XXVI INTERNATIONAL ECO-CONFERENCE® 2022
21–23th SEPTEMBER

XII SAFE FOOD

ЕКОЛОШКИ ПОКРЕТ НОВОГ САДА

PROCEEDINGS

NOVI SAD, SERBIA

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Publisher
ECOLOGICAL MOVEMENT OF NOVI SAD
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For the Publisher
Nikola Aleksic

Print
Red Copy, Novi Sad

Cirkulation
100 copies

Publication year: 2022-09-18
THE AUTORS ARE RESPONSIBLE FOR THE QUALITY
OF ENGLISH TRANSLATION

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2022

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Original Scientific paper

ANALYSIS OF THE PRESENCE OF HEAVY METALS IN THE SOILS OF THE HILLY-MOUNTAINOUS AREAS OF BALKAN PENISULA WITH THE ASSESSMENT OF ITS POTENTIAL FOR THE FRUIT GROWING: CASE STUDY OF THE LJUBOVIDJA RIVER BASIN, POLIMLJE, MONTENEGRO

Abstract

The paper presents results of the analysis of the presence of heavy metals with an assessment of its potential for the further development of fruit growing in North Montenegro, and in this specific case at the territory of the River Basin Ljubovidja, which is the hilly-mountainous area of the Balkan Peninsula. Sampling and further analysis showed that the dominant type of soil in this area is District Cambisol. In the second phase, we conducted further research on the presence of heavy metals in the area of Pavino Polje, in the municipality of Bijelo Polje, Montenegro. The results of the analysis finally showed that there is no presence of heavy metals in the samples we collected during the field visit. The studied area is recommended for the establishment of organic production. It is particularly suitable for the production of fruit growing, vegetables and fodder is also recommended.

Keywords: *Heavy metals, mountainous areas, fruit growing, organic production, Polimlje, Montenegro, Balkan Peninsula*

INTRODUCTION

At the end of the 20th century, significant changes occurred in the world: social, economic, and political (Zejak et al., 2022). Population explosion, industrialization, urbanization and exploitation of natural resources are creating problems globally (Nagpal et al., 2020). The problem of land degradation is more and more one of the most important issues that should be treated very seriously. Large quantities of different kinds of elements are discharged into the environment as contaminants each year by human activities. Heavy metal toxicity and its lack of biodegradability and long-lasting duration in the environment while entering the food chain are considered to be one the most serious potential pollutants of the ecosystem (Popović, 2002; Pakzad et al., 2016; Kastratovic et al., 2016). No or low degraded soil and well-protected lands are today a special asset of every society. Proper management of this resource is an obligation and is part of all wise decisions of those who deal with agrarian policies and sustainable management.

According to the official statistic (MONSTAT), Montenegro is with 0.84 ha per inhabitant of the total agricultural land. In relation to this criterion, the country is in the second position in the European continent after Ireland. On the other hand, this country is poor in fertile land, because many meadows have been turned into pastures, and pastures into forest land; and finally barren land counts for 23% of the territory. That is why Montenegrin agriculture is characterizing the so-called rural agriculture, i.e. production took place just for satisfying farmers' own needs (Fustic and Spalević, 2003; Fustic et al., 2005). Land degradation in Montenegro is caused by numerous natural and anthropogenic factors. The distinctly hilly and mountainous area of Montenegro (94% with a slope of over 5%), a very dynamic and scattered relief, a developed and dense network of watercourses, an abundance of precipitation (1000-5000 mm per year) and other climatic characteristics are factors of crucial importance for provoking of water and wind erosion. This is contributed by the high share of erodible and non-resistant soils substrates, the devastation of plant cover and bare land, which make up 23% of the total territory, the damages are enormous, multiple and incalculable. Another type of land degradation is conditioned by excess floods that threaten 26,000 ha in flat areas with varying intensity covering only 5% of Montenegro. Applying soil conservation measures, these potentially fertile lands should be brought to intensive agriculture production – culture for more intensive use in agriculture. Technological development caused an increase in the use of natural resources by exploitation of mineral raw materials, industrialization and urbanisation – construction of infrastructure facilities and settlements, which "consumed" a considerable area, mostly the most fertile land. With this particular form of degradation through conversion – land use change, Montenegro has lost 800-1000 ha per year in the last 40-50 years (Fustic, 2005).

In Montenegro, the transition from conventional agriculture to organic production is increasing. This method of production is well accepted by those who are engaged in soil conservation. Unlike conventional agriculture, which, due to the application of pesticides and fertilizers, led to the loss of individual plant and animal species, organic farming is based on the principles of protection and preservation of plant and animal species and the environment. Organic production is based on the biological balance of the system land – plant – animal – human. According to the Codex Alimentarius definition, it is a "holistic" production system that promotes and strengthens the agro-ecosystem and health, including biodiversity, biological cycle, and soil. Organic production is one of the world's leading trends in agriculture that is continuing to grow. Organic production of agricultural and other products is based on the application of organic production methods at all stages of production, aims to reduce the use of chemicals, and excludes the use of GMOs and products consisting of or derived from GMOs, as well as the use of ionizing radiation. Organic farming aims to produce safe food, of high quality, in an environmentally sustainable way, maintaining the genetic diversity of agro and ecosystem, preserving the environment, maintaining and improving soil fertility, reducing all forms of pollution, and producing food of high nutritional value, improving health and making a profit (Popović et al., 2014; 2019; Zejak et al., 2022; Ikanović and Popović, 2020). The land we want for the future must be carefully treated and well protected today.

MATERIALS AND METHODS

Study area. Montenegro is a country with great variability, ranging from sand and rock coasts (some corresponding to a ria coast), karst plateaus, large (intra-montane) fields, high mountains holding a (peri) glacial imprint, canyons, and more; all of it comprised in only 13 812 km^2 and within an elevation range of 2535 m. It is characterized by a Mediterranean climate, with warm and dry summers and autumns, and relatively cold winters with heavy snowfall on the continent (Zejak et al., 2022). The average altitude is 1,086 m; the lowest point: is the Adriatic Sea 0 m; the highest point: is Prokletije (Zla Kolata, 2534 m a.s.l., Dobra Kolata, 2528 m); Durmitor Kuk (Bobotov Kuk, 2522 m). According to data provided in the papers of various authors (Zejak et al, 2022; Spalevic et al., 2019; 2020), the structure of land use in Montenegro is as follows: agricultural land: 38.2% (estimated in 2018); arable land: 12.9% (estimated in 2018); crops: 1.2% (estimated in 2018); pasture: 24.1% (estimated in 2018); forest: 40.4% (estimated in 2018); other: 21.4% (estimated 2018). Irrigated land 24 km2 (2012). The Map of Montenegro with the studied region of River Basin Ljubovidja is presented in Figure 1. North Montenegro, where the studied region is located is mainly mountainous. In this neighbouring region, the highest peaks of Montenegro are found, including Komovi (2487 m a.s.l.) and Zla Kolata (2535 m a.s.l.) in the Prokletije Mountains of the same Polimlje Region. Nevertheless, this area of Polimlje is quite densely populated and includes the towns of Plav, Andrijevica, Berane, and Bijelo Polje. The rivers in this region drain to the Black Sea, and some of them form deep canyons crossing limestone formations. Further downstream, they form broader valleys flowing through softer Palaeozoic material (Spalevic, 2011).

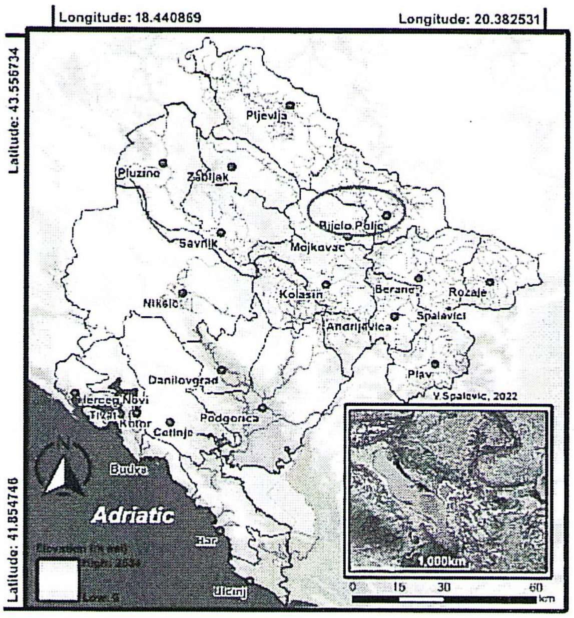

Figure 1. Map of MNE, Ljubovidja basin and Pavino Polje, (Zejak et al., 2022)

Table 1. Maximum allowed concentrations of dangerous and harmful substances in soils based on standards of Ex-Yugoslavia (mg/kg of air-dry soil)

Elemet	Official Gazette of the Republic of Serbia 23/1944	Rulebook Of Council Of Europe 2092/91	Rulebook on methods organic herbal of production, Official Gazette of FRY 51/2002
Cadmium	3	2.0	0.8
Lead	100	100.0	50.0
Mercury	2	1.0	0.8
Arsenic	25	-	10.0
Chrom	50	50.0	30.0
Nickel	300	-	-
Copper	100	50.0	50.0
Zinc	300	150.0	150.0
Boron	50	-	-
Molybdenum	-	-	10.0
Cobalt	-	-	30.0

Source: Kastori et.al., 2003.

Climate. Based data of more than 70 years (1948–2021) for temperature and precipitation, the study area is characterized by a mountain Mediterranean climate (Rajović, 2009) with rainy autumns and springs, cold winters, and a deficit of precipitation in summer months (Table 2.)

Table 2. Precipitation and temperature for the period 1948–2021 recorded at Bijelo Polje

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max daily precipitation in mm												
Max	68.6	92.8	73	93.3	42.6	58.5	97.8	55.8	95.6	157.6	101.6	79.4
Aver.	23.4	22.8	21.5	24	21.9	20.6	21.7	21.1	25.3	29	29	23.5
St.D.	15.6	18.6	13	15	9.9	12.4	15.2	11.9	17.2	24.6	16.2	14.7
Mean monthly temperatures in °C												
Max	2.9	5.8	7.8	12.6	15.8	18.2	20.8	20.9	17.7	12.6	8.6	4.4
Min	–5.6	–5.2	–0.7	6.1	9.8	14.1	16.2	14.3	11.3	6.2	–1.6	–4.7
Aver.	–1.6	0.8	4.6	8.9	13.3	16.3	18.1	17.7	14.3	9.4	4.5	0.1
St.D.	2.2	2.7	2.1	1.3	1.3	1	1.1	1.4	1.5	1.4	2.1	2.2
Max. daily temperatures in °C												
Max	15.4	20.9	25.6	28.1	32.4	35.5	36.8	39.2	36	29.5	23	19.2
Aver.	11.7	14.5	20.1	23.6	27.6	30.4	32.8	32.8	29.4	24.8	18.6	13.6
St.D.	2.8	3	3.1	2.3	2.2	2.5	2	2.5	2.6	2.6	2.8	3.3
Min. daily temperatures in °C												
Min	–27.6	–24.5	–16.5	–7.5	–4	0	1.2	2.6	–4	–7.2	–15.4	–21.7
Aver.	–15.1	–13	–8.4	–2.8	0.9	4.8	6.5	6.1	2.3	–2.5	–7.3	–12.6
St.D.	5.3	4.7	4.1	1.8	2	1.8	2.1	1.5	2.5	2.3	3.7	4.6

Source: Data from the Hydrometeorological Institute of Montenegro

The absolute maximum air temperature ever recorded was 39.2 °C. Winters are severe, with negative temperatures as low as –27.6 °C. The average annual air temperature, t0, was 8.9 °C. The average annual precipitation, H year, was 873 mm. The temperature coefficient for the region, T, was calculated at 0.99. The torrential rain, bb, was calculated at 84.7 mm.

The geological structure and soils of the area. The study area at large consists of various types of sediment, magmatic and metamorphic rocks generated in the long, Palaeozoic to Quaternary, interval. Most of the terrain is underlain by Mesozoic formations of carbonate composition, while magmatic and silico-clastic rocks are substantially less present. Paleozoic geological formations consist of sedimentary and metamorphic, silico-clastic rocks found mostly in the north-eastern parts of Montenegro, while Cainozoic rocks of carbonate and clastic composition occur almost in all regions of Montenegro. The research part related to geology and soil is based on previous geological and pedological studies (Fustic and Djuretic, 2000), who analyzed all geological formations and soils of Montenegro. Furthermore, we collected some soil samples for chemical and physical analysis. The grain size composition of the soil was determined by the pipette method. The soil samples were air-dried at 105°C sifted through 2 mm sieve and dispersed using sodium pyrophosphate. Total carbonates were determined by the volumetric Scheibler method; the soil reaction (pH in H_2O and nKCl) was determined with a potentiometer; the content of the total organic matter was determined by the Kotzman method; easily accessible phosphorous and potassium were determined by the Al-method and the adsorptive complex (y1, S, T, V) was determined by the Kappen method (Spalevic et al., 2011). Certain soil analyzes in Montenegro for the presence of heavy metals were carried out as part of the "program for testing harmful substances in the soil for the year 2007". the analyzes were done by the ministry of tourism and environmental protection. The program was implemented by the public institution "Center for ecotoxicological testing of Montenegro" in accordance with the rulebook on permitted amounts of hazardous and harmful substances in soil and methods for their testing (official gazette of the Republic of Montenegro 18/97). The investigation includes analyzing land in 15 settlements that are most exposed to pollution. The total content of heavy metals in the soil was determined after preparing the samples in a closed microwave system under high pressure Milestone Ethos 1 according to US EPA method 3051A (2007).

RESULTS AND DISCUSSION

Soil is the basic substrate for plant production, and that is why it is necessary to determine whether it is suitable for this purpose, from the point of view of the content of harmful substances and heavy metals, in order to produce health-safe food (Vukeljić et al., 2002). This is possible if the determined content of heavy metals is compared with the limit value for the respective element. The limit values for the maximum allowed concentration of heavy metals in the soil (Table 1) represent significant support in the assessment of soil pollution with these predominantly toxic elements (Kastori et al., 2003; Đukić, 2003). With the sudden scientific and technological development in all branches of the economy, the emission of heavy metals increased, which thus became significant pollutants (Vukeljić et al., 2002). Plants grown on contaminated soils and useful in nutrition endanger the life and health of people and animals (Triphati et al., 2001). The concentrations of Pb, Cd, Cu and Mn in sixteen imported NPK fertilizers, which are most often used in Serbia, were determined by the method of flame atomic absorption spectrometry. The obtained results show that the content of heavy metals in samples of different fertilizers varies significantly, which depends on the ratio of N:P:K in the examined samples of fertilizers, as well as on the origin of the fertilizers themselves. The highest content of Cu was found in coloured, mixed NPK fertilizers originating from Hungary, Greece and the Netherlands, and exceeds the value of the maximum permissible concentration of Cu that can be found in the soil. The Mn content in the Hungarian NPK fertilizer (10:10:20) is ten times higher than the average Mn content in the soil. These data indicate that it is necessary to permanently control the content of heavy metals in imported fertilizers, in order to reduce soil, underground and surface water pollution (Milinović et al., 2008). The maximum permitted amount of hazardous and harmful substances in soil (Tab. 3), in Montenegro, can lead to its pollution, and which is caused by the improper use of mineral fertilizers and plant protection products by legal and natural persons, as well as by the discharge of waste matter from various sources, are specified in the Rulebook on permitted amounts of hazardous and harmful substances in soil and methods for their testing ("Official Gazette of Montenegro", 18/97).

Table 3. Maximum allowed quantities (MDK) of dangerous and harmful substances, according to the current Ordinance

No.	Element	Chemical label	MDK in the soil in MNE, mg/kg	MDK in the soil in Serbia, mg/kg dry soil	Average value in the soil, mg/kg
1.	Cadmium	Cd	2.0	3.0	< 0.50
2.	Lead	Pb	50.0	100.0	17.37
3.	Mercury	Hg	1.5	2.0	0.0527
4.	Arsenic	As	20.0	25.0	< 5.0
5.	Nickel	Ni	50.0	50.0	17.75
6.	Fluorine	F	300.0	300.0	144.0
7.	Copper	Cu	100.0	100.0	22.5
8.	Zinc	Zn	300.0	300.0	95.0
9.	Boron	B	5.0	50	3.0
10.	Cobalt	Co	50.0	30.0	14.25
11.	Molybdenum	Mo	10.0	10.0	< 5.0
12.	Potassium	K	–	–	207.65
13.	Phosphorus	P	–	–	492.5
14.	Nitrogen	N	–	–	0.15

The research also covers the area of Bijelo Polje. The content of hazardous and harmful substances in the soil in the Municipality of Bijelo Polje was analyzed at four locations. The results of the analysis of the samples indicate the presence of lead (Pb) in concentrations above the MDK at the location of City Landfill 1. At the aforementioned location of City Landfill 1, an increased concentration of cadmium (Cd), chromium (Cr), copper (Cu), and zinc was also determined (Zn). The concentration of fluorine (F) at the Zaton 1 location is above the MDK. At the locations of City Landfill 1 and Zaton 1, there is an evident increase in lead concentration compared to the previous year, while at the other two locations, a decrease in lead concentration can be observed compared to the previous year. The content of polyaromatic hydrocarbons exceeds MDK at the location of City Landfill 1. Except for the location Zaton 1, at all other locations, there is an increase in the concentration of polyaromatic hydrocarbons compared to the previous year.

In the final report of the Ministry, it was concluded that the condition of the soil in relation to the content of dangerous and harmful substances can be characterized as satisfactory. On the basis of the monitoring carried out, at the targeted locations, it was found that in nine municipalities, it was polluted as a result of inadequate disposal of municipal waste. In the municipality of Nikšić, inadequate disposal of industrial waste causes an increased content of dangerous and harmful substances. In most municipalities, there is a negative impact of traffic, i.e. exhaust emissions, which is a significant source of pollution of the surrounding land, at the same time endangering air quality. In relation to the study area of in the Polimlje, Montenegro region, a soil samples were analyzed, from a plot of pasture/meadow culture (Figure 1) in the Pavino Polje, municipality of Bijelo Polje, at a location of the altitude of 800 m.a.s.l., with a sampling depth of 0.3 and 0.5 m of the Ah portion of the profile. Then an analysis was carried out for the presence of heavy metals by the national and authorized laboratory at the Public institution Center for Ecotoxicological Testing – CETI in Podgorica (Montenegro). This analysis by using the method AOAC (Official, method 990.08 – Metals in solid wastes, AOAC Official methods of analysis (1995), Chapter 9, p. 31). The K content was determined on an AA-6701F Atomic Absorption Spectrophotometer, and the P content was determined on the Sequential Plasma Spectrometer ICPS-7500. Both instruments are products of Shimadzu. The results of the tests in CETI-Podgorica are given in Tab.3. The majority of microelements belong to the group of heavy metals, which are characteristically toxic to plants, animals and humans in larger quantities quote from Brankov et al. (2006).

Maximum permitted amounts (MDK) of dangerous and harmful substances, according to the current Ordinance (Official Gazette of the Montenegro, No. 18/97)), it was concluded that the concentration of cadmium (Cd) is below the permitted concentration, more precisely, that it is only 0.05 mg/kg, while 2mg/kg is otherwise permitted. The concentration of 2mg/kg in the sample indicates that the presence of lead (Pb) in the controlled soil is about 30% lower than the permitted level, mercury (Hg) is only 0.005, which is a trace presence in the sample compared to the permitted 1.5mg/kg. Arsenic (As) is recorded with around 25%, and Chromium (Cr) the same with around 25%. Nickel (Ni) 17.75 mg/kg of the permitted 50 mg/kg. Fluorine (F) is recorded with about 50% of the permitted concentration, Copper (Cu) is present with 22.5mg/kg, while its presence is permitted in the amount of 100 mg/kg. Zinc (Zn) was found in the sample in a concentration of about 30% of the allowed: Boron (Bo) was recorded with 3 mg/kg, which is 2 mg/kg less than the allowed 5 mg/kg in the soil sample. Cobalt (Co) was found in the amount of 14.25 mg/kg, and the permitted concentration is 50 mg/kg. Molybdenum (Mo) is above 5mg/kg, while the permissible concentration of molybdenum is 10mg/kg of the sampled soil. The moisture content of the sampled soil during testing was 9.35%. The nitrogen content is 0.15%, phosphorus 492.5 mg/kg, and potassium 207.65 mg/kg. Based on the results (Tab. 3.) of laboratory tests in the report of Pubic institution CETI – Podgorica, it was determined that the tested soil samples corresponds to the conditions of the Rulebook on permitted concentrations of hazardous and harmful substances in soil and methods for their testing (Official Gazette of Montenegro, No 18/97).

CONCLUSION

- At the studied area of Pavino Polje, analyzes of soil samples did not determine the presence of heavy metals. As a consequence it is possible to organize organic production in this region, but it is necessary to take care of the locality itself in such a way that possible existing or potential sources of its pollution would be avoided.
- The relief, climate and soils of the North Montenegro, their existing condition and soil use would be arranged for organic agriculture, so that this area can be used for the possible production of: (1) planting of continental fruits such as raspberries, blackberries, blueberries, apples, pears and plums; (2) field crops (buckwheat, millet, potato, barley, oats, rye), and the production of (3) certain types of bulk fodder (hay, silage) for domestic animals raised in the organic farming system.
- The soil, climate and relief, with their current state and existing basic features, favour the further development of organic agricultural production, especially in the studied area and region of northern Montenegro.

Acknowledgments. The paper is funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grant numbers: 451-3-68 / 2022-14/200032.

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