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COPPER CONCENTRATION IN THE SOILS OF THE DANUBE FLOODPLAIN BETWEEN THE RIVERS TIMOK AND VIT NORTHWESTERN BULGARIA

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Abstract

This paper presents an actual and overall picture of soil contamination with copper in the Bulgarian part of the Danube floodplain between the rivers Timok and Vit. Three sampling campaigns in October 2012, April 2013, and October 2017 are carried out in the frame of two studies. The total content of copper is determined by atomic spectrometry in the soil fraction < 0.100 mm in the first study, and by X-ray fluorescence spectrometry in the soil fraction < 0.063 mm in the second survey. The copper concentration in the collected topsoil and subsoil samples ranges between 9.5 – 742.7 mg/kg with a median of 34.4 mg/kg. About 94 % of the samples exceed the background reference value, 10 % are above the maximum admissible concentration, and 3 % violate the intervention threshold. The copper content peaks in the Timok Valley and decrease downstream the Danube to nearly steady levels east of the Vidin Lowland.

Keywords: *Lower Danube, Danube's lowlands, heavy metals, wetland pollution*

1. INTRODUCTION

Copper is the fifth most produced metal with global production of more than 20 million tonnes in 2016 (Reichl et al., 2018). Activities related to extracting and processing of ores are the primary sources of metal-contaminant loads to the environment and especially to the river systems (Macklin et al., 2006). Therefore, the river valleys are one of the most affected areas in terms of heavy metal pollution, including copper. Soil contamination with the element is documented in many regions on several continents such as the valleys of Guadiamar River in Spain (Macklin et al., 1999), Elbe River (Schulz-Zunkel and Krüger, 2009), Tisa River

(Macklin et al., 2003), Iskar and Topolnitsa rivers in Bulgaria (Bird et al., 2010a; Cholakova, 2002), Timok River on the border between Serbia and Bulgaria (Brankov et al., 2012), Xiaojiang River in China (Cheng et al., 2018). According to Cheng et al. (2018), soil contamination with copper is also documented in Voghchi River in Armenia (Tepanoszan et al., 2018), Mashavera and Kazretula Rivers in Georgia (Avkopashvili et al., 2017), Aconcagua and Cachapoal Rivers in Chile (Schalscha et al, 1997), Sinú River in Colombia (Marrugo-Negrete et al., 2017) as well as rivers in Morocco (Azhari et al., 2017), Tunisia (Boussen et al., 2013), Nigeria (Obiora et al., 2016) and Portugal (Ávila et al., 2017).

Copper concentration in the Earth's crust and rocks varies between 2 mg/kg (sandstone) and 90 mg/kg (gabbro and basalt) (Reimann and Caritat, 1998). The element can be released into the environment by both natural sources and human activities like copper mining and smelting, production of non-ferrous metal alloys, coins, electrical wiring, water piping, pigments, copper-based sprays (algaecide, bactericide, molluscicide, fungicide, insecticide), phosphate fertilizer, preservatives for wood, leather, wood production, and fabrics (Reimann and Caritat, 1998; Yang et al., 2002; Wuana and Okieimen, 2011; Shalini et al., 2017).

Copper is an essential microelement for all organisms, including microorganisms, plants, animals and human beings (Reimann and Caritat, 1998; Comber et al., 2008; Wuana and Okieimen, 2011). It takes part in different enzymes which have vital functions for the metabolism of plants. The element is needed for the biological processes of photosynthesis, breathing, carbohydrate distribution, nitrogen reduction, and fixation (Pendias and Pendias, 1989). The favourable Cu content in plants is essential both for the health of the plants themselves and for their use in human and animal nutrition (Pendias and Pendias, 1989). Insufficient supply of animals and humans with the microelement leads to a decrease in the amount of haemoglobin in the blood and anaemia (Comber et al., 2008; Wuana and Okieimen, 2011, Pendias and Pendias, 1989).

The environmental quality is an essential factor for the population health (Santana et al., 2015), and it can be affected negatively by enhanced levels of copper in the soil. The element is one of the most toxic metals and can cause irritation of the nose, mouth and eyes, headache, stomach pains, dizziness, vomiting, diarrhoea, damage to the liver and kidneys and even death in prolonged exposure at high doses (Reimann and Caritat, 1998, Wuana and Okieimen, 2011). Copper is included in the Priority Pollutant List of the United States Environmental Protection Agency (US EPA), Directive 2006/11/EC/ of the European Parliament and the Council on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. The Water Framework Directive requires that the Member States identify Specific Pollutants and set standards for them. According to work by the UK Technical Advisory Group on the Water Framework Directive (UKTAG), Cu is included in the List of Specific Pollutants and Toxic Substances which are discharged in significant quantities into the water environment (UKTAG, 2013).

The industrial development in the Danube River basin has led to the accumulation of hazardous substances in the alluvial sediments along the main river and some of its tributaries (Bird et al., 2010a; Milačič et al., 2010). Historical and present mining activities have a peak in the period 1950-1987 (Winkels et al., 1998), and are considered to be the major source of heavy metal load in the Lower Danube (Bird et al., 2010b; Serbula et al., 2016; Urošević et al., 2018). A specific source of copper pollution in the Danube Valley downstream the dams of the Iron Gate seems to be the copper ore extraction in the Bor open-pit mine in the sub-catchment of the Timok River (Macklin et al., 2006). Enrichment of alluvial soil with trace elements is mostly related with the spread of contaminated river sediment throughout the floodplain (Macklin et al., 2006). It is highly dependent on the river flow regime, span, and frequency of the flood events. Despite the numerous studies on the concentration of heavy metals and metalloids in river sediments, water, plants, and animals in the Lower Danube Basin (Bird et al., 2010a; Bird et al., 2010b; Bird et al., 2010c; ICPDR, 2008; Matache et al., 2013; Ihtimanska, 2014; ICPDR, 2015; Pavlović et al., 2015; Stoyanova et al., 2018), heavy metal pollution of soil in the Danube floodplain on the territory of Serbia, Romania and Bulgaria has not been analysed in detail, yet. A preliminary investigation on trace metal spatial distribution in alluvial soils between the towns of Vidin and Turnu Măgurele was conducted in the frame of the ROBUHAZ-DUN project in 2012. Soil pollution is also studied under the project "Content of heavy metals in the soils of the Danube lowlands between the Timok River and the Vit River: relation to floodplain morphography and river dynamics". This research aims to present an actual and overall picture of the copper contamination of soils of the Danube floodplain in the Bulgarian sector between the Timok River and the Vit River.

2. STUDY AREA

The study area is located in the North-western Bulgaria and includes seven Danube's lowlands which are located between the Timok River and the Vit River: Bregovo-Novoselska (82 km2), Vidinska (134 km2), Archaro-Orsoyska (35 km2), Dolnotsibarska (21 km2), Kozloduyska (45 km2), Ostrovska (25 km2) and Chernopolska (225 km2) (Figure 1).

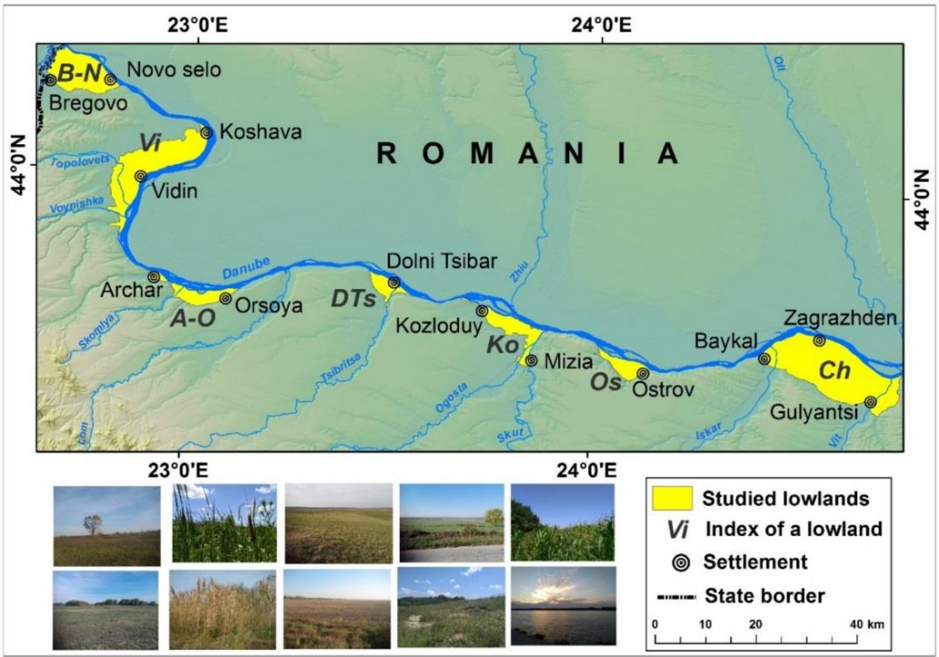

Figure 1. Designation of the studied lowlands along the Danube: Bregovo-Novoselska (B-N); Vidinska (Vi); Archaro-Orsoyska (A-O); Dolnotsibarska (DTs); Kozloduyska (Ko); Ostrovska (Os); Chernopolska (Ch)

The endpoints of the study area are located as follows: northernmost point at the mouth of the Timok River in the Danube with a latitude 44°12′48.212″N and longitude 22°40′11.203″E; southernmost point near the town of Gulyantsi with a latitude 43°36′37.282″N and longitude 24°40′48.625″E; westernmost point near the settlement Bregovo with latitude 44°10′31.809″N and longitude 22°37′34.869″E; easternmost point near the settlement Dolni Vit with a latitude 43°39′44.771″N and longitude 24°45′28.703″ E.

The climate of this region is temperate-continental. The annual mean temperature is of 11.5ºC, which is characterized by relatively cold winter and hot summer (Institute of Hydrology and Meteorology, 1983). The average value of yearly precipitation slightly decreases from the West (Novo Selo – 582 mm) to the East (Svishtov – 543 mm) (Koleva and Peneva, 1990).

The Danube's lowlands are covered with young alluvial soils (Fluvisols, FAO), alluvial meadow soils (eutric Fluvisols, FAO), sediments that are in transition to soil state and gley soils in drained areas. Gleyic Chernozems (FAO) are typically the main soil variety of the higher river terraces in the lowlands.

The investigated area occupies territories of the following districts: Vidin, Montana, Vratsa, and Pleven. The total population of the Danube's lowlands on the territory of Bulgaria between the Timok River and the Vit River is 82.222 people (National statistical institute, 2018) settled in 5 towns (Bregovo, Vidin, Kozloduy, Mizia and Gulyantsi) and 23 villages. The largest and most important economic entity is the nuclear power plant "Kozloduy". In the town of Vidin is situated a thermal power plant. The chemical industry in Vidin collapsed after the end of the communist period. Production of building materials is available in Koshava village and the town of Lom. Crop growing is predominant in the study area. Crops include the cereal and fodder grains (wheat and maize), industrial crops (sunflower) and vineyards (Bălteanu et al., 2013). There are no significant point sources of heavy metals pollution available within the territory of the investigated lowlands (Kotsev and Zhelezov, 2014).

3. MATERIAL AND METHODS

3.1 Soil sample collection

About 155 soil samples from 112 sites are collected during three field campaigns in October 2012, April 2013 and October 2017. The sampling is organized along cross-sections semi-perpendicular to the Danube River, taking into account the morphographic features of the floodplain (Figure 2).

A B

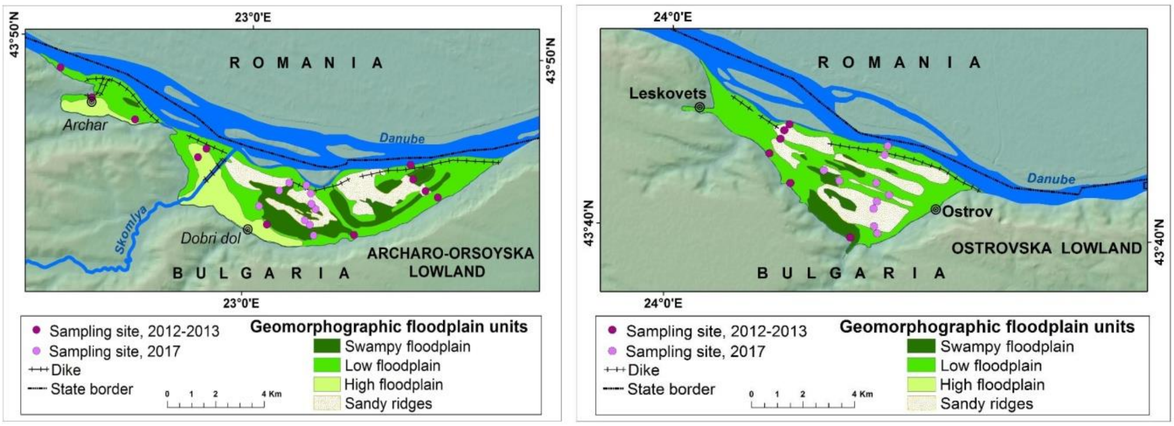

Figure 2. Distribution of the soil sampling sites: A - Archaro-Orsoyska lowland; B - Ostrovska lowland

The survey conducted in 2017 complements the previous one performed in 2012 and 2013, making the initial sampling network more complete. The first two sampling campaigns are conducted in the frame of the ROBUHAZ-DUN project (2007-2013) when 43 samples are taken from a soil depth 0-25 cm (Table 1). The rest of the samples are collected from 0-20 cm (56 samples), 20-40 cm (43 samples) and 40-60 cm (3 samples) soil depths within the project "Content of heavy metals in the soils of the Danube lowlands between the Timok River and the Vit River: relation to floodplain morphography and river dynamics" (Table 2).

Table 1. Distribution of samples by lowlands and depths, October 2012 - April 2013

No	Lowlands	0-25 cm
1	Bregovo-Novoselska	1
2	Vidinska	11
3	Archaro-Orsoyska	11
4	Dolnotsibarska	8
5	Kozloduyska	7
6	Ostrovska	7
7	Chernopolska	11
	Total	**56**

Table 2. Distribution of samples by lowlands and depths, October 2017

No	Lowlands	0-20 cm	20-40 cm	40-60 cm
1	Bregovo-Novoselska	7	6	1
2	Vidinska	10	11	0
3	Archaro-Orsoyska	10	7	1
4	Dolnotsibarska	7	6	0
5	Kozloduyska	3	2	0
6	Ostrovska	10	2	0
7	Chernopolska	9	9	1
	Total	**56**	**43**	**3**

3.2 Measurement of the content of heavy metals and metalloids in the soil

The total content of Cu in the soil samples taken in 2012-2013 is determined by atomic spectrometry for the soil fraction < 0.100 mm. The measurements are performed at the premises of the Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania.

The samples which are collected in 2017 are measured by X-ray fluorescence spectrometry (XRF). The soil material is air-dried, then crushed manually in a porcelain mortar and sieved through a < 0.063 mm wire mesh made of stainless steel. Pellets are prepared from 4 g of soil and 0.9 g of an amide wax (N.N′-Bisstearoylethylenediamide, Licowax C, Clariant).

The concentration of Cu is additionally determined in the soil fraction < 0.100 mm of 27 samples, selected from the subset of the last campaign. The results are compared with the contents of Cu in the finer fraction < 0.063 mm of the same samples and a negligible difference between the two data sets is found. The average Cu concentration in the coarser fraction is 6% lower than the average content in the finer material (Table 3). Thus, the results from the two investigations conducted in 2012-2013, and 2017 are considered comparable regarding the difference between the measured particle size fractions of the soil.

Table 3. Comparison between the copper content in the fractions < 0.100 mm and 0.063 mm

No	Sample code	Danube lowland	Geomorphographic floodplain units	Depths, cm	Cu in fraction < 0.063 mm [mg/kg]	Cu in fraction < 0.100 mm [mg/kg]
1	2a	Bregovo-Novoselska	Low floodplain	0-20	120.8	156.0
2	2b	Bregovo-Novoselska	Low floodplain	20-40	139.5	116.2
3	2c	Bregovo-Novoselska	Low floodplain	40-60	80.7	76.2

4	3a	Bregovo-Novoselska	Low floodplain	0-20	329.2	361.8
5	3b	Bregovo-Novoselska	Low floodplain	20-40	234.4	250.1
6	5a	Bregovo-Novoselska	Low floodplain	0-20	353.8	340.0
7	5b	Bregovo-Novoselska	Low floodplain	20-40	334.5	349.5
8	6a	Bregovo-Novoselska	Low floodplain	0-20	742.7	862.7
9	6b	Bregovo-Novoselska	Low floodplain	20-40	526.6	568.4
10	13a	Vidinska	Low floodplain	0-20	435.3	283.5
11	13b	Vidinska	Low floodplain	20-40	680.3	349.2
12	16a	Vidinska	Low floodplain	20-40	21.2	21.0
13	20a	Vidinska	Low floodplain	0-20	49.4	51.0
14	20b	Vidinska	Low floodplain	20-40	47.4	50.1
15	26a	Archaro-Orsoiska	Sandy ridges	0-20	32.8	12.7
16	26b	Archaro-Orsoiska	Sandy ridges	20-40	23.4	9.2
17	27a	Archaro-Orsoiska	Swampy floodplain	0-20	55.6	43.7
18	30a	Archaro-Orsoiska	Sandy ridges	0-20	37.8	36.2
19	31a	Archaro-Orsoiska	Swampy floodplain	0-20	54.2	60.0
20	31b	Archaro-Orsoiska	Swampy floodplain	20-40	56.4	59.6
21	34a	Dolnotsibarska	Low floodplain	0-20	27.2	25.6
22	34b	Dolnotsibarska	Low floodplain	20-40	25.6	25.1
23	36a	Dolnotsibarska	Low floodplain	0-20	23.6	22.6
24	36b	Dolnotsibarska	Low floodplain	20-40	24.2	23.6
25	53b	Chernopolska	Swampy floodplain	20-40	61.4	67.6
26	58a	Chernopolska	Low floodplain	0-20	32.8	34.6
27	58b	Chernopolska	Low floodplain	20-40	28.0	28.1
Average value					169,6	158,7

3.4. Statistical analysis

The statistical analysis of the obtained data is performed with several brands of software. Microsoft Office Excel Software, version 2016 is used to calculate means, medians and standard deviations, as well as for plotting histograms. SPSS (IBM), version 25, is used to calculate the coefficient of determination and correlation. In this study, the Pearson correlation is applied. ArcMap (ArcGIS, ESRI) version 10.5 is used for classification of the soil samples.

4. RESULTS AND DISCUSSION

Concentrations of Cu in the soil samples are presented in series of maps (Figures 3 and 4) as proportional circles relative to the following threshold concentrations: “background” (16 mg/kg), maximum admissible concentration (150 mg/kg) and intervention value (500 mg/kg). The mean concentration (median) of the element in floodplain sediment of Europe according to the FOREGS Geochemical Atlas of Europe (Salminen et al., 2015) is accepted as a reference value (background). The other two soil quality standards are adopted from the Bulgarian legislation, namely the Regulation 3/2008 for the thresholds of harmful substances in soil. The latter thresholds consider the negative impact of hazardous chemical substances on the environment and human health. The values of the soil quality standards are pH-dependent and specific for several classes of land-use as follows: arable land; permanent grass plots; settlements, parks and sports grounds, and industrial sites. In this study, we used the values for soils in arable lands with pH interval 6.0-7.4, which are the most representative for the Danube wetlands of Bulgaria (Table 4).

Table 4. Maximum admissible concentration (MAC) for arable lands and intervention value for copper in soil

pH (H_2O)	MAC for arable lands (mg/kg)	Intervention value (mg/kg)
<6.0	80	500
6.0 – 7.4	150	500
>7.4	300	500

Source: Regulation 3/2008 for the thresholds of harmful substances in soil

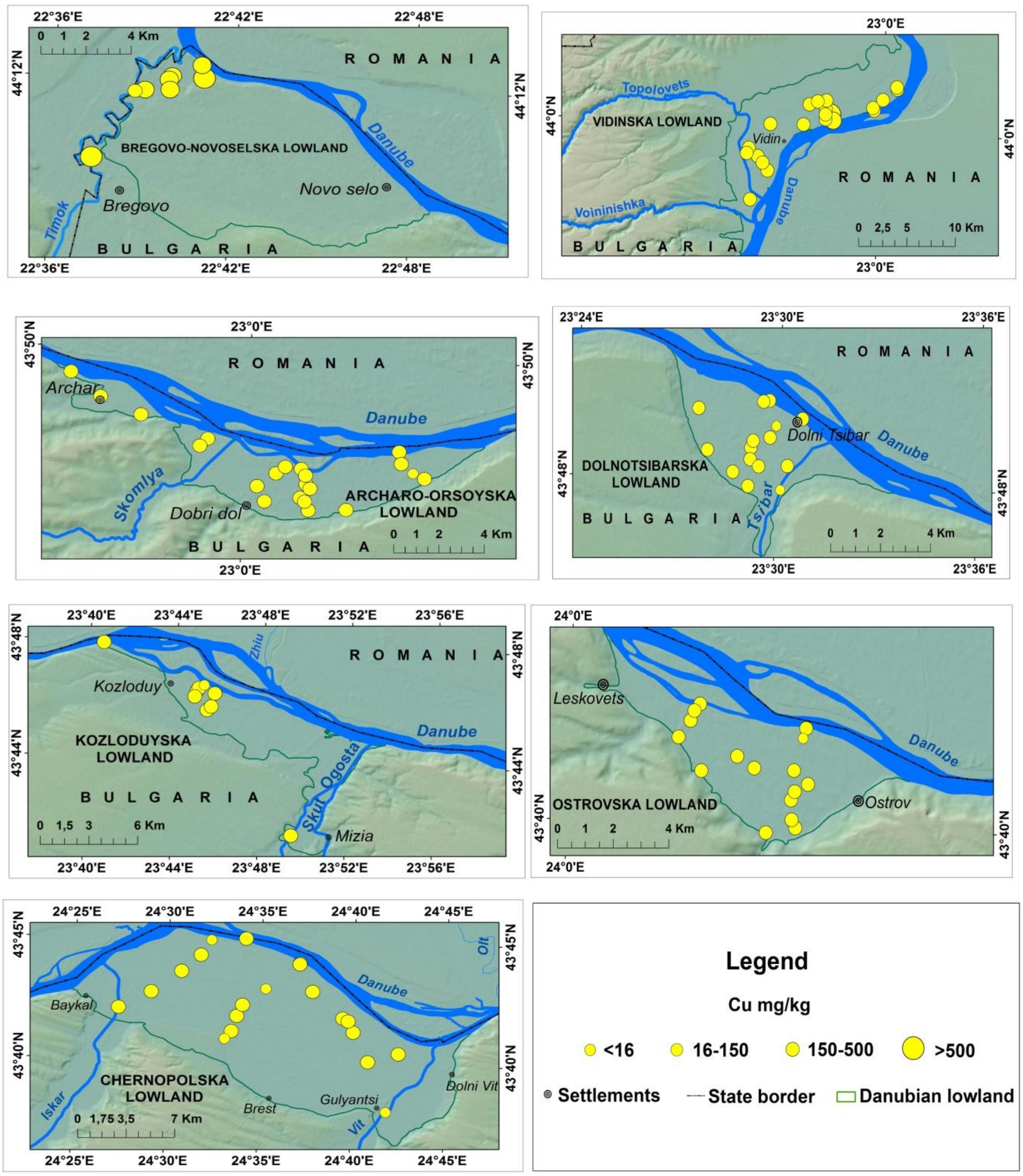

Figure 3. Copper distribution in the topsoil (0-20 cm; 0-25 cm) of the lowlands

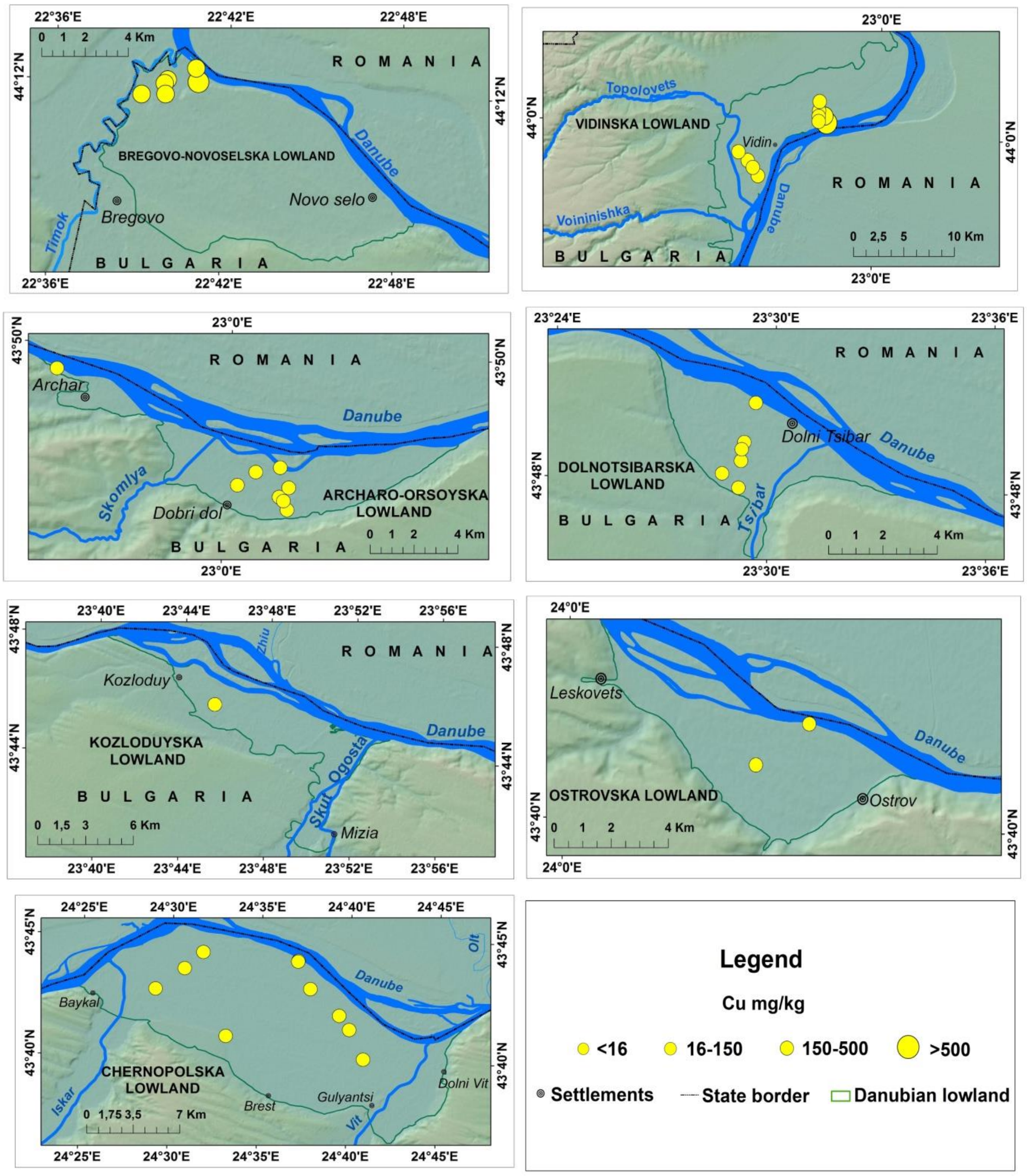

Figure 4. Copper distribution in the subsoil (20-40 cm) of the lowlands

The concentration of Cu in the collected soil samples ranges between 9.5 – 742.7 mg/kg with a mean (median) of 34.3 mg/kg and standard deviation 125.6 mg/kg (Table 5).

Table 5. Basic statistics of Cu concentration in soil, mg/kg

Set of samples	No	Mean	Median	Min	Max	Std. dev.	Samples >background[1], %	Samples >MAC[2], %	Samples >IntV[3], %
Topsoil	112	69.9	32.8	9.5	742.7	118.4	91.96	7.96	2.65
Subsoil	43	92.5	34.4	17.4	680.3	143.0	100	16.28	4.65
All samples	155	76.2	34.3	9.5	742.7	125.6	94.19	10.26	3.21

[1]Mean (median) for Cu concentrations in floodplain sediment in Europe (Salminen et al., 2015); [2]Maximum admissible level (Regulation 3, 2008); [3]Intervention value (Regulation 3/2008)

Samples of topsoil have similar average content (median) of Cu to that of the subsoil. The lowest and the highest extreme values are alike for the two depth intervals of soil, and the standard deviations for topsoil and subsoil differ by 17 %.

Almost all the samples (94 %) exceed the background reference value. Copper concentration is over the MAC threshold in nearly 10 % of the collected samples. Five of them (3%) are higher than the intervention value. Violations of the MAC threshold are more often for the subsoils compared to topsoils, the difference being more than 50%.

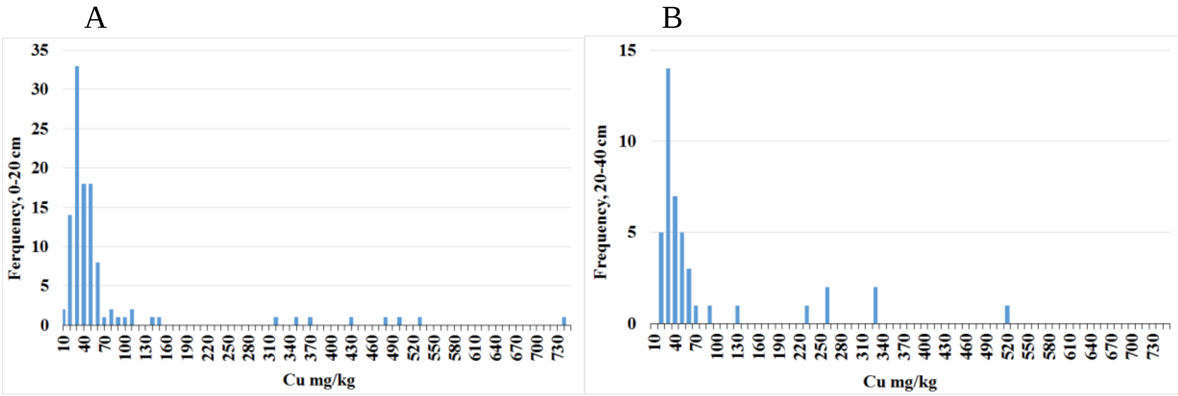

Figure 5. Histograms of Cu concentrations in the soil samples: A - topsoil (N 112); B - subsoil (N 43)

The histograms of the data for topsoil and subsoil show a similar distribution pattern with higher frequency for the lower values and a tail extended to the higher ones (Figure 5).

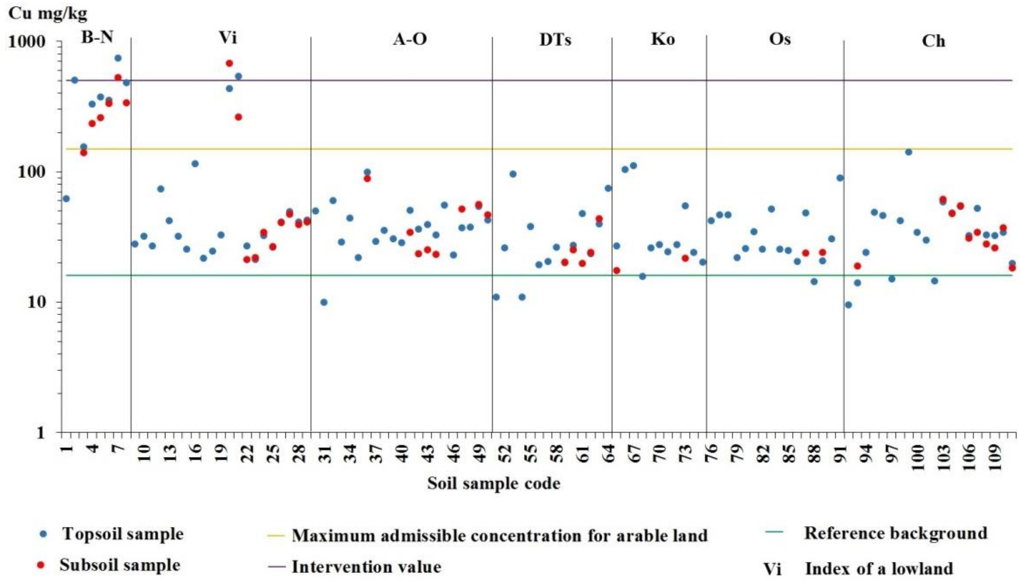

Figure 6. Concentration of copper in topsoil and subsoil in Danube's lowlands labelled with the same indexes as in Figure 1

Both histograms are markedly skewed to the right with coefficients of skewness 4.68 for topsoil and 5.07 for subsoil. The kurtosis is 23.88 and 29.76, respectively. These coefficients are higher than the indexes of normal distribution. According to Myers (1997), histograms of this type are usual for contaminated soil and groundwater (Ersoy et al., 2004).

The highest concentrations of Cu are registered in the soil of the valley of Timok River within the Bregovo-Novoselska Lowland, ranging between 61.9-742.7 mg/kg (Figure 6). All samples except one exceed the MAC threshold, and 21% of them have Cu above the intervention value. Similar contaminant levels are measured in some soil samples from the river banks of the lowland of Vidin, which are located nearly 60 km downstream of the confluence of the Timok into the Danube River. Contaminant levels in soil drop steadily below the MAC value from the river point downstream of the Archaro-Orsoyska Lowland. This pattern is very close to the findings of an earlier survey of trace metals content in the river channel and floodplain sediment of the Danube in the Bulgarian sector (Bird et al., 2010a).

Comparison between Cu concentrations in topsoil and subsoil shows significant positive correlation r (43) = 0.907 ($p < 0.001$). The linear regression between the two variables has a coefficient of determination R^2 of 0.82 (Table 6).

Table 6 Coefficient of determination (R square) in SPSS

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	0.907[a]	0.823	0.819	71.7505

[a] Predictors: (Constant), Cu mg/kg, topsoil

The slope of the regression line shows that similar changes in the contaminant content in the topsoil and subsoil can be expected from site to site, although the changes in the subsoil are likely to be slightly smaller (Figure 7).

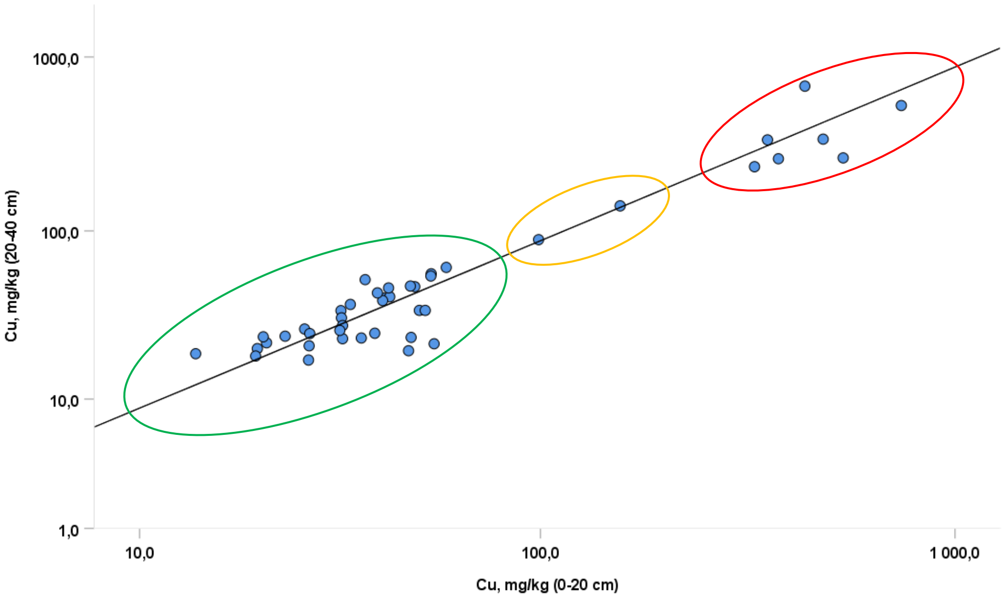

Figure 7. Copper in topsoil samples plotted against copper in subsoil samples

The statistical results could be interpreted as a similar spatial distribution pattern of Cu in the soil depth up to 40 cm within the studied Danube's wetlands. The likeness can be due to several reasons, the most important being the impact of the same group of factors across the study area and their small change for a long period of time. Since many samples are taken from arable lands, the compliance of the results for the two soil depths may be aided by the mixing of material in the ploughing process. The appearance of homogeneous surface sediment deposits with a thickness of at least 40 cm could be another reason for the similar Cu contents in the topsoil and subsoil samples at particular sites of sampling.

Three groups of soil sampling sites could be distinguished on the plot. The most contaminated points within the red ellipse are located in the Timok Valley. The two distinct dots in the yellow circle depict spots in the Vidin Lowland which are frequently flooded by the Danube. The sites in the other lowlands, including the floodplain around Vidin protected from inundation, are grouped at the beginning of the graph due to their lowest concentrations of copper. The three groups reflect the difference in the flooding regime of the wetlands and their distance from the mouth of the Timok River. The Timok River is identified as a significant source of Cu-contaminated sediment loads to the Danube by many studies (ICPDR, 2003; Bird et al., 2010c). The distribution of the soil sampling sites on the graph confirms these findings. Intensive soil contamination with Cu can be expected in all the areas between the Timok River and the town Vidin which are not protected from flooding. We witnessed the inundation of the common floodplain of the Danube and Timok rivers during the spring flood in 2013 when a colourful mixture of suspended sediments from both rivers was depositing in the backwaters. A similar accumulation of sediment-associated Cu occurs in the floodplain sections between the banks of the Danube and the dykes many kilometres downstream the main river. All islands in this stretch of Danube are affected by the same processes of contaminant deposition and should also be included in the category of the wetlands which are expected to be highly contaminated with copper.

Since the flooding regime has a significant impact for the dispersal of sediment-associated Cu across the Danube Floodplain, a comparison of the metal concentration in soil between sites with a different frequency of inundation from the Danube is performed. No one of the studied sites in the valley of Timok is completely protected from inundation and deposition of contaminated sediment because the area behind the Danube dyke is occasionally affected by spills directly from the Timok River. Therefore, the Timok Valley is not taken into account in the comparative analysis of data on flooded and non-flooded areas.

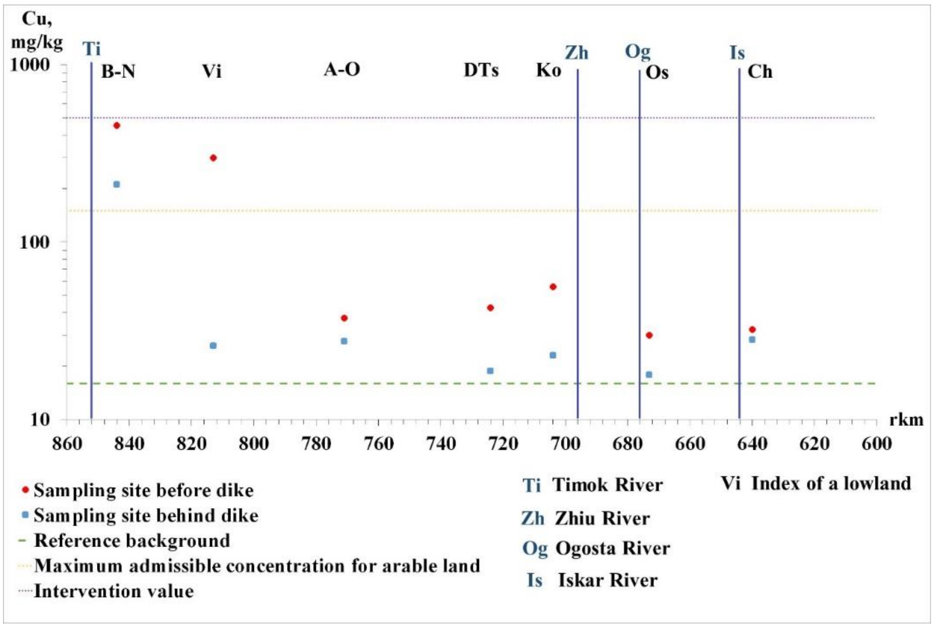

Figure 8. Average copper content in topsoil and subsoil in the individual Danube's lowlands labelled with the same indexes as in Figure 1

The average concentrations of the contaminant in soils of frequently inundated areas, and in soils protected from flooding are calculated. The results show distinctly elevated contents of Cu in the floodplain sections between the dykes and the Danube banks compared with the areas behind the levees for all investigated lowlands (Figure 8). One possible explanation is the fact that all these lowlands except Timok Valley are well protected against flooding from Danube and accumulation of sediment-associated Cu behind the dykes is rather incidental. It could be suggested that the major part of the Cu load was received in the wetlands before the construction of the flood protection facilities in the late 40s of the 20th century. This period precedes the peak of the trace metal contamination in the Lower Danube (Winkels et al., 1998) and the rate of Cu accumulation was presumably not so high. However, the copper levels in the flood-protected areas show a slightly decreasing trend with increasing the distance from the Timok's mouth. This tendency probably reflects the impact of the tributary river on the Danube floodplain at the very beginning of the last century.

The biggest difference between Cu concentrations in inundated and protected lands is found for the lowland of Vidin due to its proximity to the confluence of the Timok River in the Danube. The pollutant levels before and behind the dykes are much closer for the rest of the wetlands downstream of Vidin, indicating the dampening impact of the Danube tributary due to dilution of the contaminated sediments along the main river. The almost parallel change in the average concentrations of copper in front and behind the dykes along the river shows the impact of the same factors on the formation of the metal concentrations in the soils of the Danube lowlands in the periods before the construction of the dykes and after that.

5. CONCLUSIONS

Copper exceeds the maximum admissible concentration (150 mg/kg) in 10% of the measured soil samples, and it could be considered a pollutant of concern in the Bulgarian lowlands along the Danube. The soil contamination with copper is the most intensive in the common floodplain of the Timok River and Danube as well as in the frequently flooded areas in the lowland of Vidin. The contaminant concentrations in soil decrease with increasing the distance from the confluence of the Timok River in the Danube. The results indicate that the Timok River is probably the main supplier of copper to the floodplain of the Danube in the section between the rivers of Timok and Vit. Results did not show a significant difference between Cu levels in topsoil (0-20 and 0-25 cm) and subsoil (20-40 cm). Spatial distribution patterns of the element in all the studied lowlands seem to be similar for both sampling depths, considering the significant positive correlation of Cu concentrations in topsoil and subsoil. The dykes constructed before the peak of the industrial contamination of the Lower Danube restrain the deposition of sediment-associated Cu in most of the wetlands, thus avoiding more intensive soil pollution.

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