Original scientific paper
Оригиналан научни рад
UDC: 504.05:631.4(497.6RS)
DOI: 10.7251/AGREN1601019P

University of Banjaluka, Faculty of Agriculture
Agro-knowledge Journal

State of Heavy Metals Pollution of Flooded Agricultural Land in the North Part of Republic of Srpska

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Abstract

This paper presents the results of the research of soil contamination in flooded area located at the confluence of Bosna and Sava rivers. The sampling was performed according to a network of points Etrs89 reference European Network based on grid points of 500 m x 500 m. The total number of soil samples was 31 and 13 samples of sediment-mud. In the soil samples and sediment-mud samples various parameters were analyzed: pH H2O and 1 M KCl, humus (method by Tjurin), and the readily available phosphorus and potassium (AL method). The interpretation of total content of heavy metals in the soil was conducted according to Dutch Soil Remediation Circular (2009). The samples were analyzed for the total content of heavy metals: Pb, Cd, Cr, Ni, Zn, Cu (aqua regia digestion, AAS) and the elevated concentrations of Ni. However, Ni content in mud was from 240.5 mg/kg to 294.5 mg/kg, in soil it was from 128.9 mg/kg to 452.1 mg/kg. All mud samples were alkaline, and 79% of soil samples were alkaline and of neutral reaction. The analysis indicated that the flood in May 2014 was not caused by soil contamination with heavy metals, which however contributed to the increase of the overall content of these elements in the soil.

Key words: flood, contamination, soil, mud, heavy metals

Introduction

In mid-May 2014, Bosnia and Herzegovina suffered major floods after the rainfalls that exceeded the record of the last 120 years, ever since the measurements had been made. During the period of just 48 hours (13-14, May 2014) about 150 l/m^2 fell in some areas of BiH (EC, UN, WBG, 2014). According to the national authorities, 60 towns and cities were severely or slightly affected, occupying the area of a total of approximately 10.000 km^2 - 13.000 km^2. There were over 3000 landslides, which, in addition to all other damages, moved mines and warning signs to unknown locations. Large areas of fertile land were flooded and planted crops destroyed. The most affected areas were in the mouths of the rivers that flow into the Sava River (Vrbas, Bosna and Drina). The Sava River broke through an embankment near Bijeljina and flooded Semberija, affecting 10.000 ha of agricultural land (ECHO Joint Assessment Report, 2014*)*. The water stayed there for 2 to 30 days.

This paper presents the results of the research of soil contamination in the flooded area of Šamac municipality, located at the confluence of Bosna and Sava rivers. The Bosna River (271 km length, 10.457 km^2 catchment area) flows through the once industrially most developed areas of Bosnia and Herzegovina (Zenica - ironworks, Kakanj - coal mines, power plants, Maglaj – cellulose and paper factory, Doboj, Modriča - oil refinery etc). The largest part of industrial plants, as well as the settlements, are located along the Bosna river, and there was a threat of sediment sludge deposited in flooded areas containing hazardous and harmful substances in concentrations which are hazardous to human and animal health. The layers (soil, sludge) from the upper flows of Bosna River are deposited in the area of 2845 ha of flooded area, which is located at the confluence of Bosnia River to Sava. The duration of the flood wave was up to 23 days. The maximum height of water in flooded areas was 3 m. The layer thickness was up to 1m.

Material and Methods

The locations for sampling were determined on the basis of the EU reference network grid points of 500x500. The sampling was performed according to a network of points ETRS89 references European Network grid points of 500 m x 500 m. Depending on the duration of the flooding, the sampling was made on the network of: 2 km x 2 km – in the areas with shorter periods of flooding (up to 4 days); 1 km x 1 km – in the areas with longer periods of flooding (4 - 15 days); 500 m x 500 m – in the areas with long periods of flooding > 15 days.

The sampling was made in addition to the existing network, and only in cases of extreme danger from contamination in the field and the area itself, it was not included into the reference network points. The following samples were taken from the selected areas: sediment-mud if there was any and with the thickness ranging from over 0.5 cm and samples of arable soil layer (0-25 cm).

The sampling locations were found by GPS. The samples of soil and sludge were taken from the area of a circle with radius (r) of 15 m. The average sample consisted of 13 individual samples, 12 individual samples were taken from the intersections of main directions (N, E, S and W) and the diameter of the concentric circles r = 2.5m; r = 10m and r = 15m. The 13^{th} sample was taken from the center of the circle (Predić et al, 2013).

All surfaces were geo positioned. Photos were taken, as well as basic information about the plot, the length and type of flooding, crop conditions and damage. 31 soil samples and 13 samples of sludge were taken. In the soil samples and sediment-mud samples various parameters were analyzed: pH H_2O and 1 M KCl, humus (method by Tjurin), the readily available phosphorus and potassium (AL method), the total content of heavy metals Cd, Pb, Ni, Cr, Cu, Zn (aqua regia digestion, AAS). Interpretation of total content of heavy metals in the soil was conducted according to Dutch Soil Remediation Circular (2009).

Results and Discussion

The Bosna River at the confluence of the Sava River in May 2014 flooded an area of 2845 hectares, of which 1942 ha (68%) is agricultural land, and 903 ha (32%) of non-agricultural land. The flooding period was from 2 to 22 days. The thickness of the sediment-mud after the runoff of water was from 0.5 to 10 cm.

The results of basic parameters of soil fertility (Table 1) indicate that it is the soil of different levels of fertility, which is related to the land use and soil type. In the sediment-mud humus content varies from 1.3 to 4%, while the content of easily available phosphorus and potassium varies within the limits of low and medium *(phosphorus*) to very good content (*potassium).* The reaction (pH value) in all samples of sediment-mud is alkaline (pH 7.8 -8.5 in H_2O). The soil samples reaction is in the range of slightly acid (pH of 6.5 in H_2O) to alkaline (8.4 pH in H_2O) which is clearly related to the existing soil types.

Along the Bosna river and Sava river there are Calcaric Fluvisols (*FAO Soil Classification)*, and the central parts of floodplains are dominated by Eutric Fluvisols with smaller areas of Mollic Gleysols.

Tab.1. The results of analysis of main parameters of sediment-mud and soil fertility
Резултати анализе основних параметара плодности у муљу и земљишту

Sample *Узорак*	pH		Humus	mg/100g	
	H_2O	KCl	%	P_2O_5	K_2O
Sediment-mud *Седимент-муљ*	7.80 – 8.34	7.00 – 7.50	1.3 – 4.0	4.5 – 12.7	12.0 – 39.4
average	8.11	7.27	2.41	7.53	23.18
std	0.15	0.12	0.81	2.35	7.84
rsd	1.86	1.71	33.63	31.25	33.82
Soil / *Земљиште*	6.03 – 8.25	4.60 – 7.49	1.1 – 11.2	1.2 – 43.1	10.9 – 62.9
average	7.76	6.86	2.17	14.42	21.47
std	0.56	0.66	0.58	11.41	10.27
rsd	7.18	9.61	26.77	79.14	47.83

Tab. 2. The results of total content of heavy metals in sediment-mud and soil
Резултати укупног садржаја тешких метала у узорцима муља и земљишта

Sample *Узорак*	Pb mg/kg	Cd mg/kg	Cr mg/kg	Ni mg/kg	Zn mg/kg	Cu mg/kg
Sediment Iv *Седимент Iv*	18.5 - 34.0	0.05 - 0.3	18.3 - 57.4	240.5-294.5	102.3-171.4	41.5 - 58.2
average	26.9	0.1	36.6	270.9	150.6	49.6
std	4.8	0.1	13.7	15.6	21.1	5.9
rsd	16.6	110.3	37.3	5.8	14.0	11.8
Soil Iv *Земљиште Iv*	10.8 - 70.0	0.05 - 1.3	7.5 - 76.3	128.9-452.1	59.7 - 276.2	25.7 - 85.3
average	32.2	0.1	48.2	280.7	117.4	44.4
std	14.9	0.2	16.6	53.5	40.0	13.5
rsd	46.5	198.7	34.5	19.1	34.1	30.4
Increased content *Повећан садржај*	85 - 150	0.8 – 5.0	130 - 250	35 - 100	140 - 500	36 - 100
Contaminated *Контаминирано*	> 150	> 5	> 250	> 100	> 500	> 100

The total content of lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn) and copper (Cu) in sediment-mud and soil (Table 2) was within expected concentration according to the Dutch Soil Remediation Circular (2009).

The results given above (Table 2) indicate that the content of total Nickel (Ni) in all soil and sediment-mud samples is above 100 mg/kg, which

makes these soils contaminated by Ni. The content of Ni in tested sediment-mud samples is equal and it is within the intervals from 240.5 mg/kg to 294.5 mg/kg. The content of Ni in arable soil layers is within the wider range from 128.9 mg/kg to 298 mg/kg, and in one sample it was even 452.1 mg/kg (location 8, Tab.3).

Tab. 3. The total content of Ni, Zn and Cu in sediment-mud and soil at the same locations
Садржај укупног Ni, Zn *и* Cu *у муљу и земљишту на истим локацијама*

Location *Локација*	Ni mg/kg		Zn mg/kg		Cu mg/kg	
	Sediment- mud *Седимент - муљ*	Soil	Sediment- mud *Седимент - муљ*	Soil	Sediment- mud *Седимент - муљ*	Soil
5	274.9	251.8	154.3	106.9	50.7	46.3
8	294.5	452.1	155.2	183.0	43.2	85.3
9	276.2	236.8	163.8	91.9	57.9	41.4
10	241.0	128.9	102.3	73.7	41.5	29.7
16	280.8	238.0	157.4	80.2	51.7	36.5
18	281.2	242.7	169.8	84.9	57.3	39.4
25	275.6	269.8	143.9	94.1	42.0	33.3
27	271.6	248.7	150.1	73.6	46.4	37.7
28	267.4	247.8	101.4	79.3	45.7	38.2
75	284.3	249.4	171.4	85.9	58.2	42.0
77	261.8	253.3	155.8	92.5	51.7	42.4

In order to determine if it is an isolated case of contamination of wider area around the location 8, there have been two more samples taken from the network of 500 m x 500 m. The analysis results have shown that this is an isolated case of contamination because the content of total Ni in the topsoil, at one location totalled 294.7 mi/kg, and at another location 268.9 mg/kg, which is within the limits laid down by Ni in most soil samples. In addition, it was noted that in the previous floods, the location 8 had higher layer of sediments deposited with thickness ranging (thick) 1 - 2 m, which after the floods was incorporated into an existing plot. For this reason, when taking samples from the arable layer/topsoil (0 - 25cm) in reality (in principle) the deposited material is taken against the sediment that is mixed with a small proportion of soil from the existing plot. Such a situation with the location 8 explains the illogical results obtained in comparison with the results from other locations i.e. that the concentration of nickel (Ni), zinc (Zn) and copper (Cu) are higher in the soil than in the sediment.

Although the content of Nickel determined within the entire area is above 100 mg/kg, the soils along Bosna and Sava rivers contain higher

concentrations of Nickel than the soils of other flooded areas. Table 3 illustrates the results of the total content of Ni, Zn and Cu from 13 locations from which the samples of soil and sediment were taken.

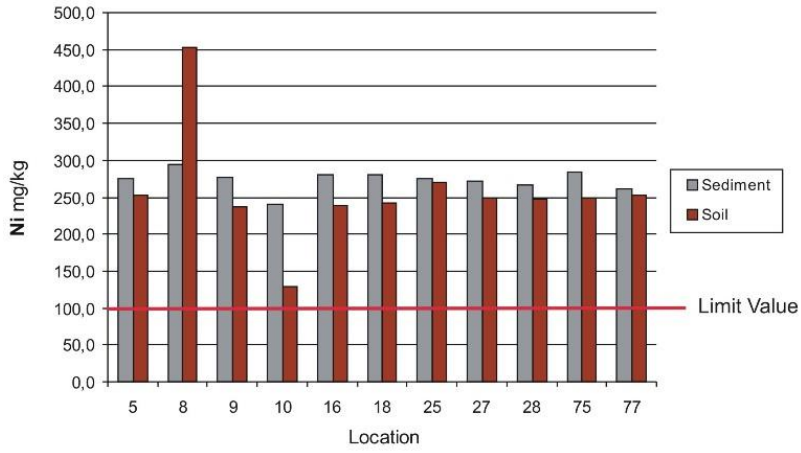

Fig.1. Content of total Ni in sediment-mud and arable topsoil (0 - 30cm) in flooded area
Садржај укупног Ni *у муљу и плављеном пољопривредном земљишту (0-30цм)*

Except for the location number 8 which was explained above, the Ni (Fig. 1.), Zn and Cu content in the sediment-mud is greater than the contents of these elements in the top layers of soil.

The data of vertical and horizontal distribution of Ni suggests that the increased nickel content in the soil of natural origin is a result of flooding of these areas and deposition drifts containing serpentine minerals with natural sites from the upper stream of the Bosna River. This fact is confirmed by the research in the same period (May 2014) conducted by the Federal Institute for Agropedology Sarajevo. In samples of the sludge in flooded areas in the middle course of the Bosna river (the locality of Zavidovići) high concentrations of total Ni were found at a maximum of 752 mgNi/kg (Bukalo et al 2014). According to geological data on soils (Mojičević et al., 1976), in the mid flow of the Bosna River and its tributaries, there are serpentinite and peridotite layers.

These minerals and rocks are the main carriers of nickel and chromium in nature (Massoura et al., 2006; Reimann et al., 2014).

Similar results were achieved by Novkovic et al. (2008) in the researches of Ni content in agricultural land in the lower valley of the Vrbas River. The valley of the Vrbas River runs parallel to the Bosna River Valley (about 50-70 km west). The nickel content within the flooded area of the Sava

river basin is lower and is generally in the range of 50 to 100 mg/kg (Ministry of Agriculture and Environment Protection of the Republic of Serbia, 2014). All samples of sediment-mud were of alkaline reaction, and 84% of soil samples is alkaline, slightly alkaline and neutral reaction which are the conditions in which heavy metals are in the insoluble and hardly soluble forms so it can be said that the level of potential risk from the adoption of increased concentrations of Ni, Zn and Cu by the root system of cultivated plants, is low. However, in soil samples of poor acidic reaction there is a possibility that, in certain circumstances, a longer retention of surface water or high groundwater levels create reducing conditions which can lead to conversion to a solution of one part of heavy metals and their adoption by the root system of plants.

Conclusion

Floods have affected a large area of land with plenty of water, which was brought silt (a potential source of pollution) deployed over a large area in a layer of a few millimetres up to 10 cm.

The content of the tested heavy metals in sediment-mud is slightly different from the contents of these elements in the topsoil so that we can claim that the flood in May 2014 did not pollute the land with hazardous and noxious substances, but in some areas it caused a slight increase of the level of some elements in the soil.

The data of vertical and horizontal distribution of Ni suggests an increased nickel content in the soil of natural origin as a result of flooding of these areas and deposition drifts containing serpentine minerals with natural sites from the upper stream of the Bosna River.

Soil pH is alkaline in 85% of samples, as well as in all samples of sediment-mud, as this is the condition in which heavy metals (nickel) are insoluble forms, so that the level of potential risk from the adoption of higher concentrations of nickel by the root system of cultivated plants is very low.

The flood in May 2014 actualized the necessity of establishing a system of permanent monitoring of agricultural land through the establishment of permanent stations for monitoring of agricultural land following the European principles, but in line with our circumstances and the economic situation.

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Стање загађења плављеног пољопривредног земљишта тешким металима у сјеверном дијелу Републике Српске

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Сажетак

У овом раду су представљени резултати истраживања контаминације земљишта у плављеним подручјима на ушћу ријека Босне и Саве. Узорковање земљишта и муља је извршено по Европској референтној мрежи тачака 500м x 500м (Etrs89 references European Network). Укупно је узет 31 узорак земљишта и 13 узорака седимената - муља. У узорцима је анализиран pH у води и 1 M KCl, садржај хумуса (метода по Тјурину) и лако приступачни фосфор и калијум (AL метода). Интерпретација укупног садржаја тешких метала у земљишту извршена је према Dutch Soil Remediation Circular (2009). Узорци су тестирани на садржај тешких метала Pb, Cd, Cr, Ni, Zn, Cu (aqua regia метод, AAS) а у узорцима су идентификоване повишене концентрације Ni. Садржај Ni у муљу је износио од 240,5 мг/кг до 294,5 мг/кг, а у земљишту од 128,9 мг/кг до 452,1 мг/кг. Сви узорци муља су алкалне, а 79 % узорака земљишта су алкалне и неутралне реакције. Истраживање је показало да поплава у мају 2014. године није била узрок контаминације земљишта тешким металима, али је допринијела повећању укупног садржаја тешких метала у земљишту.

Кључне ријечи: поплава, загађење, земљиште, муљ, тешки метали

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Received: September 13, 2016
Accepted: December 08, 2016