International Journal for Research in Applied Sciences and Biotechnology

ISSN: 2349-8889
Volume-7, Issue-3 (May 2020)

www.ijrasb.com

https://doi.org/10.31033/ijrasb.7.3.2

Influence of the Spreča River Flooding on Individual Physicochemical Parameters of Soil

Melisa Ahmetović[1], Husejin Keran[2], Indira Šestan[3], Amra Odobašić[4], Asmira Čanić[5], Halid Junuzović[6] and Nisveta Hrnjić[7]

[1]Sen. Asst., Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

[2]Full Prof. Dr., Department of Physical Chemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

[3]Asst. Prof. Dr., Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

[4]Full Prof. Dr., Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

[5]Lab. Asst., Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

[6]Sen. Asst., Department of Analytical Chemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

[7]Institute of Public Health of the Central Bosnian Canton, Travnik, BOSNIA & HERZEGOVINA

[1]Corresponding Author: melisa.ahmetovic@untz.ba

ABSTRACT

During the last few years, we have witnessed more frequent floods affecting the northeastern part of Bosnia and Herzegovina, the valley of the Spreča River. Flooded soil has undergone various changes, in terms of numerous deficiencies and heavy metal contamination, where such soil represents a great danger both for people and animals. Therefore, in this paper the physicochemical analysis of soil and degree of pollution is determined. The aim of soil sampling and analysis is to determine its status after water withdrawal, in terms of nutrient supply, and to determine possible chemical pollution. Based on the results obtained, agricultural producers will receive recommendations regarding restoration of production on these areas, the choice of cultivated culture, corrective measures or remediation of these areas.

As part of the analysis, hygroscopic moisture, acid-base soil status, oxidoreduction potential, organic matter content, carbonate content and heavy metals content were determined. Based on the performed analyzes, the soil was shown to be of neutral character (determined in 1M KCl), and weakly alkaline (determined in distilled H_2O) with predominantly reducing condition prevailing in the soil. The conducted analyzes have shown that the soil is very poor in humus, and that the heavy metals content is within the limit values determined by the Rulebook on Determination of Allowed Quantities of Harmful and Dangerous Substances in Soil and Method of Testing there of ("Official Gazette of Federation of Bosnia and Herzegovina", number 52/09). Therefore, from the aspect of the pollution degree, the soil from this plot belongs to the first class when it comes to iron, manganese, cadmium and lead, to the second class when it comes to zinc, and the third class when it comes to copper.

Keywords**--** heavy metals, physicochemical analysis, soil, pollution degree

I. INTRODUCTION

Water is one of the most important life factors of all living beings. Its lack causes the cessation of life functions of the organism. Shortage in plant production, as well as excess water, is undesirable because it causes a decrease in yield. In our agricultural production we are experiencing water shortages, but also in the last few years we are experiencing flood surpluses. Due to the flooding of agricultural area, unfavorable conditions are created, undesirable changes of mineral substances occur, concentrations of ferrous and sulfur ions increase, as well as increased concentrations of heavy metal ions. [1] All these complex phenomena manifest in different strengths and affect plants themselves depending on their resistance.

The Spreča River is the largest watercourse in Tuzla Canton, with the largest agricultural areas and industrial complexes. It is the largest recipient of most wastewater from Tuzla Canton, and supplies water to the largest artificial hydro-reservoir in Bosnia and Herzegovina, Modrac. At the time of heavy rainfall occurring almost every year in spring and fall, the Spreča River floods the agricultural land in its immediate vicinity, which has an impact on both biodiversity and natural values, as well as on the quality of soil affected. As the riverbed of the Spreča River is not regulated (neither its cleaning nor deepening was performed), we witness that the flood covers the coastal area downstream of the accumulation Modrac, where water after intensive release from the dam of the Modrac lake floods larger areas and remains on agricultural areas even after the river returns to its trough.

Taking care of the interactions between sustainable agriculture, environmental protection and

ISSN: 2349-8889
Volume-7, Issue-3 (May 2020)

https://doi.org/10.31033/ijrasb.7.3.2

anthropogenic impact on ecosystems requires the determination of heavy metal concentrations in agricultural land that was directly affected by floodwaters, which were the carriers of various pollutants of anthropogenic origin. Therefore, the aim of this paper is to determine the contamination of agricultural land, as well as how to determine the actual condition of soil quality and make further recommendations regarding the use of the land. To understand the connection between the processes leading to environmental protection, sustainable agriculture and anthropogenic impact on ecosystems along the Spreča River, it is necessary to determine the heavy metal concentrations in agricultural land in flooded areas, as heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem by: direct ingestion or contact with contaminated soil, food chain (soil-plant-human or soil-plant-animal-human), drinking contaminated groundwater, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity [2]. Therefore, pollution risk assessment is an effective way to solve the issue of contamination in a cost-effective way while preserving public health and ecosystems [3].

As an important factor in the testing of heavy metals, pH reaction and humus were analyzed, and besides pH reaction of soil and humus, carbonate content and oxidoreduction potential were made.

II. EXPERIMENTAL PART

2.1. Material

The agricultural land after the flood, in the lower basin of the Spreča River, at the site in Brijesnica Velika, at a depth of 30 cm, was taken as the material for analysis. The soil was cleaned of other impurities (pieces of glass, roots) and then left to air dry for seven days. After air drying, the sample was ground in a mortar and prepared for analysis.

2.2. Methods

Within the framework of the physicochemical analyzes, the following parameters were tested: hygroscopic moisture content, acid-base status, organic matter content, oxidoreduction potential, carbonate content and heavy metals content.

Hygroscopic moisture content was determined by the gravimetric method and calculated according to the following relation:

$$\text{hygroscopic moisture content } (\%) = \frac{m_2 - m_3}{m_2 - m_1} \text{x}100 \quad (1)$$

m_1- mass of the empty glass container;
m_2- mass of the glass container with soil sample before drying;
m_3- mass of the glass container with soil sample after drying.

The acid-base status was determined by the electrochemical method, measured on a pH meter Mettler Toledo 220. The pH value of the soil was measured in H_2O (active acidity) as well as in 1 M KCl (substitution acidity).

Organic matter content was determined by the Tyurin method (bichromate method), and in addition to the analysis of the soil sample, a blind test was performed whereby the organic matter content was calculated according to the following relation:

$$\% \text{ humus} = \frac{(a-b) \cdot 0{,}0005172 \cdot 100}{m} \quad (2)$$

a- volume of Mohr salt (ml) used for blank titration x 0.1x10;
b- volume of Mohr salt (ml) used for soil sample titration x 0.1x10;
m- mass of soil sample.

Oxidoreduction potential was determined in the solution of the analyzed soil and distilled water after stirring for 30 minutes, after which the electrode potential was measured in mV and the rH value was calculated according to the following relation:

$$rH = \frac{E}{28.9} + 2 \text{ pH} \quad (3)$$

Carbonate content was determined by the titrimetric method, when the soil sample was dissolved in HCl, heated and cooked until carbonate was destroyed and then titrated with sodium hydroxide solution (0.1 M NaOH) with methyl orange as an indicator.

$$\% \text{ CaCO}_3 = \frac{(100-a) \cdot 0.005 \cdot 100}{\text{g of soil}} \quad (4)$$

a- ml of used base (0.1 M NaOH);
0.005= g $CaCO_3$ which binds 1 ml 0.1 M HCl.

Concentration of essential and toxic heavy metals was determined after the soil sample was overflowed with aqua regia (3:1), and then heated to boiling and filtered through filter paper-black paper, after which the concentrations of Fe, Mn, Pb, Cd and Zn were determined from the filtrate at Perkin Elmer atomic adsorption spectrophotometer.

2.3 *Determining the pollution degree of soil*

Determining the pollution degree of soil contamination is a proven way to determine the soil quality, respectively based on the established actual state of the soil, it is possible to provide remediation measures. In many European countries, studies are being conducted on the content of toxic metals in soil, with the aim of managing its flow through the ecosystem and implementing safeguards. [4]

ISSN: 2349-8889
Volume-7, Issue-3 (May 2020)

https://doi.org/10.31033/ijrasb.7.3.2

The usual approach in determining the degree of soil contamination by heavy metals is to determine how much soil is affected by them (natural or anthropogenic). For soil used for agricultural purposes, it is necessary to determine the pollution degree (PD) in order to categorize the soil present. [5] The pollution degree is calculated from the following relation:

$$PD\ (\%) = \left(\frac{C_{m.sample}}{C_{lim.value}}\right) x\ 100 \quad (5)$$

C $_{m.sample}$ – metal concentration in the test sample (mg/kg)
C $_{lim.value}$ - limit value of metal concentration in soil (mg/kg).

Based on the obtained values, the classification of soil for agricultural production is made (Table 1).

Table 1: Classification of soil for agricultural production

Class	Class definition
I	PD<25 %, clean soil, suitable for agricultural production
II	PD=25-50 % soil of increased pollution, cultivation of plants with the necessary protection against the heavy metals imission
III	PD=50-100 % soil of high pollution, cultivation of plants with increased protection measures against heavy metals imission
IV	PD=100-200% polluted soil and unsuitable for cultivation of plants, necessary remedial measures
V	PD>220% extremely polluted soil, ban on the cultivation of plants for human and animal use, necessary to perform comprehensive remediation and recultivation measures.

III. RESULTS AND DISCUSSION

Physicochemical analysis was performed on the soil sample, including the pH reaction of the soil, humus content, oxidoreduction potential, moisture content, carbonate content and heavy metals content. Based on the obtained parameters, the pollution degree (PD) was determined and further measures are recommended.

3.1 Moisture content

The moisture content in the surface layers of the soil is an important parameter in agriculture [6]. Soil moisture is a crucial variable in governing the water and heat among land surface and atmosphere through plant transpiration and soil evaporation [7]. Moisture content determined by the gravimetric method was 4.16%. This moisture content can be considered relatively small, since the soil does not retain a large amount of water in its structure and will not cause the particles to adhere and change the granulation.

3.2 pH value

Soil pH value is probably the most informative measurement that can be made to determine soil characteristics. Soil pH values near two to three indicate the presence of free mineral acid. In soils with higher pH values, hydrolysis of basic cations tends to maintain a stable pH with dilution. A major factor influencing pH soil value is the salt content of the soil solution. [8]

According to the obtained values, the pH value of the soil determined in H_2O was 7.60, while the pH value determined in 1 M KCl was 6.79. Based on the table 2 it has been determined that the soil is of neutral character, which favors the cultivation of almost all field crops.

Table 2: Soil pH value determined in 1 M KCl

Reaction	pH
Very acidic	< 4.5
Acidic	4.5 – 5.5
Weakly acidic	5.5 – 6.5
Neutral	6.5 – 7.2
Weakly alkaline	7.2 – 8
Alkaline	8 – 9
Very alkaline	>9

The slightly higher pH value determined in distilled water is probably caused by the waste alkaline sludge resulting from the blowdown of boiler plants, delamination of cauldron machines, leachates from slag and ash landfills, as well as other sludge streams which arrive through water and remain on the soil after the flood, which have carbonate and which give the soil a higher pH value.

3.3 Organic matter content (humus)

Organic matter content in the soil is a general indicator of soil fertility. The Tyurin method determined the humus content of 0.513 % in the analyzed sample, i.e. <1, which by Gračanin classification indicates that the soil is poor in humus (Table 3), indicating that the humus was probably washed out during the flood, whereby is covered with sediment of different granulation.

Table 3: Limit values for humus content in soil (Method by Gračanin)

Soil supply	Humus (%)
Very poor in humus soil	<1
Poor in humus soil	1-3
Enough humus soil	3-5
Rich in humus soil	5-10
Extremely rich in humus soil	>10

Organic matter on agricultural areas in the flooded zone is of great importance for many processes

ISSN: 2349-8889
Volume-7, Issue-3 (May 2020)
https://doi.org/10.31033/ijrasb.7.3.2

that take place in the surface layer of soil and its characteristics. Naturally, organic matter is mineralized, which releases the biogenic elements that the plant adopts and incorporates into its structure during the growth and development phase. Therefore, defiance of organic matter in the soil leads to decreased activity of microorganisms, which reduces production of ammonia and hydrogen sulphide, i.e. their oxidation is reduced to strong acids which would lower the pH value.

3.4. Oxidoreduction potential

The soil analysis showed that predominantly reducing conditions prevailed in the soil, since the calculated rH value was less than <20, i.e. -17.31 mV. (Table 4.)

Table 4: rH value of the soil

rH	Type of process
28-34	Oxidation conditions
22-25	Reduction conditions
<20	Dominant reduction conditions

According to many researches, it is assumed that the initial rapid drop of Eh dried soil, which occurs immediately after the flood, causes H_2 gas to emerge as a decomposition product in the soil, with this H_2 formation difficult to experimentally prove due to its small amount. [9]

3.5 Carbonate content

Carbonate (C) is a natural constituent of many soils, occurring as weakly soluble, alkaline-earth carbonates, mainly as $CaCO_3$ (calcite) or as dolomite [10]. The pH of carbonate soils is mainly controlled by the amount of calcium carbonate in the soil profile and often ranges 7.5 to 8.2. Existence or absence of calcium carbonate has an important effect on soil pH and thus controls a number of chemical reactions in relation to nutrient availability for plants and mobility of these elements in soil [11]. The distribution and amount of carbonates influence soil fertility. The increase of calcium carbonate in soil usually leads to many problems related to fertilization and nutrient availability. The extent and rate affect the amount of carbonates in the soil, the chemical and physical nature of the carbonates (e.g. particle size and mineralogy) [12, 13].

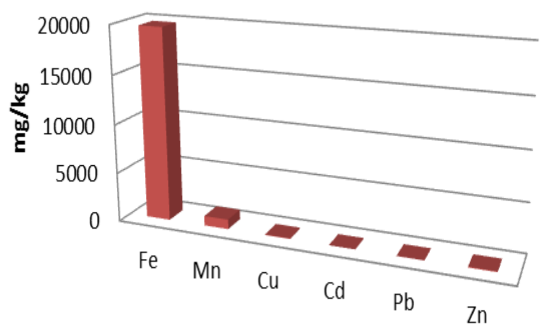
Carbonate content determined by the titrimetric method was 82.5 %, which shows that the analyzed soil contains high value of $CaCO_3$, which justifies the measured pH in distilled H_2O which was 7.60. Such a high carbonate value indicates that the sediment and sludge that flow through the water remains in the soil.

3.6 Heavy metals content

The conducted soil analysis showed the highest concentration of Fe in the soil (19,719. 5 mg /kg) followed by manganese (985.52 mg/kg). Manganese content is significantly lower than iron, as much as 20 times lower. Given that in Regulations for determination of permissible levels of harmful and dangerous substances in soil no maximum permissible concentrations of Fe and Mn in soil are prescribed, these values of Fe and Mn are considered to be essential elements, with no real risk of toxic effects on agricultural products and food of plant origin.

The content of Pb was 14.1 mg/kg, which according to the Rulebook on Determination of Allowed Quantities of Harmful and Dangerous Substances in Soil and Method of Testing thereof ("Official Gazette of Federation of Bosnia and Herzegovina", number 52/09) within the limit values for silt-loam soil. The content of Zn and Cu is also within the limit values for silt loam soil, where according to the Rulebook on determination of allowed quantities of harmful and dangerous substances in soil, the limit values for Cu are 65 mg/kg and for Zn 150 mg/kg.

Cd content was not found in the analyzed soil.



	Fe	Mn	Cu	Cd	Pb	Zn
mg/kg	19719,5	985,52	54,7	0	14,1	73,67

Figure 1: Presentation of total concentrations of heavy metals in soil

3.7. The pollution degree (PD)

Soil pollution is defined as the accumulation in the soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease causing agents, which have adverse effects on plant growth and animal health [14]. There are many different ways in which soil can be contaminated, such as: landfill; discharge of industrial waste into the soil; percolation of contaminated water into the soil; decay of underground storage tanks; overuse of pesticides, herbicides or fertilizers and the most common chemicals involved in causing soil pollution are: petroleum hydrocarbons; heavy metals; pesticides, solvents [15].

Table 5: Pollution degree of soil by individual metals

Pollution degree (PD)					
Fe	Mn	Cd	Zn	Cu	Pb
-	-	-	49.11	84.15	17.625

ISSN: 2349-8889
Volume-7, Issue-3 (May 2020)

https://doi.org/10.31033/ijrasb.7.3.2

Based on the calculated values, it was found that the lowest PD has Pb, whose value was 17.625, which also represents the lowest level of pollution from metals whose presence has been proven. The largest PD has Cu, with 84.15%, while the PD of zinc is slightly lower and it amounts to 49.11%. According to the criterion, the soil in this area belongs to class I when it comes to iron, manganese, cadmium and lead, to class II when it comes to zinc, and to class III when it comes to copper.

Since the analyzed soil is located near the Spreča River, and is most commonly used for growing corn and as a meadow, the necessary measures for protection against heavy metal immission, i.e. monitoring of these heavy metals in the soil, should be carried out during further use and cultivation of plants. Since these metals are also essential elements in the soil, their monitoring is of great importance both for the growth and development of plants and for livestock fed from this soil.

IV. CONCLUSION

The analysis of the soil sample taken after the flood showed that it was a land of neutral character (pH_{KCl} = 6.79) and weakly alkaline (pH_{H2O} = 7.60), in which dominant reducing conditions prevailed. The soil is very poor in humus which indicates that the content of the humus is probably washed away during flooding and covered with other sediment.

The results of the analysis of heavy metals, toxic (Cd and Pb) and essential (Fe, Mn, Zn) indicate quite heterogeneity of the sample with a wide range of minimum and maximum values, with a high concentration of Fe 19,719.5 mg/kg and Mn 985.52 mg/kg, while the concentrations of Pb and Zn were within the limit values for the silt-loam soil. (According to the Rulebook on Determination of Allowed Quantities of Harmful and Dangerous Substances in Soil and Method of Testing thereof ("Official Gazette of Federation of Bosnia and Herzegovina", number 52/09).

Considering that no maximum permissible concentrations of Fe and Mn in soil are prescribed in the rulebooks on determination of allowed quantities of harmful and dangerous substances in soil, these values of Fe and Mn are considered to be essential elements, with no real risk of toxic effects on agricultural products and food of plant origin.

It was found that the lowest pollution degree (PD) has Pb, whose value was 17.625%, which also represents the lowest pollution degree from metals whose presence was proved. The largest PD has Cu, with 84.15%, while the PD of zinc is slightly lower and it amounts to 49.11%. According to the criterion, the soil in this plot belongs to class I when it comes to iron, manganese, cadmium and lead, to class II when it comes to zinc, and to class III when it comes to copper. As the analyzed soil is used mainly as a meadow, further monitoring of these metals in the soil is necessary for the cultivation of corn, so that no adverse effects can occur for both plants and livestock fed from this soil.

REFERENCES

[1] Đaković, B. (1960). Štete od poplave u poljoprivrednoj proizvodnji. *Agronomski glasnik, 10* (5-6), 260-266
[2] M. J. McLaughlin, B. A. Zarcinas, D. P. Stevens & N. Cook. (2008). Soil testing for heavy metals. Communications in Soil Science and Plant Analysis, 31(11-14), 1661-1700. https://doi.org/10.1080/00103620009370531
[3] T. J. Schmugge, T. J. Jackson and H. L. McKim (1979). Survey of Methods for Soil Moisture Determination. *NASA Technical Memorandum So 6ST (NASA-Tb-80656)* 1180-22756.
[4] Meni Ben-Hur and Marcos Lado. (2007). Effect of soil wetting conditions on seal formation, runoff, and soil loss in arid and semiarid soils — a review. *Australian Journal of Soil Research, 46*(3), 191-202. https://doi.org/10.1071/SR07168
[5] Kisić I., Bogunović I., Bilandžija D. (2017). The influence of tillage and crops on particle size distribution of water-eroded soil sediment on Stagnosol. *Soil & Water Res.*, 12, 170-176.
[6] G. Civeira. (2019). *Introductory Chapter: Soil Moisture In: Soil Moisture*. GABRIELA CIVEIRA: Intech Open. DOI: 10.5772/intechopen.83603. Available at: https://www.intechopen.com/books/soil-moisture/introductory-chapter-soil-moisture.
[7] GWRTAC. (1997). *Remediation of metals-contaminated soils and groundwater*. Tech. Rep. TE-97-01 GWRTAC, Pittsburgh, Pa, USA,, GWRTAC-E Series.
[8] G. W. Thomas. (1996). *Soil pH and Soil Acidity. In: Methods of Soil Analysis: Part 3 Chemical Methods, 5.3*. Soil Science Society of America, Inc., American Society of Agronomy, Inc, pp. 475-490.
[9] Yamane, I., & Sato, K. (1968). Initial rapid drop of oxidation-reduction potential in submerged air-dried soils. *Soil Science and Plant Nutrition, 14*(2), 68–72. https://doi.org/10.1080/00380768.1968.10432011
[10] L. E. Allison and C. D. Moodie. (1965). *Carbonate. In: Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties, 9.2*, American Society of Agronomy, Inc., pp. 1379-1396
[11] F. Sarmadian, A. Keshavarzi and A. Malekian (2010). Continous mapping of topsoil calcium carbonate using geostatistical techniques in a semi-arid region. *Australian Journal of Crop Science, 4*(8), 603-608.
[12] Y. S. Hamid (2009). *Dissolution Kinetics of Carbonates in Soil*. Ph.D. Dissertation, Szent Istvan University, Godollo.
[13] M. C. del Campillo, J. Torrent and R. H. Loeppert (1992). The reactivity of carbonates in selected soils of southern spain. *Geoderma, 52* (1-2), 149-160. doi:10.1016/0016-7061(92)90080-Q

ISSN: 2349-8889
Volume-7, Issue-3 (May 2020)
https://doi.org/10.31033/ijrasb.7.3.2

[14] Okrent D. (1999). On intergenerational equity and its clash with intragenerational equity and on the need for policies to guide the regulation of disposal of wastes and other activities posing very long time risks. *Risk Analysis*, 19, 877-901.
[15] M. Aqeel Ashraf, Mohd. Jamil Maah and Ismail Yusoff (2014). *Soil Contamination, Risk Assessment and Remediation. In: Environmental Risk Assessment of Soil Contamination.* Available at: https://www.intechopen.com/books/environmental-risk-assessment-of-soil-contamination
[16] Vukadinović, V., Lončarić, Z. (1997). *Ishrana bilja. Poljoprivredni fakultet u Osijeku,Osijek*. Available at: http://www.secerana.com/documents/Ishrana_bilja.pdf
[17] Vukadinović, V., Bertić, B. (1989). *Praktikum iz agrokemije i ishrane bilja. Poljoprivredni fakultet u Osijeku, Osijek. Available at: http://ishranabilja.com.hr/literatura/Praktikum%20iz%20ishrane%20bilja.pdf*
[18] N. Grabić (2016). *Ukupne i raspoložive frakcije mikroelemenata u tlu, Završni rad, Poljoprivredno-prehrambeni fakultet*, Osijek. Available at: http://www.ptfos.unios.hr/index.php/o-fakultetu/natjecaji/festival-znanosti-arhiva/festival-znanosti-2016
[19] I. Šestan, A. Bratovčić. (2018). *Teoretske osnove sa eksperimentalnim vježbama iz pedologije i agrohemije. Tehnološki fakultet*, Tuzla.
[20] N.Hodžić (2016). *Kontaminacija poljoprivrednog zemljišta teškim metalima u plavnim područjima rijeke Spreče sa prijedlogom mjera za remedijaciju, Magistarski rad*, Tehnološki fakultet Tuzla.