Serbian Journal of Geosciences 9 (2023)
University of Niš, Faculty of Sciences and Mathematics
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Some potentially toxic elements (Pb, Zn, As, Cd, Cu, Ni, and Cr) in overbank sediments of smaller water courses from the Drina River basin (Republic of Serbia)

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Received 25.12.2023. · Accepted for publication 12.02.2024. · Published 10.03.2024.

Keywords:

PTE, overbank sediments, limit maximum values, remediation values

Abstract

The Drina River belongs to the Black Sea basin. It is formed by the confluence of the Tara and Piva rivers in Šćepan polje. The toponyms of Podrinje preserve the names of localities that bear witness to mining. There are also names that refer to families that founded hamlets, villages and towns. The area of the Drina basin is about 19,900 km^2 large. A total of 68 samples from watercourses east of the Drina (areas of the Republic of Serbia) were analyzed. For the sake of instructivity, the Drina basin is divided into two parts: the northern one and the one formed by the rivers whose recipient is the Lim river. This makes an approximately equal division of the Drina basin. Total concentrations of selected heavy metals - potentially toxic elements (PTE) were analyzed. These values were compared with the limit maximum allowed values, i.e. remediation values. In the northern part of the Drina basin, locally, some heavy metals reach limit maximum values, and locally also remediation values. Increased concentrations of analyzed potentially toxic elements can also originate from mining activities (tailings). In the southern part of the Drina basin, locally much fewer elements reach these values. Remediation contents of Ni and Cr in the southern part of the basin are probably of geogenic origin.

1. INTRODUCTION

PTE in overbank sediments represent a big problem since they are highly migratory, so they can easily reach the hydrosphere and biota, i.e. the food chain. Their origin can be anthropogenic or geogenic. These elements deposited in the sediments during subsequent floods can be remobilized and become a source of contamination again (Sanjuán et al., 2018). These elements can also originate from rocks - the geological basement on which soil with sediment was developed (Salminen et al. 1998, Dorfer et al. 2018a, Dorfer et al. 2018b).

Smaller watercourses from the Drina basin sometimes have the characteristics of torrential flows. Climatic influences also play a role in PTE sensations in sediments (Gor, 2009). The above can lead to the interference of PTE (Peh and Miko, 2001; Veljković et al. 2019).

There are no systematized data about the presence and concentration of PTE in soils from the Drina basin. Good soil and water quality is often quoted without systematic research. Sporadic research was done, usually after floods, which often occurs in this part of Serbia. Traces of mining are largely present in the researched area. Investigations of overbank sediments, which were carried out during the preparation of the Geochemical Map of Serbia, for the first time systematically treated PTE in overbank sediments of the Drina (Đokić, 2019, 2023).

In this paper an attempt was made to recognize the influence of the geological base, mining, or their joint influence (synergy) and/or to separate them, in relation to the total contents of PTE or their indications.

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2. MATERIALS AND METHODS

Investigating area

Drina river belongs to the Black Sea Basin. It is formed by the confluence of Piva and Tara near Šćepan Polje in Montenegro (fig. 1). It has a length of about 346 km and is the largest tributary of the Sava river. Its catchment area includes the southwestern and western parts of Serbia, the northern part of Montenegro and the eastern part of Bosnia and Herzegovina. The direction of the river flow is from south to north. One of its characteristics is that it defines the Tara Mountain massif from the northwest and north side. River Drina is one of the cleanest watercourses in Serbia.

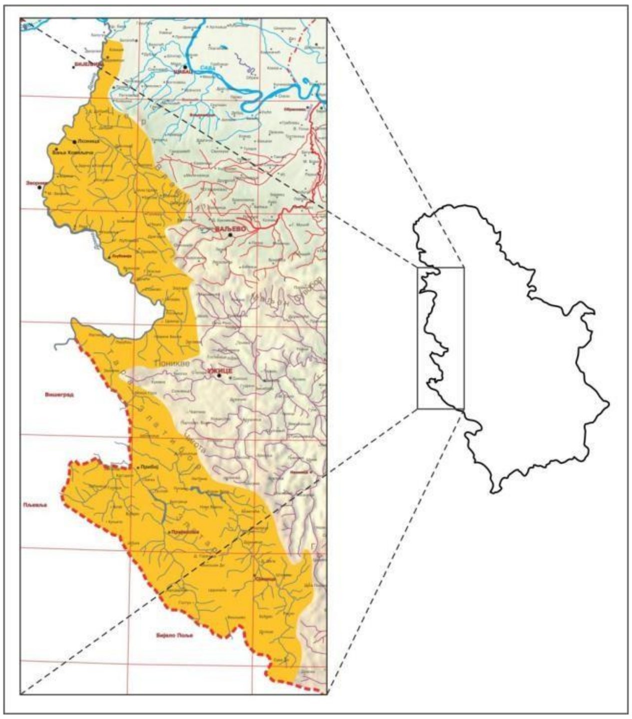


Figure1. Spatial position of the Drina basin

Sampling

The collecting of samples was carried out according to the recommendations for preparation of the "Geochemical map of Serbia 1:500,000, stream, overbank and floodplain sediments" (Đokić 2016). The coordinates of the samples were determined using a global positioning device type GARMIN-GPSmap60CSx. The depth of sampling is from 0cm to 10cm. In order to avoid the influence of organic matter, the samples were collected under the humus layer. Collecting was done with an EikelKamp probe with a soil sampling attachment, and a shovel with a stainless-steel blade. Samples were collected at least 100 m from settlements and 500 m from industrial and mining facilities. Each sample represents a composite of 10 individual subsamples to be more representative of the location (Đokić 2016). A total of 68 samples (680 sub-samples) were collected. Samples from the Drina basin were collected in 2019 and 2023 (Đokić 2019 and 2023).

Analytical preparations, procedures, methods and concentration limits

The collected samples were dried at room temperature in atmospheric conditions for 60 days, after which they were quartered. The reduced sample was dried in a porcelain container, in a dryer, at a temperature of 40° C. Weighing 100g of the sample was ground and sieved to a grain size of <100µm. The sample prepared in this way was chemically analyzed. Chemical analyses of the samples were carried out in the accredited laboratory for chemical tests of the Institute of Mining and Metallurgy Bor. Elements whose origin can be related to mining have been selected. The elements cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), arsenic (As), copper (Cu) and chromium (Cr) were examined by the spectrometric method in induced coupled plasma (ICP-MS). The lower limit of determination of Zn is 0.001%, As <1mg/l; Pb, Cu <0.5 mg/l; Ni, Cr<0.1 mg/l and Cd <0.05 mg/l, (in Đokić 2017 and 2018).

The obtained total concentrations of elements were compared with the valid instructions on the limit maximum and remediation contents of selected heavy metals (Official Gazette of RS, no. 30/2018 and 64/2019).

Geological composition

Podrinje has a very complex geological composition). It consists of formations of the Quaternary and Neogene cover and magmatic rocks, formations of the Jadar terrane and Dinarides (Kalenić et al., 2015, Fig. 2).

The formations of the Quaternary and Neogene cover are generally light blue and yellow in color, and the formations of the Jadar terrane and the Dinarides are darker brown and green in color (more details in Kalenić et al., 2015).

The formation of the Quaternary cover consists of: gravels, sands and siltstones, bed facies gravels and sands, river terrace, terrace 7-9, terrace 20 -30, cones and blues in cutting, gravels, sands and siltstones, moraines: rubble, gravels and gravelly clays.

The Neogene cover and magmatic rocks consist of: clastites, pelites with coal, sea bridge, clastites, pelites and carbonates; marine Baden, clastites, pelites and carbonates with tuffs, basalts, trachybasalts, clastites, pelites and carbonates with pyroclastites, granitoids.

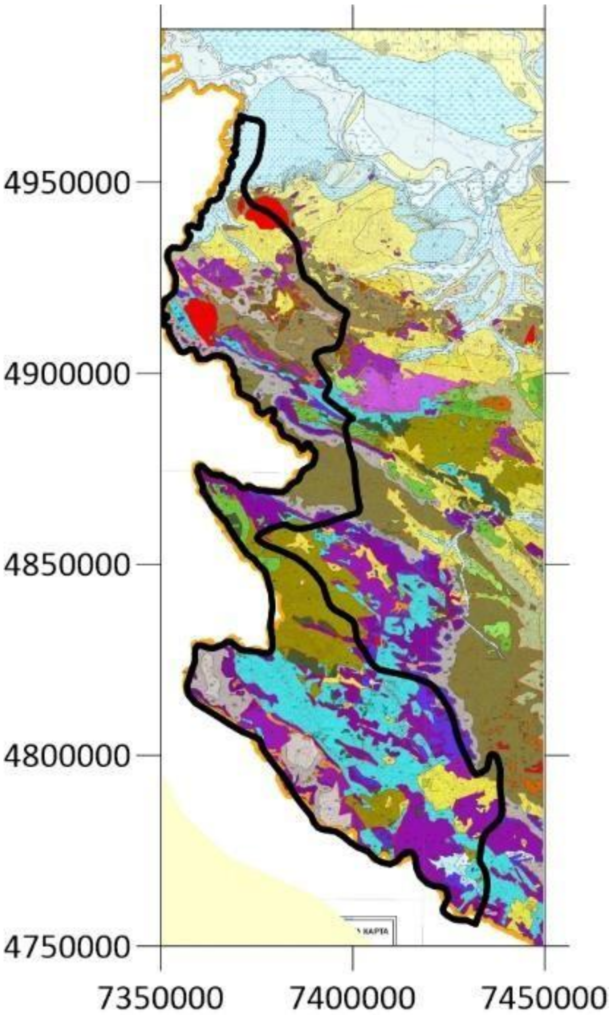


Figure 2. Geological map of the Republic of Serbia 1:300 000. Detail, after Kalenić et al, 2015.

The black line defines the boundaries of the Drina watershed.

Formations of the Jadar terrane consist of: conglomerates, sandstones, rarely limestones, massive limestones, porphyrites (andesites) and pyroclastites, dolomites and dolomitic limestones, limestones (ooid, bioturbated, etc.), bituminous limestones, fusulinide limestones, sandstones and siltstones with lenses of fusulinide limestones, siltstones with clasts and olistoliths, layered limestones with clay interlayers, massive limestones and siltstones, sandstones and siltstones.

The formations of the Dinarides are: clastites, limestones and marls, siltstones with inclusions of sandstone, limestone and ophiolitic rocks, diabases and spilites, serpentinites and serpentinized peridotites, massive limestones, limestones with cherts, quartz conglomerates, sandstones, siltstones, claystones and limestones, sandstones, siltstones and limestones, sediments of braided rivers.

3. RESULTS AND DISCUSSION

The Drina River is one of the cleaner watercourses in Serbia. Nevertheless, numerous traces of mining have been recorded in its basin. These traces go back to the pre-antique period. In the past, in Serbia, mining activities, together with the accompanying downstream jobs, constituted one of the leading industrial branches. Mines were often the driving force of the entire social development. Traces of mining on Bobija are certainly from the pre-Roman period. It is known that copper was mined in Rabelje, and lead, zinc and barite in Tisovik. Numerous underground mining works from the past ages confirm mining, mining tools and accessories found in old mining works, as well as numerous and very striking Saxon mounds in Lonjin and Rujevac. In 1828, the state even bought lead in Krupanj from the locals who smelt it at this location (Đokić et al., 2010). The characteristics of Podrinje are mining activities on the one hand, and highly developed agricultural production on the other.

Systematized data on mining in these areas is missing. From the beginning of the 19th century, the notes of Baron Herder are important, who, as an excellent expert in geology and mining, noted that generally "mines are unearthed improperly, so nothing can be said about their behavior" (Herder, 2014).

Numerous tailings were left behind by the mining activity. The Veliki Majdan Pb-Zn tailings, barite (Bobija), and tin ores (Zajača, Stolice, Džavrin Potok, Zavorje, Dolovi, Brasina, Kik and Dolić) remained behind the processing of predominantly lead-zinc ore. Increased concentrations of the heavy metals just analyzed were recorded at most of the tailings. White blooms were also recorded on some of them, which confirm high concentrations.

In 2010, the Geological Survey of Serbia investigated the larger tailings deposits of the Podrinja (Đokić et al. 2011). On this occasion, basic information about larger tailings ponds in these areas was systematically collected. This informations are related to their size, and to chemical, mineralogical and particle size characteristics. The design, and especially the interpretation of the results obtained from this project, were greatly influenced by the experiences and recommendations of the EU (Directive of the European Parliament, COM:2003.).

In recent history, studies of these tailings that were carried out in Serbia, were financed from foreign funds (Nishikawa, 2008, Pleiades, 2017/2020).

The paper contains data from the project "Geochemical map of Serbia 1:500,000, stream, overbank and floodplain sediments in 2018 and 2023." The analyzed heavy metals can also come from mining activities, actually they can be related to tailings.

LEAD. This element has a pronounced chalcophile character, so it is connected to sulphide minerals, most often galena (PbS). The mean concentration of lead in the earth's crust is 14 ppm (Jović, 2004). Limit values for this element are 85ppm, and remedial values are 530ppm. Lead in the environment originates mainly from anthropogenic sources (lead mines and smelters, metallurgical plants, vehicle exhaust gases, production of accumulators and batteries, certain pesticides, etc.). All these activities were recorded in these regions. This heavy metal occurs in concentrations above the limit values in 9 samples in the northern part of the Drina basin. In concentrations that exceed remediation values, it occurs in one sample collected in the northern part of the Drina basin in the Krupinska river watercourse (Fig. 3). Lead is quickly absorbed into the bloodstream and has a negative effect on the central nervous system, the bloodstream, the immune system and the kidneys (Šarkanj et al., 2010.).

ZINC. This heavy metal is characterized by its chalcophile character. It occurs in nature in the form of sulfide-sphalerite (ZnS).The average content of Zn in the Earth's crust is 75 ppm (Jović, 2004). Limit values for this element are 140ppm, and remedial values are 720ppm. This element occurs in concentrations above the limit in 7 analyzes in the northern part of the Drina basin, and only in one in the southern part (Lim), i.e. in the Uvac watercourse (Fig. 3).

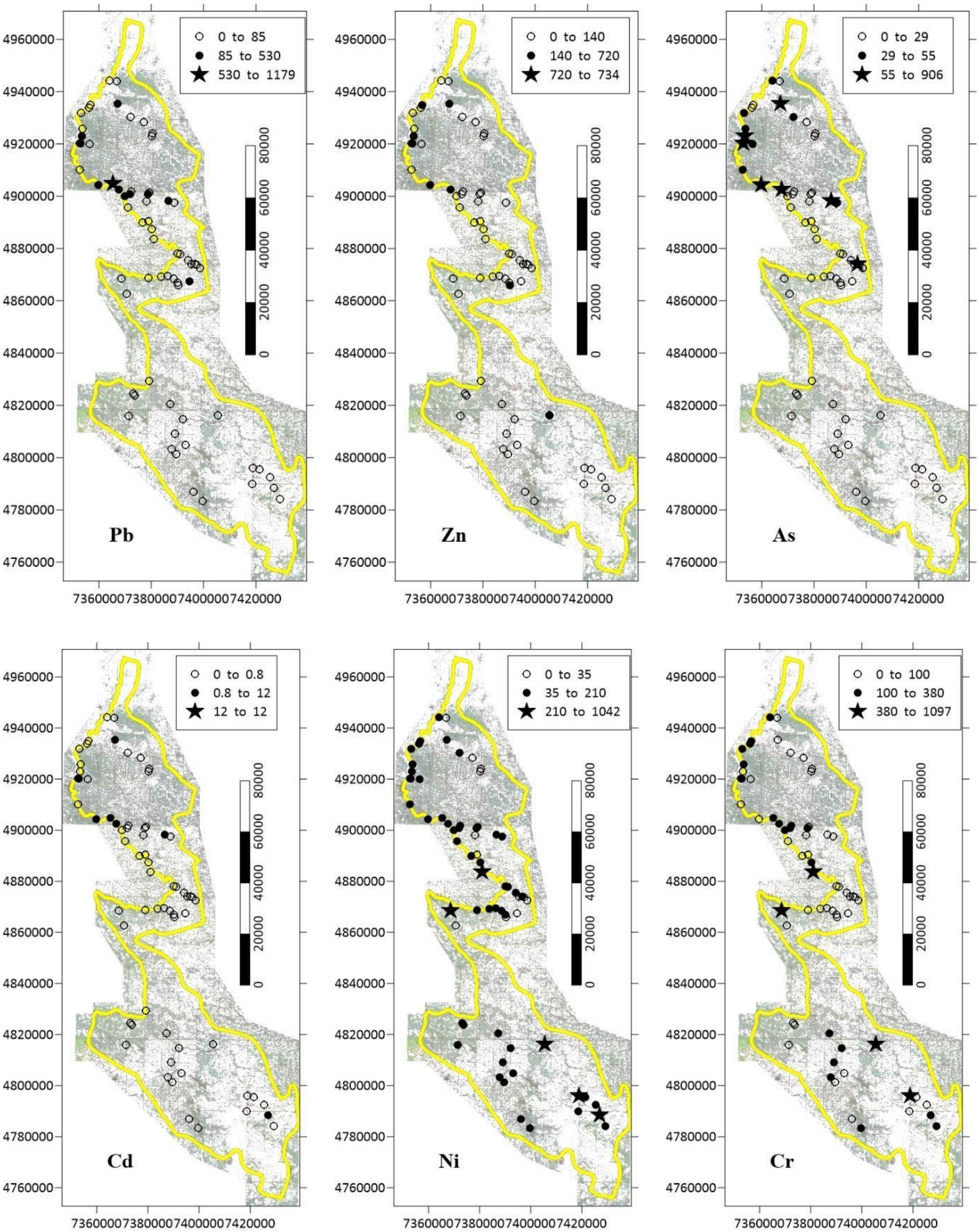
ARSENIC. This is a chalcophile element. It occurs in nature in sulfides: arsenopyrite (FeAsS), realgar (AsS) and orpiment (As2S3). Its mean content in the Earth's crust is 1.5 ppm (Jović, 2004). Limit values for this element are 29ppm, and remedial values are 55ppm. There are opinions that this element reaches the biosphere from anthropogenic sources, which is possible in these areas. Arsenic is very mobile and this allows it to contaminate much larger surfaces very easily. This element occurs in contents above the limit and remediation values in 7 samples and only in the northern part of the basin (Fig. 3). Arsenic toxicity causes changes in the skin, causes neurotoxicity and carcinogenicity. Increased concentrations link it to diabetes and hypertension (Šarkanj et al., 2010.).

CADMIUM. This element occurs with an average concentration in the earth's crust between 0.1 and 0.5 ppm. Limit values for this element are 0.8ppm, and remedial values are 12ppm. This element has no essential biological functions, but is found in more than 1000 species of flora and fauna. It is the most dangerous heavy metal in the soil and environment. This element occurs in contents above the limit at 6 locations in the northern part of the basin, and at only 1 in the southern part (Lim), namely in the Vapa watercourse (0.83ppm, Fig. 3). Cadmium can replace zinc, calcium and potassium in the body and is difficult to remove. Cadmium is primarily toxic to the liver and kidneys, then the digestive tract (Šarkanj et al., 2010.).

NICKEL. This metal is present in the earth's crust in a mean concentration of about 80ppm. Limit values for this element are 35ppm, and remedial values are 210ppm. The origin of nickel is probably geogenic. This element occurs in most samples in contents that are above the limit. It occurs in contents that are above remediation in two samples in the northern parts of the basin and in three in the southern parts (Fig. 3). Nickel is also considered to be an essential element for the body, although nickel deficiency has not been observed in humans. Dermatitis caused by even the smallest intake of food containing nickel can appear (Šarkanj et al., 2010.).

CHROMIUM. This element occurs in the earth ́s crust in a concentration of 100ppm (Jović, 2004). Limit values for this element are 100ppm, and remedial values are 380ppm. The main sources of anthropogenic chromium are metallurgical plants, cement production, burning of fossil fuels, fertilizers and waste sludge. This heavy metal occurs in contents above remediation in two samples from the northern part of the basin (Bačevačka river and Aluški stream) and in two samples from the southern part (Uvac 1 and 2, Fig. 3). Chromium intake imbalance causes stomach problems (Šarkanj et al., 2010.).

COPPER. This element has a siderophile and chalcophile character. It is present in the Earth's crust as sulphide-chalcosine, coveline (CuS) and chalcopyrite (CuFeS2). The mean content in the Earth's crust is 55ppm (Jović, 2004). Limit values for this element are 36ppm, and remedial values are 190ppm.The content of this element exceeds the limit in 9 samples in the northern part of the basin and in 7 samples in the southern part (Fig. 3). An imbalance in the intake of this element, above all insufficient intake of copper in the body, can lead to major consequences for human health. This affects hemolytic anemia, kidney, liver and brain damage as well as increased blood pressure (Šarkanj et al., 2010.)



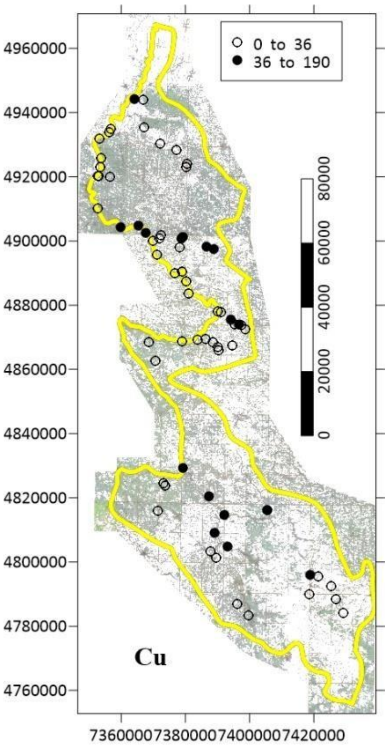


Figure 3. Concentration of PTE, Drina basin, Legend● normally, border maximal values,★ remediation values. The yellow line defines the boundaries of the watershed.

4. CONCLUSION

Drina is an international river. There are numerous objects in its basin that can affect the quality of overbank sediments. In the paper, analyzes are given only for the total concentrations of metals, which origin may be different. It is very likely that the anthropogenic factor (recorded and unrecorded historical tailings) has a decisive influence on the increased concentrations, especially in the northern parts of the basin. The evident influence of historical tailings has not been sufficiently analyzed.

Smaller watercourses in the Drina basin also have the characteristic of torrential flows. Suspended material transported by smaller watercourses during frequent floods is deposited as overbank sediment in the soil on the banks. This sediment can affect, above all, the chemical properties of the soil. However, the greatest influence on the structure, mineralogical and chemical composition of the soil has the geological base on which the soil was developed. This especially applies to the parts of the basin whose recipient is Lim. The climate has a great influence on these properties.

However, determining the unambiguous origin of these heavy metals in sediments is very complex. It is practically impossible to make unequivocal conclusions, especially in these locations, which have a very complex geological structure. Certainly, in the so far indicated locations more detailed research is necessary.

The fact that the Drina catchment area is extremely rich in forest is also of great importance. This region is extremely suitable for the development of animal husbandry, agriculture and tourism.

ACKNOWLEDGMENT:

Most of the data that were used in paper were collected during the realization of the project and project annex of "Geochemical map of the Republic of Serbia 1:500 000 (stream, overbank and floodplain sediments)". The project and the project annex were realized in 2016, 2019, 2023. The realization of the projects is financed with funds from the budget of the Republic of Serbia.

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