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Heavy metal determination in agricultural soil collected from Brăila County

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Abstract
This is a study conducted on agricultural soil collected from village of Dudescu, Zăvoaia Commune, Însurăței City, Brăila County. In this case soybeans, sunflowers, corn and wheat have been cultivated prior the soil sampling. The soil was analyzed using an ED-XRF and the results indicated, in general, elements concentrations within normal values, indicating a good soil quality. The exceptions in this study, which have exceeded the normal legal values, were: chromium (Cr), nickel (Ni) and arsenic (As). To assess the level of soil pollution, different types of indexes were calculated such as the migration index (MI) and the ecological risk potential (RI).

Keywords: soil analysis, agriculture, migration index, ecological risk of heavy metals in vegetables, XRF.

1. INTRODUCTION

According to the human needs, soil can provide physical support for the entire infrastructure and for all the raw materials. In the last years the human needs are exponentially growing, subjecting soil to an unprecedented pressure. Foremost among these pressures is the demand of food production. This is a problem because, more than always, soil is receiving many pollutants from various sources that accumulate with negative effects on human health. In the case of agricultural soil, the pollution with heavy metals influences the soil solution quality that transfers the pollutants to crops and ground waters. To ensure future sustainability in agricultural soils is important to careful monitor the level of pollution. In normal conditions, the presence of some elements in this type of soils is due to the parent material and remains low. But in some cases, due to the anthropogenic inputs such as contaminated irrigation water or an excessive use of agrochemical products can increase the level and the type of pollutants [1,2].

2. EXPERIMENTAL

This study focuses on the quality of agricultural soil in the village of Dudescu, Zăvoaia Commune, Însurăței City, Brăila County, where soybeans, sunflowers, corn, and wheat have been cultivated. Soil samples were collected, on October 2022, from 0, 5, and 30 cm of depth. After being allowed to dry, plant residues were removed, and the samples were grounded and encapsulated. Special capsules were qualitatively and quantitatively analyzed for major and minor elements using an ED-XRF spectrometer, Niton XLTj-793 [3]. Once the elemental concentrations were identified, they were interpreted using specific equations to estimate the level of pollution. Each soil sample was analyzed tree times for 240 seconds (the average was used), using two filters: the first one determining elements from K to Cu, and the second one determining elements from Zn to Sb.

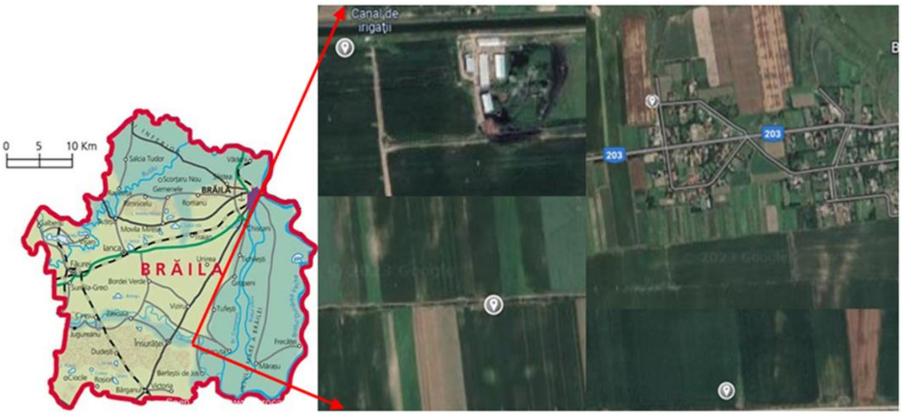

Figure 1. Satellite image of the sampling locations

3. RESULTS AND DISCUSSION

In order to identify the level of pollution in agricultural areas, the following calculations were performed: **the migration index (IM)** and the **ecological risk potential (RI)**.

The **migration index (IM)** is calculated to assess the degree of mobility of elements using the formula **(1)**:

$$\mathrm{IM} = \sum_{i=1}^{n}\left(\frac{P}{P_T}\right)d \quad (1)$$

Where: n represents the number of sample layers, P is the concentration of the element in layer n, P_T is the total concentration across layers, and d represents the depth of the layer. In the presented case, n equals 3 with values ranging from 0.3, 5, and 30 cm. This factor can vary from 1 if the element is entirely accumulated in the first centimeter and maximally up to 30 if it is accumulated in the last 30 centimeters. The migration potential is classified into 4 classes based on the obtained values: A (<5) very low; B (5-10) moderate; C (10-20) high; D (>20) very high [4, 5].

The **ecological risk potential (RI)** was calculated to determine the ecological risk by assessing the ecological risk of heavy metals in vegetables. RI was calculated using the equation **(2)**:

$$\mathrm{RI} = \sum E_i = \sum T_i \cdot \frac{C_i}{B_i} \quad (2)$$

In this case, C_i represents the determined concentration of the element in the soil sample, B_i is the background concentration, and T_i is the toxicity coefficient. E_i is the total ecological risk index. Since toxicity coefficients (T_i) were identified only for Zn = 1, Cr = 2, Cu = 5, Pb = 5, Ni = 5, As = 10, Cd = 30, and Hg = 40, in this study, the total ecological risk index was determined only for these elements. The values of E_i are classified as follows: $E_i < 40$ low risk, $40 \leq E_i < 80$ moderate risk, $80 \leq E_i < 160$ high risk, $160 \leq E_i < 320$ higher risk, and $E_i > 320$ severe risk. The values of RI are classified as follows: $R_i < 150$ low risk, $150 \leq R_i < 300$ moderate risk, $300 \leq R_i < 600$ high risk, and $R_i \geq 600$ severe risk [6, 7].

Table 1. Migration index

Elements	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Rb**	**Pb**
Soybean	9.43	2.33	nd	11.77	5	11.91	11.50
Sunflower	10.36	14.11	5	11.49	11.97	11.66	11.27
Wheat	11.64	11.79	5	13.05	nd	11.07	17.21
Corn	12.77	12.24	5	12.57	0.3	11.89	11.93

Soybean crops (*Glycine max (L.) Merr.*) grow efficiently when the soil is fertile, with a medium loamy texture and a pH of 7.8 units. Soybeans are a rotation crop, typically used after wheat and corn crops to minimize the possibility of occurrence of various cereal diseases and optimize soil nutrient value. Soybeans should not be planted after alfalfa, beans (for grains), rapeseed, and sunflowers where the presence of white mold (*Sclerotinia sclerotiorum*) has been identified. This pathogen uses the soybean plant as a host, persisting until the appearance of other crops. Moreover, it is recommended not to plant multiple soybean crops in succession, as it can lead to the spread of diseases from one crop to another and soil erosion issues [8].

At this location, the heavy metal concentrations that exceeded normal values were: As, Ni and Cr.

Table 2. Ecological risk of heavy metals in vegetables (EI)

RI	**Depth (cm)**	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
Soybean	**0**	5.84	15.47	nd	0.46	nd	4.53
	5	6.22	11.75	nd	0.33	19.68	4.47
	30	3.93	nd	nd	0.41	nd	4.31
EI		15.99	27.21	nd	1.20	19.68	13.30
Sunflower	**0**	4.57	13.38	nd	0.40	18.06	4.22
	5	6.54	nd	6.26	0.37	23.50	3.30
	30	4.13	11.62	nd	0.37	20.78	4.20
EI		15.24	24.99	6.26	1.14	62.34	11.72
Wheat	**0**	5.29	16.76	nd	0.61	nd	3.20
	5	4.51	nd	6.64	0.47	nd	3.19
	30	4.94	10.58	nd	0.68	nd	7.28
EI		14.74	27.35	6.64	1.76	nd	13.67
Corn	**0**	4.42	14.00	nd	0.46	23.16	3.31
	5	4.81	14.37	5.58	0.41	nd	3.91
	30	5.37	15.28	nd	0.50	nd	3.63
EI		14.60	43.66	5.58	1.36	23.16	10.83

Arsenic (As) was only identified at a depth of 5 cm, with a concentration exceeding the normal values by more than 1.97 times. Its presence at 5 cm may indicate anthropogenic pollution or the presence of a clay layer, which facilitates its accumulation. The current value did not exceed the alert threshold concentration, which is equal to 15 mg kg^{-1}. Regarding the values characterizing the ecological risk of heavy metals in plants, for Arsenic (As), both the Ecological Index (EI) and Risk Index (RI) indicated a low risk. The Migration Index calculated for As had a value of 5, indicating moderate migration.

Nickel (Ni) was identified in the top 5 cm of the soil, and it was absent at 30 cm depth. This, along with the decreasing trend of concentrations with depth, indicates anthropogenic pollution. The maximum identified value is 61.86 mg kg^{-1}, which is more than 3 times the normal value for Ni in soil, which is approximately 20 mg kg^{-1} according to regulations. The value at 5 cm is equal to 46.99 mg kg^{-1}, which is 2.35 times higher than the normal value. Regarding the values characterizing the ecological risk of heavy metals in plants, for Nickel (Ni), both the Ecological Index (EI) and Risk Index (RI) indicated a low risk. The Migration Index calculated for Ni had a value of 2.33, indicating very low migration.

Even though there are elevated concentrations of **chromium (Cr)**, they do not exceed the alert threshold for less sensitive areas, which is 100 mg kg^{-1}. It is observed that, in the case of soybean cultivation, the maximum concentration is at 5 cm. Nonetheless, the trend is decreasing with depth, indicating anthropogenic pollution. Some soil properties related to flooding or irrigation, can lead to a pH change that may allow the transformation of stable Cr III into mobile Cr IV [4]. For this reason, frequent monitoring of Cr concentrations is recommended. According to the calculated equations, the Migration Index (IM) value for soybean cultivation (9.43) is found to be in class B, with moderate migration potential.

Sunflowers (*Helianthus annuus L.*) grow worldwide, on all continents, and belong to the *Asteraceae* family, the largest family of *Angiosperms* with origins in North America. These types of crops are among the most important seed crops used for oil production, alongside palm oil (*Elaeis guineensis Jacq.*), soybeans (*Glycine max (L.) Merr.*), and rapeseed (*Brassica napus L.*), playing a significant role in the world's economy. Sunflower seeds have a high-quality oil content (ranging from 38% to 50%), primarily used for consumption. The rest parts left after oil extraction is used for animal feed. Additionally, the oil can be used in the pharmaceutical and cosmetic industries, in floriculture, honey production and biodiesel production. The life cycle of a sunflower crop can vary between 80 and 130 days, depending on the planting and harvesting dates. Due to its excellent adaptability, sunflowers are used as a rotation crop, especially in soils previously used for wheat cultivation [9].

At this location, the heavy metal concentrations that exceeded normal values were: arsenic (As), nickel (Ni) and chromium (Cr).

Arsenic (As) was identified at all depths, with a maximum concentration of 11.75 mg kg^{-1} and a minimum of 9.03 mg kg^{-1}. These concentration values exceed normal values but do not exceed the alert threshold concentration of 15 mg kg^{-1}. Regarding the values characterizing the ecological risk of heavy metals in plants, for arsenic (As), both the EI and RI indicated a moderate risk. The MI calculated for As had a value of 11.97, which places it in class C, is implying a high risk of migration.

Nickel (Ni) was identified at the surface with a concentration of 53.5 mg kg^{-1} and at 30 cm with a slightly lower concentration of 46.47 mg kg^{-1}. Both values exceed the normal values of nickel in soil according to regulations, which are set at 20 mg kg^{-1}, but they do not exceed the alert threshold of 75 mg kg^{-1}. Regarding the values characterizing the ecological risk of heavy metals in plants, for nickel (Ni), both EI and RI indicated a low risk. The MI calculated for Ni had a value of 99.97, indicating very high migration, placing the element in class D.

Even though there are elevated concentrations of **chromium (Cr)**, they do not exceed the alert threshold for less sensitive areas, which is 100 mg kg^{-1}. It is observed that, in the case of sunflower cultivation, the maximum concentration is at 5 cm (98.10 mg kg^{-1}). Nonetheless, the trend is slightly decreasing with depth, indicating anthropogenic pollution and the possible presence of clay at the 5 cm depth. According to the calculated equations, the IM value for sunflower cultivation (10.36) was found to be in class C, indicating a high migration potential. Regarding the values characterizing the ecological risk of heavy metals in plants, for sunflower cultivation, both the Ecological Index (EI) and Risk Index (RI) indicated a low risk.

In the case of soil for **cereal crops (wheat and corn)**, the heavy metal concentrations that exceeded normal values were nickel (Ni) and chromium (Cr).

For **wheat cultivation**, **nickel (Ni)** was identified at the surface with a concentration of 67.05 mg kg^{-1} and at 30 cm with a slightly lower concentration of 42.33 mg kg^{-1}. This, along with the decreasing trend of concentrations with depth, indicates anthropogenic pollution. Both values exceed the normal values of nickel in soil according to regulations, which are set at 20 mg kg^{-1}, but they do not exceed the alert threshold of 75 mg kg^{-1}. Regarding the values characterizing the ecological risk of heavy metals in plants, for nickel (Ni), both the EI and RI indicated a low risk. The MI calculated for Ni had a value of 11.79, placing the element in class C, indicating a high migration potential.

For **corn cultivation**, **nickel (Ni)** was identified at the surface with a concentration of 56.01 mg kg^{-1}, at 5 cm with 57.48 mg kg^{-1}, and at 30 cm with the highest concentration of 61.13 mg kg^{-1}. The very slight upward trend of concentrations with depth suggests the presence of pollution from the parent material, but the small variation between concentration values can also indicate long-term and systematic pollution with this element. All values exceed the normal values of nickel in soil according to regulations, which are set at 20 mg kg^{-1}, but they do not exceed the alert threshold of 75 mg kg^{-1}. Regarding the values characterizing the ecological risk of heavy metals in plants, for Ni, both the EI and RI indicated a moderate risk. The MI calculated for Ni had a value of 12.24, placing the element in class C, indicating a high migration potential.

For **wheat cultivation**, **Cr** was identified at all studied depths. The values ranged from a maximum of 79.35 mg kg^{-1} at 0 cm to 67.68 mg kg^{-1} at 5 cm. At 30 cm, an intermediate value of 74.13 mg kg^{-1} is present. Although these are elevated concentrations, they do not exceed the alert threshold for less sensitive areas, which is 100 mg kg^{-1}. The concentration trend is decreasing with depth, indicating possible anthropogenic pollution. According to the calculated equations, the IM values for wheat cultivation (11.69) include it in class C, indicating a high migration potential. Regarding the values characterizing the ecological risk of heavy metals in plants, for wheat cultivation, both the EI and RI indicated a low risk.

For **corn cultivation**, **Cr** was identified at all studied depths. The values ranged from a maximum of 80.49 mg kg^{-1} at 30 cm to 66.27 mg kg^{-1} at 0 cm. At 5 cm, an intermediate value of 72.19 mg kg^{-1} is present. Although these are elevated concentrations, they do not exceed the alert threshold for less sensitive areas, which is 100 mg kg^{-1}. The trend is increasing with depth, indicating a possible pollution from the parent material. However, the pollution seems to be systematic and consistent, as the concentrations are similar. Such pollution may be due to irrigation with contaminated water. According to the calculated equations, the IM value for wheat cultivation (12.77) class C, indicating a high migration potential. Regarding the values characterizing the ecological risk of heavy metals in plants, for wheat cultivation, both the EI and RI indicate a low risk.

4. CONCLUSIONS

The crops are irrigated with water from the Ialomița-Călmățui irrigation system, so the source of irrigation is the water from the Danube river. Therefore, we can assume that the link between the presence of chromium (Cr) and nickel (Ni) elements at all locations with values above the normal ones is attributed to the existing pollution in the Danube water. In [8], in the Galați - Danube Delta area, in the spring of 2019, Ni was presented as belonging to class 3, with a mention of moderate to strong pollution. Additionally, [10] in a study on sediments taken from the Romanian section of the Danube, confirms some exceedances of normal values for Ni and occasionally for Cr. Ni and Cr are less mobile metals; they bind to silicates [11], hence the constant concentrations across soil samples.

In the case of pollution with nickel and chromium, soils can be remediated using spinach crops (*Spinacia oleracea*) [4]. The concentrations of chromium have decreased slightly in the case of cereal crops, as it has been proven that wheat and corn uptake Cr from the soil [12].

From the soil belonging to cereal crops, arsenic (As) is absent, which is attributed to the uptake of this element by cereals. In the study by [13], it is shown that the ability of cereals to take up As from the soil is significant.

In general, except for chromium (Cr), nickel (Ni) and arsenic (As), which have exceeded the normal legal values, all the other elements have shown lower values, indicating a good soil quality.

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