery et al., 2013). Interest in selenium concentrations in the environment stem from the dual role of selenium as an essential nutrient at low concentrations and as toxic substance at higher levels of concentrations (Hagarova et al., 2005). Selenium usually occurs in association with various sulphide minerals/metallic ores in which it replaces sulphur atoms and only forms minerals

with elements having a comparatively high atomic number, e.g., Pb, Hg, Bi, Ag, Cu etc. Particularly, selenium has strong affinity for copper and accumulation of copper in ores is usually accompanied by concentration of selenium (Tarin, 2006). In surface waters, Se is found mostly as selenate and selenite, which are both highly bioavailable species allowing for bioaccumulation and biomagnification posing a threat to aquatic wildlife (Savery et al., 2013). Mercury is one of the most hazardous environmental pollutants with a large number of physical and chemical forms. Mercury is released into the environment from three major sources: natural deposits in soils, anthropogenic release, and wet and dry atmospheric deposition from both of these sources (Jagtap et al., 2015). Although all forms of mercury are poisonous, alkylmercury compounds are of special concern because of their easy penetration through biological membranes, efficient bio-accumulation, high volatility and long-term elimination from tissues. In the aquatic environments, mercury accumulates in sediments, where the methylation and demethylation processes preferably seem to occur (Berzas Nevado et al., 2010). The major discovery in recent years that Se can inhibit the toxicity and enrichment of MeHg in aquatic organisms has provided a potential approach to solving problems of Hg contamination in water (Zhang, 2014). A large number of scientific studies have confirmed that interactions between selenium and mercury are a very important topic of study for the systematic understanding of the environmental behaviour, fate and toxicological effects of Hg (or Se). Research (Yang et al., 2008) indicates that adding Se to lake sediments can significantly reduce the formation of MeHg in these sediments.

Mercury in contaminated sediments could be extracted by various chemical reagents in order to determine the different mercury species and partitions, providing useful information of toxicology, bioavailability and biochemical reactivity. Unfortunately, at present, neither specific extractants nor standard protocols exist for the isolation of particular mercury species (Issaro et al., 2009). Hagarová et al. (2005) report that the application of extraction methods to

selective removal of selenium is complicated by the fact that selenium may exist in more than one oxidation state (selenate (VI), selenite (IV), elemental selenium (0) and selenide (II)), each of which has a unique behaviour. Selenium determination with microwave digestion with aqua regia is recommended in paper Prachei et al. (2010). The determination of Hg total content in sediments with aqua regia is proposed by the U.S. Environmental Protection Agency (1986). In paper Rezende et al. (2011) is recommended the aqua regia digestion procedure for As and Hg determination in sediments, and obtained results are with high precision and accuracy.

In the presented manuscript, the arsenic, mercury and selenium levels in the Serbian River and artificial lake sediments were determined using microwave digestion with aqua regia and extraction with ammonium–acetate. The main objective of this study was to determine the distribution of studied elements in sediments and to estimate the degree of contamination and potential risk of ecological damages, on the basis of: calculation of pollution indexes (Igeo and EF), comparison with the corresponding sediment quality guidelines, comparison of the obtained results with those found in the literature, and prediction of mobility of studied potential harmful elements. There were also calculated Se:Hg and S:Se ratios, and were determined content of several ancillary parameters: Al, Fe, Mn, Ca, Mg, C, H, N, and S. In order to establish relationships among elements and determine the common source (and/or carrier substances), a correlation and cluster analysis was performed. To our knowledge, this is the first systematic investigations of arsenic, mercury and selenium content in river and artificial lake systems from Serbian localities.

2. Materials and methods

2.1. Study area and sampling sites

Serbia has many rivers and lakes. Serbia's rivers belong to the drainage basins of the Black, the Adriatic, and the Aegean seas, where the largest and the most important in the area is the Black Sea drainage basin covering an area of 81,261 km² or 92 % of the territory of Serbia. The number of natural lakes in the total area is relatively small; however, when the increasing number of artificial reservoirs is included, the hydrographic networks become richer and more complex (Dević et al. 2014). Most lakes of Serbia are artificial, created by damming numerous rivers of Serbia for the purpose of obtaining hydroelectric power or as water reservoirs.

A total of 48 surface sediment samples were collected from Serbian rivers (36) and artificial lakes (12) during 2008. Sampling site numbers are denoted with the brackets: the Tisa (9), the Danube (6), the Sava (4), the Ibar (2), the Great Morava (2), the West Morava (2), the South Morava (2), the Nišava (2), the Tamiš (1), the Vrbas (1), the Topčiderska River (1), the Porečka river (1), the Kolubara (1), the Pek (1) and the Toplica (1) - *rivers* and the the Barje (3), the Čelije (3), the Vrutci (1), the Garaši (1), the Bojnik (2) and the Bovan (2) - *lakes*. Locations of the sampling sites are shown in Figure 1 and Table 1. The sampling of sediments in this research was conducted using a Van Veen grab sampler, designed to collect an accurate representative sediment sample. The sediment samples were stored at 4 °C to prevent changes in the chemical composition. The micro and macroelemental levels were determined in the granulometric fraction, i.e., < 63 µm of the bottom sediment sample (grab sample). Analysis of the metal concentration in the fine sediment fraction (less than 63 µm) is recommended as these particles are the most important sources of bioavailable metals in sediments (Villaescusa–Celaya et al., 2000), as well as for comparability of data to other river basins (Milačič et al., 2010).

The moisture content of each sample was determined by drying a separate 1 g sample in an

oven (105 ± 2 °C) until a constant weight was reached. From this, a correction to dry mass was obtained, which was then applied to all reported metal content results.

2.2. Chemical analysis

2.2.1. Digestion with aqua regia

Total As, Hg, Se, Al, Fe, and Mn levels were determined using microwave digestion with aqua regia. Approximately 500 mg of sample sediment and 12 mL of aqua regia (9 mL HCl and 3 mL HNO₃) were added to a microwave vessel (DIN 38414 S7 1983, SW-846 EPA Method 3051a 2007). Microwave digestion was performed in a pressurised microwave oven (Ethos 1, Advanced Microwave Digestion System, Milestone, Italy) equipped with a rotor holding 10 microwave vessels (PTFE). During digestion, the temperature of the microwave oven was raised to 165 °C over 10 min (holding time 0 s), then to 175 °C over 3 min, after which it was maintained at 175 °C for 10 min (max power 1200 W) (Rönkkömäki et al., 2008). One control vessel per rack contained a temperature and pressure probe. The vessels were removed from the oven after the temperature had dropped to less than 50 °C and the pressure to less than 69 kPa. At the end of the digestion cycle the vessels were allowed to cool to room temperature before continuing the sample preparation, to align with security protocols and to avoid the leakage of volatile substances. After cooling, the sample digests were filtered with Whatman No. 42 filter paper, to remove solids which remained after the microwave digestion process. The digests were then transferred into a flask, diluted to 100 mL with 1 M HNO₃ and stored in a polyethylene bottle at 4 °C until needed for analysis (Sakan et al., 2011).

2.2.2. Extraction with 1 M $\text{CH}_3\text{COONH}_4$

A 40-mL aliquot of a 1 M $\text{CH}_3\text{COONH}_4$ solution was added to 1 g of sediment in a 50-mL centrifuge tube. The suspension was shaken on a shaker for 2 h in a room at 20 ± 2 °C (Todorović et al. 2001; Sakan et al. 2009; Petrović et al., 2010; Sakan et al. 2012). The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min. Then, the supernatant was decanted and diluted to 50 mL with 1 M HNO_3 and stored in a polyethylene bottle at 4 °C until needed for analysis.

2.2.3. Determination of element content

In this research, the following elements were determined in each sample: As, Hg, Se, Al, Fe, and Mn. The analytical determination of the studied elements was realised with an atomic emission spectrometer with an inductively coupled plasma iCAP-6500 Duo (Thermo Scientific, United Kingdom). The detector was a RACID86 Charge injector device (CID). For As, Hg, and Se determination, ICP OES coupled with hydride generation technique was used. Hydride technique was used to minimize interferences from sample matrices.

Analytical grade chemicals were used throughout the study without any further purification. The metal standards were prepared from a stock solution of $1,000 \text{ mg L}^{-1}$ by successive dilutions. The concentrations obtained for all the elements in the blanks were close to the detection limit of the method, indicating that contamination was not a problem in the digestion.

The wavelengths used in this analysis were: As - 189.0 nm, Hg - 194.2 nm, Se - 196.0 nm, Mn - 257.6 nm, Fe - 261.1 nm, Ca - 184.2 nm, Mg - 279.5 nm, and Al - 237.3 nm. The detection limit was determined as three times the standard deviation of the blank

measurements. The obtained values were (in mg kg⁻¹) were: As - 0.0001, Hg - 0.0001, Se - 0.0001, Mn - 0.03, Al - 0.5 and Fe - 0.3.

The obtained results are expressed in mg kg⁻¹ dry sediment.

2.2.4. Elemental Analysis

The determination of C, H, N, and S content in the investigated sediments was performed by elemental analysis, using the Vario EL III C, H, N, S/O elemental analyser (Elementar). Determined C content represented total carbon content, i.e. sum of inorganic and organic carbon.

2.3. Contamination indexes

The *index of geoaccumulation* (I_{geo}), originally introduced by Muller (1979), was employed here to separate the anthropogenic influences on the sediment from the natural influences (Li et al., 2016). The index is defined by the following equation:

$$I_{geo} = \log_2(C_n / 1.5 B_n),$$

where C_n is the measured sediment concentration of the element of interest (n) and B_n is the geochemical background concentration of element (n). The I_{geo} classifies the sampling locations into seven classes as follows: $I_{geo} \leq 0$ – practically uncontaminated; $0 < I_{geo} < 1$ – uncontaminated to moderately contaminated; $1 < I_{geo} < 2$ - moderately contaminated; $2 < I_{geo} < 3$ - moderately to heavily contaminated; $3 < I_{geo} < 4$ - heavily contaminated; $4 < I_{geo} < 5$ - heavily contaminated; and $5 \leq I_{geo}$ - extremely contaminated.

The *enrichment factor (EF)* was calculated according to the following equation:

$$EF = (C_{n(sample)}/C_{ref(sample)}) / (B_{n(background)}/B_{ref(background)}),$$

where $C_{n(sample)}$ is the content of the examined element in the examined environment; $C_{ref(sample)}$ is the content of the reference element in the examined environment; $B_{n(background)}$ is the content of the examined element in the reference environment, and $B_{ref(background)}$ is the content of the reference element in the reference environment (Bernalte et al., 2105). Five contamination categories are recognized on the basis of the enrichment factor: $EF < 2$ (deficiency to minimal enrichment), $EF = 2-5$ (moderate enrichment), $EF = 5-20$ (significant enrichment), $EF = 20-40$ (very high enrichment), and $EF > 40$ (extremely high enrichment).

2.4. Statistics and data processing

In order to establish relationships among elements and determine the common source (and/or carrier substances), a correlation matrix was calculated for the elements in the sediments. Hierarchical Cluster Analysis also was performed to classify the sediments according to the values of the studied variables into clusters and generate dendrogram. Data were analyzed using SPSS 21.0.

3. Results and discussion

3.1. The accuracy check

The accuracy of the analytical procedures applied was checked by analysis of the certified reference material (BCR-143R, 'Sewage sludge amended soil'). The materials were handled according to the supplier's specifications. The percentage recovery for Hg and Mn was obtained as: $[(\text{measured concentration in mg kg}^{-1}) / \text{mean certified value for CRM in mg kg}^{-1}) \times 100]$. The determined concentration for Hg was 1.03 mg kg^{-1} , which is 93.6% of the certified values. The determined concentration for Mn was 822 mg kg^{-1} , which is 95.8 % of the certified values. Good agreement between determined and the certified values confirming the accuracy of the obtained result.

The precision is expressed as relative standard deviations. The relative standard deviations of the means of duplicate measurement were less than 10% for all the measured elements.

3.2. Mercury, arsenic and selenium content in sediment

The total As, Se and Hg contents in studied sediments are summarized in Table 1, while the contents of determined ancillary parameters (Al, Fe, Mn, Ca, Mg, C, H, N, and S) are summarized in Supplementary Table 1. Comparison of the obtained results in this research with those found in the literature for the elements in soil and sediments from India, China, Spain, Armenia, France, Gana, Scotland, Danube and Sava river is shown in Table 2.

In general, contents of elements vary along studied localities (Table 1). The total content of As in sediment were in the range $4.10\text{-}103 \text{ mg kg}^{-1}$. The average content of As in the sediment ($19.0 \pm 16.5 \text{ mg kg}^{-1}$) was comparable to that of the sediment from Yangtze river (Tang et al. 2014), Sava river (Milačić et al., 2010), Danube river (Woitke et al. 2003), and was significantly lower compared with the values reported by Patel et al. (2005) for sediment from central India. Average concentration of As found in this study was also lower than values reported in Dhivert et al. (2015). However, the average concentration of As was found to be

slightly higher in this study compared with the values reported by Xu et al. (2016) - for soil from China (Beijing), Roig et al. (2011) - for river sediments (Spain), Tepanosyan et al. (2016) - for topsoil (Armenia), and Frémion et al (2016) – for Loire river sediments (France). Comparison of As content in Tisa river sediments in this study with those published for Tisa sediment in Sakan et al. (2012) indicate that values in this study was higher than values in Sakan et al. (2012). Possible reason for this maybe fact that in this research was determined total content of As (by aqua regia), since in Sakan et al. (2012) present results for total extractable amount of As represented as the sum of As released in all five fractions of sequential extraction. As extractant in residual fraction in Sakan et al. (2012) is used 6M HCl, not aqua regia.

Total Hg content ranged from bellow detection limit to 0.72 mg kg^{-1} . Hg pristine concentrations vary between 0.08 and 0.4 mg kg^{-1} (Issaro et al., 2009), indicating mercury emissions from anthropogenic sources in the studied area. Results of comparisons of the obtained results with other published results for mercury (Table 2) indicate that mercury contents in Serbian river and lakes are higher that the levels measured in topsoil in Armenia Tepanosyan et al. (2016) and river sediment from Spain (Roig et al., 2011), but roughly similar to measured values in soil from China (Xu et al., 2016), river sediments from Ghana (Oppong et al., 2010), Sava river (Milačič et al. 2010) and Tisa river (Sakan et al. 2012). The sediments mercury contents measured in this study area, however, lower than those found in soil from sewage irrigation area of northwest China (Chen et al. 2016). The average contents of Hg found in this study is similar to measured values of Hg in Danube river and Danube tributaries (Woitke et al. 2003), but on some location along the entire course and some tributaries, maximum values were higher than studied values.

Total Se content in this study ranged from 0.056 to 1.000 mg kg^{-1} (Table 1). The river and lakes sediments selenium contents are higher than the levels measured in soils from China (Lv

et al. 2014), but similar to measured values in Scottish topsoil (Shand et al., 2010), Finnish sediment (Koljonen et al., 1974), and soils from China (Yu et al., 2014).

To estimate the environmental status of sediments and to determine the potential risk of ecological damage, the Hg, As and Se contents in the sediment were compared with the corresponding sediment quality guidelines (SQGs, Table 2): US EPA benchmarks (US EPA 2007; de Castro–Catalá et al., 2016), PEC - probable effect concentrations (Ingersoll and MacDonald 2007) and Serbia national legislation (Republic of Serbia 1994). Screening ecological benchmarks are used to identify chemical concentrations in environmental media that are at or below thresholds for effects to ecological receptors. No benchmarks were exceeded for Se, but for As and Hg on some sites measured values exceeded the benchmarks (Fig. 2, Table 2). Lemly (2002) also described the sedimentary toxic effect threshold for Se in sediment as 2 µg/g, which is in accordance with US EPA benchmarks. The fact that Se levels were less than the international threshold levels suggests the very probable absence of risk of contamination with this element over the catchment.

The collation of contents of As and Hg with maximum acceptable concentrations (MAC) approved by Serbian legislation (Table 2) showed that only arsenic exceeded MAC on some localities: Great Morava, West Morava, Ibar and Toplica (rivers) and Barje (artificial lake). Data from Table 2 further indicate that most of sediments exceeded PEC values for As, but did not exceeded for Hg. PEC (probable effect concentrations) are SQGs that were established as concentrations of individual chemicals above which adverse effects in sediments are expected to frequently occur. Thus, it is possible to conclude that on studied localities Hg was found to be present in slightly elevated concentration. The highest Hg content was found at site West Morava. Elevated Hg content in this river was also shown in paper Milošković et al. (2016).

High content of arsenic on some localities are mainly caused by pollution with exogenous substances. Stafilov et al. (2010) report very heavy pollution with As of the area around the Ibar and Sitnica valleys. Devic et al. (2016) reported high levels of As in river water in Serbia. The authors explain that, with the use of arsenic-containing herbicides, high concentrations of naturally occurring arsenic in some quaternary sedimentary aquifers, and as a consequence of mining activities. These results suggest that a large proportion of the Serbian population is chronically exposed to As. High content of arsenic in river and lake sediments indicate that arsenic pollution problem that lasts longer period of time.

The box-plot (Supplementary Fig. 1) show that Se and As have some outliers and extreme values. Since that Se content not exceeded MAC values, it can be supposed that geology is the primary control on the selenium concentration in sediments. This is partially because of different background Se content in different regions.

In the sediment samples which are analyzed in this paper shown that elevated concentrations of elements, mainly those that exceed the MAC, in most cases were detected in samples of river sediments. It is possible to assume that this is due to the fact that the artificial lake reservoirs are usually built in rural areas, where the less anthropogenic pollution. Unlike lakes, rivers often flow through the towns, but these bodies of water more or less burdened with micronutrients, toxic substances, organic or inorganic, waste materials, depending on the type and industrial process which, particularly in Serbia, without needed and compulsory technology treatment directly discharged into them.

3.3 Se:Hg ratio

It was proposed as early as 1972 that the Hg-to-Se molar ratio should be used as a reference standard for Hg pollution (Ganter et al., 1972). However, this proposal has attracted little

attention because the specific underlying mechanism has only gradually become clear in recent years (Zhang et al., 2014). In Burger et al. (2012) was written that Ralston (2008) suggest that selenium:mercury molar ratios above 1 are protective for adverse mercury effects. The Se:Hg ratio are calculated for studied sediments and results are shown in Table 1. The ratio $\text{Se:Hg} > 1$ was observed in sediments with lower mercury and higher selenium content, suggest a protective effect of Hg toxicity. For sediments with higher Hg content, Se:Hg was < 1 , which indicates that the higher content of selenium is required in order to neutralize the negative impact mercury effects. In general, when the concentration of Se is significantly higher than that of Hg, Se plays a dominant role in Hg assimilation processes.

3.4. S:Se ratio

Malisa (2001) reported that S/Se ratios are distinct in different rock types and can thus be used to elucidate the origin of rocks, ores, and sediments. The obtain values for S:Se ratios in studied sediments in present research (3586-35000, Table 1) are in accordance for values in clayey and organic-rich sediments (1000-10000) for most of the studied samples, but in some areas, obtained Se/S ratio was higher. This ratio in sediments depends on the abundance of selenium during sedimentation, since there is a usually about the same amount of sulphur present, which can be bound to sediments (Malisa, 2001). High value for S/Se ratios at some locations in this research may be a consequence of geochemical composition of sediment.

3.5. Analysis of the easily soluble element fraction of sediments

In order to estimate the extent of pollution of selected elements in sediments, extraction in $\text{CH}_3\text{COONH}_4$, was performed. The neutral 1M ammonium acetate extraction method is the

most widely used procedure to extract water-soluble and rapidly exchangeable fractions. The percentages of the extracted elements in the soluble fraction compared to the total content obtained with aqua regia digestion were calculated and results shown in Supplementary Fig. 2 only for As, since the extracted amounts of Se and Hg in this fraction was below detection limits. Other studies also shown that a significant proportion of insoluble and non-bioavailable elemental Se naturally present in sediment (Wiramanden et al. 2010). Sakan et al. (2012) reported that in investigated river and alluvial sediment mercury is quite stable and present low chemical availability, which is comparable with data found in this study.

Data from Supplementary Fig. 2 showed that the percentages of the easily soluble metal fraction of arsenic were in general below 10%, indicating its low mobility into the aquatic environment. Obtained results are comparable to results for Sava River (Milačič et al. 2010) and Tisa river and Danube alluvial sediments (Sakan et al. 2012).

3.6. Determination of background values

The selection of appropriate background values is very important in assessment of the sediment contamination level, based on ecological risk-assessment criteria, such as I_{geo} and EF (Li et al., 2016; Sakan et al., 2015). Unfortunately, no earlier background data for the three selected element were available for the study area. The As and Hg data reported in Woitke et al. (2003) were chosen as the background values for the current study due to the following reasons: (i) contaminated and mineralogically and texturally comparable river sediments, (ii) similarity with other published background values (Table 2) and (iii) similarity with US EPA benchmarks (Table 2).

3.7. The index of geoaccumulation

The calculated values for I_{geo} are shown on Figure 3. I_{geo} for As ranging from < 0 to 1.93, indicating practically uncontaminated to moderately contaminated sediments; for Hg, I_{geo} was from < 0 to 0.87, indicating practically uncontaminated to moderately contaminated sediment. The percentage of sediments that had $I_{geo} < 0$ were 45.8% for As and 75.0% for Hg. The percentage of samples that had $0 < I_{geo} < 1$ were 47.9% for As and 25% for Hg. Only three sediments (Ibar (2) and Barje lake (1)) had $I_{geo} > 1$ for As (6.2%), indicating moderately contaminated areas. The average pollution levels in Serbian river and artificial lakes expressed in terms of geoaccumulation indexes of As and Hg indicate that the environment is uncontaminated to moderately contaminated. Therefore, although there was a significant proportion of samples for which As and Hg exceeded the benchmarks, they had the least number of samples that exceeded the I_{geo} values when background values were taken into consideration.

3.8. Enrichment factor

The calculated EFs are shown in Figure 4. EF values range for As was from 0.113 to 3.537 (mean 0.586). All values of EF for Hg were below 2, indicating deficiency to minimal enrichment with Hg on studied localities. The EF values of As indicate deficiency to minimal enrichment to moderate enrichment (EF ranged from 0.11 to 3.54). The calculated values of EF indicate that 95.8% sites for As had values for $EF < 2$ (deficiency to minimal enrichment). Two stations in the studied area had values > 2 for As (moderate enrichment), for Ibar river (stations 1280 and 1281). Obtained results are consistent with the results of I_{geo} .

3.9. Correlation analysis

The correlation coefficients between each pair of variable elements in the sediments were calculated using the Pearson correlation matrix approach and values are shown in Supplementary Table 2. The results obtained show that there are both positive and negative correlations between the elements with regard to their source. Results of correlation analysis indicate that Hg does not show a significant correlation with any of the elements. The lack of significant linear correlation between Hg and the other studied elements suggests that its sources were quite different from those of the others. As is positive correlated with: Fe, Mg and S, and Se are positive correlated with C and S. Correlation between Se and S is highly significant. Positive correlation among As and Fe is also shown in paper Chen et al. (2016), which may indicate that As is present as insoluble Fe-arsenate complexes. Also, arsenate (As(V)) is expected to be very sparingly soluble in most environments, because of a very efficient inner-sphere complexation adsorption mechanism on Fe and Al oxides (Gustafsson and Tin, 1994). Frémion et al. (2016) found that a correlation between As and major elements could reflect the fact that after their release in aquatic medium, they sorb through time onto Al- and Fe-oxides present in high concentration in sediments matrix. As and S may form very insoluble compounds, such as arsenopyrite (Gustafsson and Tin, 1994). Positive correlation of As with Mg may be due to Mg has the capacity to precipitate with arsenate (Fendorf et al., 2010). The positive correlation between Se and S reflect the association of Se with various sulphide minerals. Because of the similar ionic radii of sulphide ion and selenide ion, selenium readily substitutes for sulphur ion sulphide minerals. Correlation of Se with total carbon content indicates that selenium in sediments accumulated via organic matter also, which is in accordance with the results of Wiramanden et al. (2010). Čuvardić (2003) show that in sedimentary rocks, Se is bond to organic fractions. Wiramanden et al. (2010) suggest

that microbial activity may be very important in the biogeochemical cycling of Se in fresh-water ecosystems.

Fe is negatively correlated with Ca and C, and positively with K, Mn, and H. Obtained correlations may be consequence of different origin of elements; Ca and C represented carbonates, and Fe is mainly present in form oxide. Fe oxides are building associations with Mn oxides and clay minerals in soils and sediments. The positive correlations of total C with Ca, Mg, and N confirmed dual nature of carbon content, since that total carbon includes inorganic and organic sample constituents. Inorganic carbon forms are present in soils and sediments typically as carbonates (represented with Ca and Mg in this research) and total N content represent organic matter. Nitrogen in soil and sediment is mainly derived by decomposition of the plants and animals or plankton and plays an important role as a source of nutrients (Avramidis et al., 2015).

3.10. Cluster analysis (CA)

The results obtained by CA (R mode) are presented by dendrogram, where the distance axis represents the degree of association between groups of variables, i.e. lower the value on the axis, the more significant the association. According to the dendrogram (Supplementary Fig. 3), two main clusters can be observed. Cluster one consists of H, N, Se, S, Fe, K, Mn, and As. Cluster two consists of Ca, C, Mg and Hg. The first cluster, based on the degree of dependence on elements, can be divided into three subclusters H and N (1), Se and S (2) and Fe, K, Mn, and As (3). H and N were significantly correlated with each other indicating adsorption of organic matter to clay minerals; Se and S represented sulphides and Fe, K, and Mn present Fe and Mn oxides and associations of these oxides and clay minerals in

sediments. As(V) is very strongly sorbed by Fe/Mn oxides (Li et al. 2016), which explain the presence of arsenic in this subcluster.

The second cluster can be divided into two subclusters: Ca, C, and Mg (1) and Hg (2). As expected, Hg was isolated from the other elements, which is indicative of lack of association with the others in the sediments. Ca, C, and Mg represented carbonates and form separate sub-cluster.

Results obtained by applying this multivariate method are consistent with those obtained by content distribution in sediments and inter-element relationships of studied elements.

4. Conclusion

Sediment pollution with As, Hg, and Se is a widespread concern due to the global distribution of these elements and the associated potential for toxicity, bioaccumulation and biomagnification. In the Serbian river and artificial lake sediments studied, mercury was found to be present in slightly elevated concentration. High content of arsenic on some localities, mainly caused by pollution with exogenous substances indicate that arsenic pollution problem that lasts longer period of time. Elevated concentrations of elements, mainly arsenic, in most cases were detected in samples of river sediments, since artificial lake reservoirs are usually built in rural areas, where the less anthropogenic pollution rivers often flow through the towns. Concentration of total selenium content in sediments is too low to be of toxicological significance in the aquatic environment.

The average pollution levels in studied sediments, expressed in terms of geoaccumulation indexes of As and Hg indicate that the environment is uncontaminated to moderately contaminated. All values of EF for Hg were below 2, indicating deficiency to minimal enrichment with Hg on studied localities. The calculated values of EF for As indicate that 95.8% sites for As had values for $EF < 2$, indicating deficiency to minimal enrichment. Two

stations in the studied area had values > 2 for As, indicating moderate enrichment. These sediments were taken from Ibar river, and obtained values may be explained by increased load of As due to anthropogenic pressures in these region. The percentages of the easily soluble metal fraction of arsenic were in general below 10%, indicating its low mobility into the aquatic environment.

Due to the potential risk of arsenic and mercury pollution in sediment, with potential impacts on the entire ecosystem, pollution prevention and remediation measurements seem essential, especially in areas where we found increased levels of this element.

Acknowledgements

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Fig. 1. Location map of sampling sites.

Fig. 2. Hg, As, and Se content (mg kg^{-1}) in sediments from rivers and lakes.

Fig. 3. Arsenic (a) and mercury (b) index of geoaccumulation of studied sediments.

Fig. 4. Enrichment factors values of Hg (a) and As (b) at each sampling site.

Table 1 Content of studied elements (mg kg^{-1}), dry weight basis and Se:Hg and S:Se ratios

Table 2 The average contents and ranges of As, Hg, and Se, compared with data reported in other sediments and soils and quality guidelines (in mg kg^{-1} , only if it is not otherwise stated)

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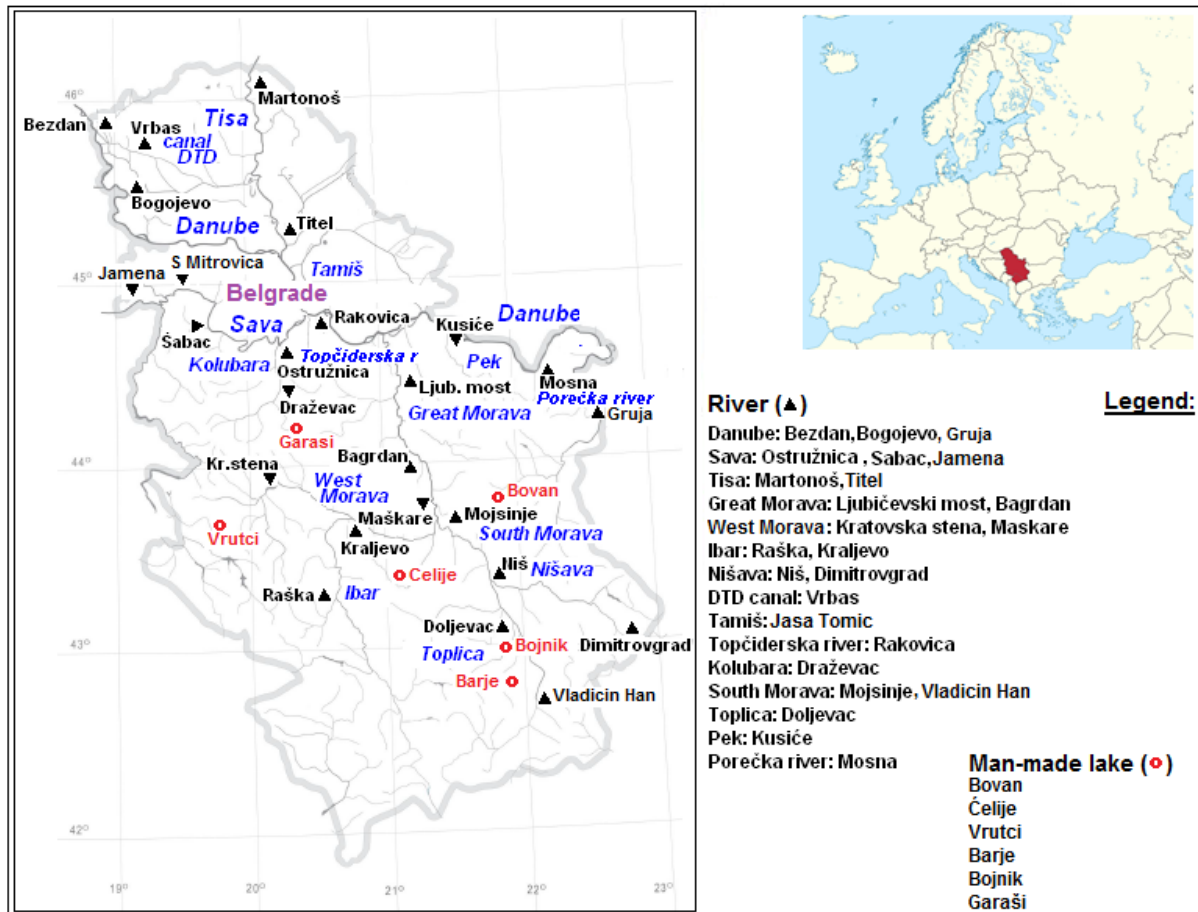


Figure 1

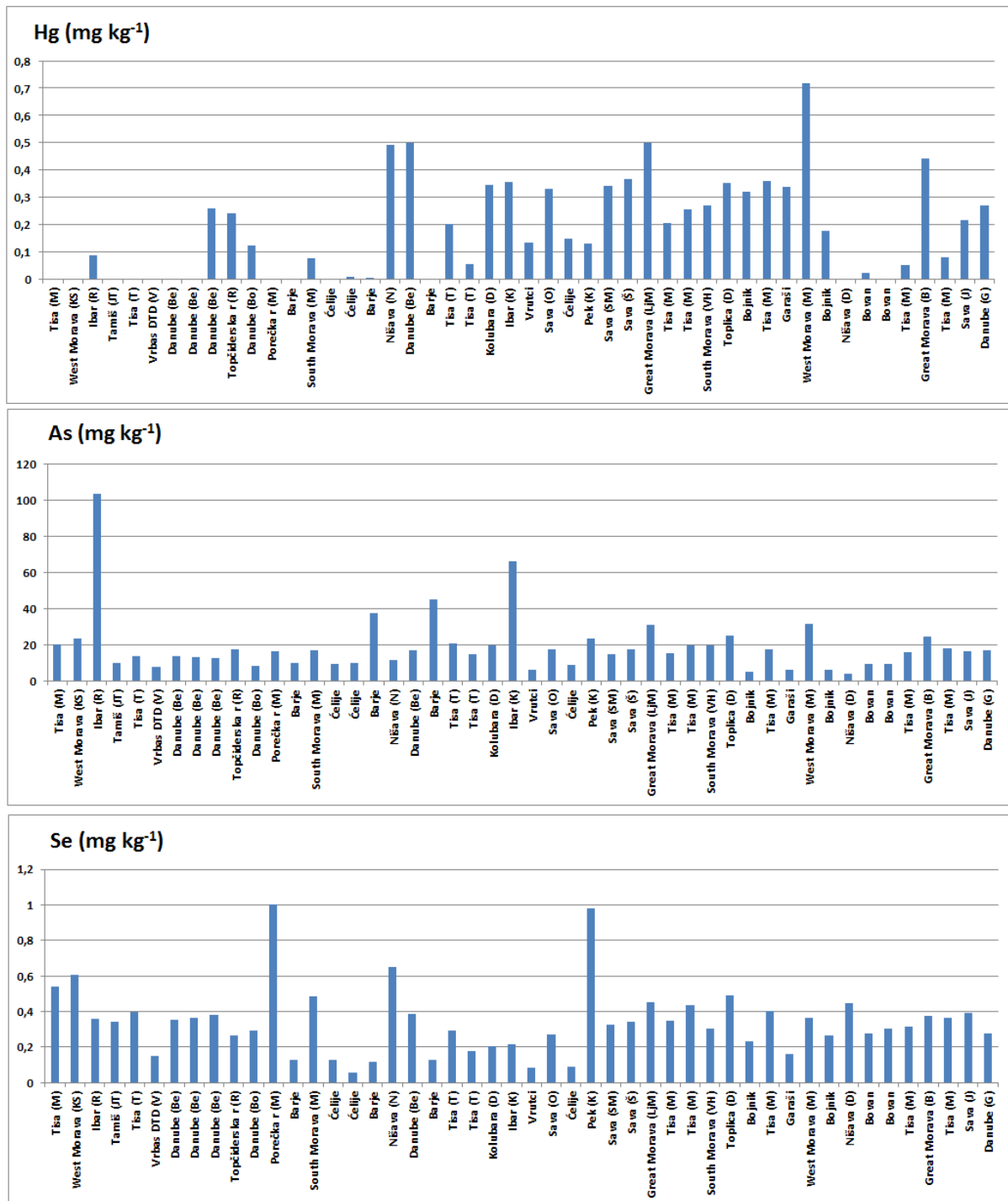


Figure 2

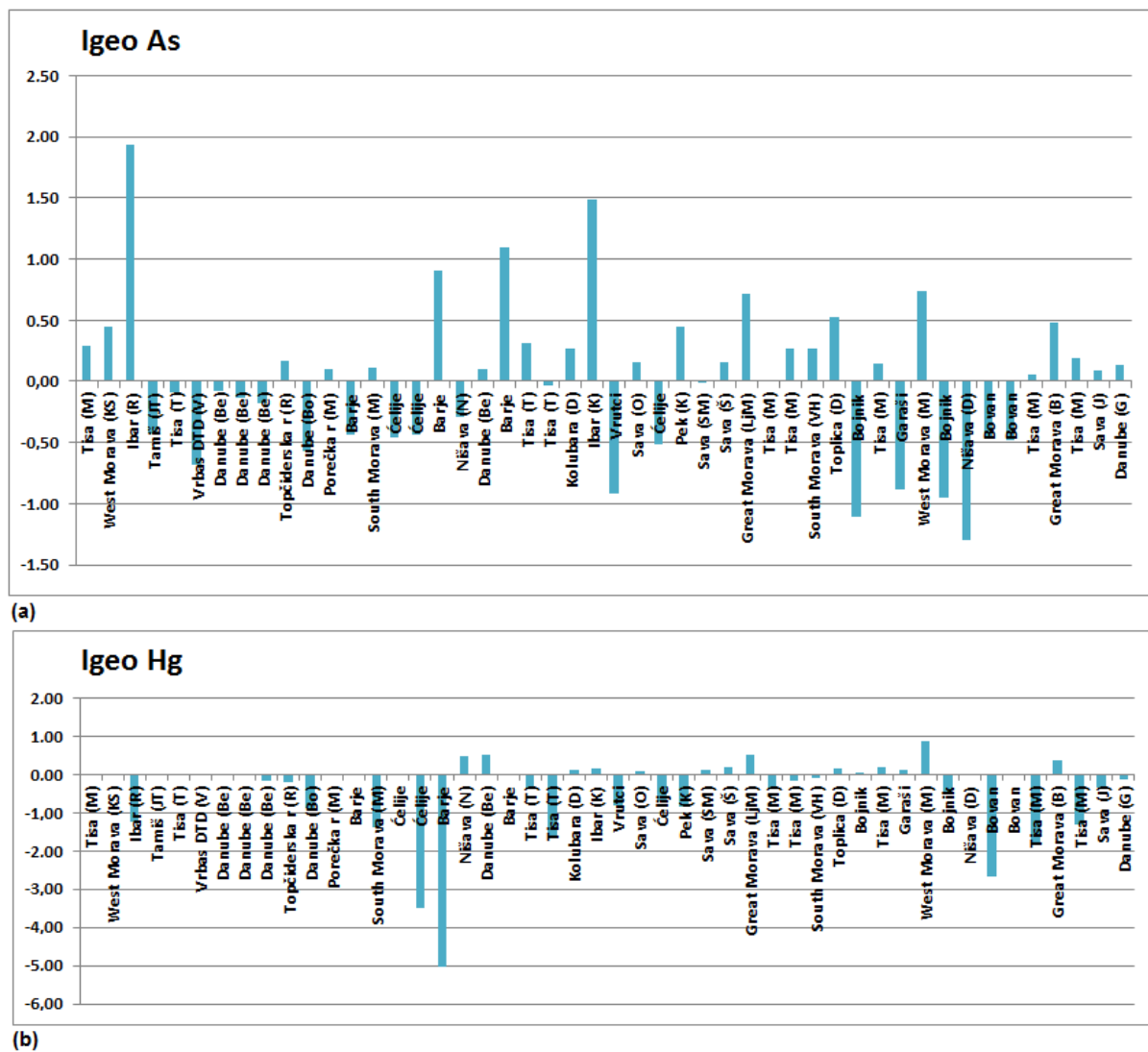
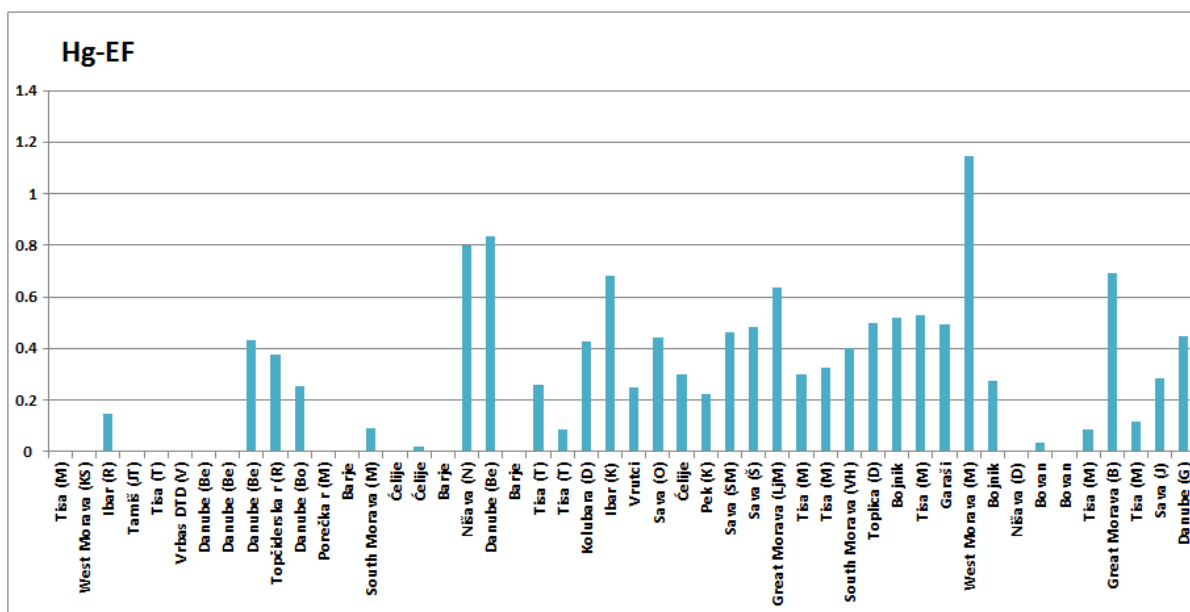
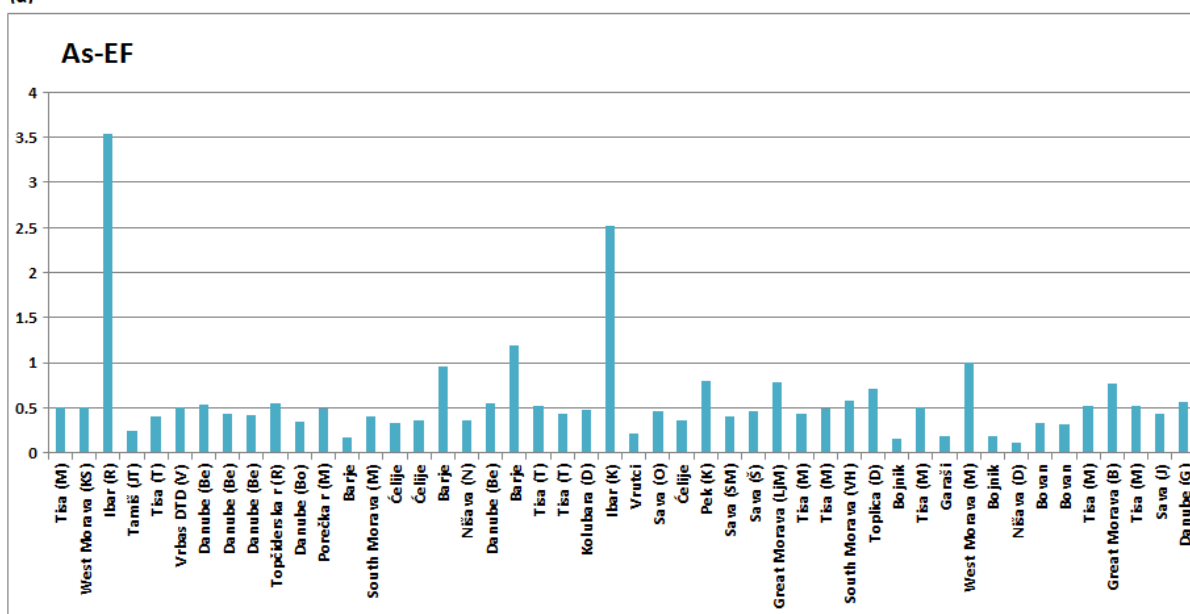


Figure 3



(a)



(b)

Figure 4

ACC

Table 1Content of studied elements [mg kg⁻¹], dry weight basis and Se:Hg and S:Se ratios

Number	Sampling location	R/L [#]	Hg	As	Se	Se:Hg	S:Se
1	Tisa (Martonoš)	R	< dl*	20.1	0.542		6827
2	West Morava (Kratovska stena)	R	< dl	23.5	0.605		8099
3	Ibar (Raška)	R	0.086	103	0.357	4.15	13165
4	Tamiš (Jaša Tomić)	R	< dl	9.77	0.341		8504
5	Tisa (Titel)	R	< dl	13.6	0.399		6266
6	Vrbas DTD (Vrbas)	R	< dl	7.58	0.152		13158
7	Danube (Bezdan)	R	< dl	13.8	0.352		5682
8	Danube (Bezdan)	R	< dl	13.1	0.365		5753
9	Danube (Bezdan)	R	0.259	12.5	0.382	1.47	5131
10	Topčiderska river (Rakovica)	R	0.242	17.6	0.266	1.10	7143
11	Danube (Bogojevo)	R	0.123	8.44	0.291	2.37	6873
12	Porečka river (Mosna)	R	< dl	16.6	1.004		3586
13	Barje	L	< dl	9.69	0.128		14922
14	South Morava (Mojsinje)	R	0.075	16.8	0.486	6.48	5967
15	Čelije	L	< dl	9.46	0.128		15391
16	Čelije	L	0.009	9.70	0.056	6.22	35000
17	Barje	L	0.002	37.2	0.117	58.50	16667
18	Nišava (Niš)	R	0.492	11.2	0.650	1.32	5538
19	Danube (Bezdan)	R	0.500	16.6	0.388	0.78	5052
20	Barje	L	< dl	44.7	0.127		15354
21	Tisa (Titel)	R	0.203	20.4	0.290	1.43	6897
22	Tisa (Titel)	R	0.056	14.4	0.176	3.14	11080
23	Kolubara (Draževac)	R	0.345	19.5	0.206	0.60	9466
24	Ibar (Kraljevo)	R	0.357	66.0	0.216	0.61	12130
25	Vrutci	L	0.135	5.96	0.084	0.62	22619
26	Sava (Ostružnica)	R	0.331	17.6	0.272	0.82	7132
27	Čelije	L	0.147	8.95	0.090	0.61	21889
28	Pek (Kusiće)	R	0.130	23.4	0.983	7.56	6419
29	Sava (Sremska Mitrovica)	R	0.341	14.8	0.323	0.95	6037
30	Sava (Šabac)	R	0.368	17.5	0.342	0.93	5702
31	Great Morava (Ljubičevski most)	R	0.500	30.7	0.451	0.90	4279
32	Tisa (Martonoš)	R	0.206	15.1	0.347	1.68	5620
33	Tisa (Martonoš)	R	0.254	19.6	0.433	1.70	4411
34	South Morava (Vladičin Han)	R	0.271	19.6	0.301	1.11	6379
35	Toplica (Doljevac)	R	0.352	25.2	0.491	1.39	3951
36	Bojnik	L	0.321	4.95	0.230	0.72	8435
37	Tisa (Martonoš)	R	0.360	17.4	0.400	1.11	4875
38	Garaši	L	0.337	6.2	0.159	0.47	12327
39	West Morava (Maskare)	R	0.717	31.3	0.363	0.51	7218
40	Bojnik	L	0.178	5.81	0.263	1.48	7338
41	Nišava (Dimitrovgrad)	R	< dl	4.10	0.446		4731
42	Bovan	L	0.021	9.41	0.274	13.05	7080
43	Bovan	L	< dl	9.29	0.301		6412
44	Tisa (Martonoš)	R	0.051	15.8	0.316	6.20	6203
45	Great Morava (Bagrdan)	R	0.441	24.3	0.373	0.85	5308
46	Tisa (Martonoš)	R	0.08	18.2	0.365	4.56	5342
47	Sava (Jamena)	R	0.217	16.3	0.390	1.80	5000
48	Danube (Gruja)	R	0.269	17.1	0.276	1.03	7609
Median			0.141	16.4	0.332		
GM**			0.134	15.3	0.292		
HM***			0.081	12.8	0.242		
Avg			0.183	19.0	0.340	3.95	8874
Max			0.717	103	1.004	58.5	35000
Min			< dl	4.10	0.056	0.47	3586
SDEV			0.180	16.48	0.191		

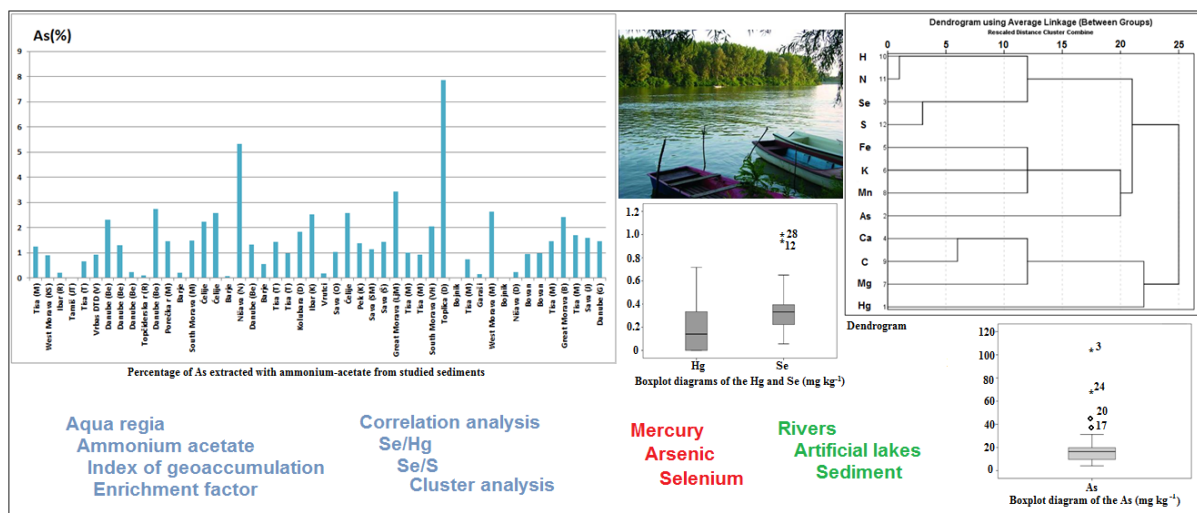
[#] River/Lake; *below detection limit (< 0.0001 mg kg⁻¹); ** geometric mean; *** harmonic mean

Table 2

The average contents and ranges of As, Hg, and Se, compared with data published for other sediments and soils and sediment quality guidelines (in mg kg⁻¹, only if it is not otherwise stated)

	As	Hg	Se	Literature
Sediment (Kupa river, Croatia)	ND-12.96 (5.036±2.829)	13.4-206 (86.8±48.2)**	0.12-1.26(0.61±0.26)	Frančičković-Bilinski (2007)
Sediment (rivers***, Slovenia)	10.87-30.46 (17.33±6.94)	121-1087 (425±312) **	0.34-2.72(1.26±0.57)	Frančičković-Bilins. et al. (2006)
Sediment (Sava river****)	1.89-46.01(14.13±7.94)	16.8-6918(1163-1415)**	ND-3.94(1.25±0.81)	Frančičković-Bilinski (2008)
Sediment (central India)	19-489 (105*)			Patel et al. (2005)
Soil (northwest China)	6.28- 12.96 (9.88)	0.52-5.05 (1.39)		Chen et al. (2016)
Background	11.70	0.13		Chen et al. (2016)
Scottish topsoils			0.19-1.46	Shand et al. (2010)
Finnish sediment (silt)			(90**)	Koljonen T (1974)
Finnish sediment (clay)			(320**)	Koljonen T (1974)
Soil (northeast-southwest China)			0.08-0.215	lv et al. (2014)
Soil (China, Fujiang River B)			(0.200)	Yu et al. (2014)
Soil (China, Beijing)	4.05-18.3 (8.38)	0.01-0.67 (0.07)		Xu et al. (2016)
Sediments (river, NE Spain)	1.09-13.17	ND-0.22		Roig et. (2011)
Topsoil (Yerevan, Armenia)	0.050-4.900 (0.050)	0.010-0.270 (0.115)		Tepanosyan et al. (2016)
Sediments (Rhue river, France)	9.4			Frémion et al. (2016)
Sediment (Upper Loire River, France)	44.7			Dhivert et al. (2015)
Sediment (Yangtze River, China)	17.0			Tang et al. (2014)
Sediment (River Pra Basin, Ghana)		0.390-0.707		Opong et al. (2010)
Sediment (Sava river, spring - outfall)	7-25	0.2-0.6		Milačić et al. (2010)
Sediment (Danube river)	9.0-68.9 (17.6±1.9)	<0.10–2.37 (0.22±0.05)		Woitke et al. (2003)
Sediment (Danube-tributaries)	8.1-388 (20.1±15.9)	<0.10–2.56 (0.22±0.21)		Woitke et al. (2003)
Sediment-background values	10	0.2		Woitke et al. (2003)
Sediment (this study)	4.10-103 (19.0±16.48)	<dl[#]-0.72 (0.18±0.18)	0.06-1.00 (0.34±0.19)	
MAC (Serbia)	25	2		Republic of Serbia (1994)
Benchmarks	9.8	0.18	2	US EPA 2007
PEC	25	1.1		MacDonald and Ingersoll (2002)

ND: not detected; * mean; **µg kg⁻¹; *** Savinja, Voglajna, and Hudinja; ****Slovenia and Croatia); dl[#]- 0.0001 mg kg⁻¹; ND- Not Detected



Graphical abstract

Highlights

Estimation the anthropogenic input of As, Hg and Se > Combination of different methods for estimation of the environmental status > Risk assessment of contamination > Calculation of contamination indexes - index of geoaccumulation and enrichment factor

> As in sediments of the studied area have potential risk

ACCEPTED MANUSCRIPT