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Determination of pollutant elements in agricultural soil using X-Ray Fluorescence Spectrometry

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Abstract
This study investigates the impact of agricultural practices on soil quality in Fundeni Commune, Galati County, with a particular focus on the potential contamination by heavy metals. Soil samples were collected from representative agricultural areas, including a vegetable garden, an alfalfa field, and two vineyards. The concentrations of heavy metals were determined using X-ray fluorescence (XRF) spectroscopy, allowing both qualitative and quantitative assessment. The analytical results indicated that, while the majority of measured elements were within permissible limits, certain samples exhibited concentrations exceeding the normal thresholds for arsenic (As), zinc (Zn), chromium (Cr), nickel (Ni), copper (Cu), and cadmium (Cd), suggesting localized contamination potentially linked to agricultural inputs.

Keywords: agriculture, heavy metals, soil, XRF.

1. INTRODUCTION

In rural areas, gardening is a popular activity that, in addition to maintaining physical and mental well-being, can also provide food, such as fruits and vegetables, at a lower cost compared to market prices. Commercially available fruits and vegetables are often chemically treated, which has led to a significant number of health problems in humans. Thus, gardening provides fresh produce to support and maintain a healthy diet.

In urban areas, garden plots are typically located near roads or industrial activities that emit contaminants, which, over time, can have negative health effects on residents. In contrast, rural areas are generally free from such pollution sources, and any exceedances of normal concentration levels are usually due to parental material, accidental pollution or the improper use of fertilizers and other soil amendments [1].

Since most villagers grow their own fruits and vegetables, it is crucial to quantify metal concentrations to assess the risks they may be exposed to.

Metals in garden soil can pose a hazard through ingestion, inhalation, and dermal absorption. Several studies have highlighted the relation between metal concentrations in garden soil and the risk of cancer, as well as the accumulation of metals in the different organs of the human body [2].

2. EXPERIMENTAL

The soil samples were collected from Fundeni commune, Galati County. Galati County is located in southeastern Romania, at the southern extremity of the Moldavian Plateau, with a latitude of 45°27' North and a longitude of 28°02' East, covering a total area of 4,466 km² [3].

Fundeni commune is situated in the lower Siret River floodplain, on its left bank, in the southeastern part of Galati County. It is bordered by the Siret River and Nămoloasa commune to the southwest, Tudor Vladimirescu commune to the southeast, and Liești commune to the north and northwest. The commune consists of three villages: Fundeni, Lungoci, and Hanu-Conachi. Fundeni village is the second-largest village in the commune.

The local relief is a well-defined unit corresponding to the lower Siret floodplain. The southwestern area consists of a wide plain and local floodplain terraces, while the northern and northwestern regions feature slightly elevated terraces, where the well-known Hanu-Conachi sand dunes are located. The predominant soil types in Fundeni commune include leached chernozem with sandy deposits (81%), alluvial soils (12%), sands (6%), and saline soils (1%).

The commune is home to a notable natural reserve, declared a protected area under Law No. 5/2000. This reserve, known for its shifting sands, unique flora, and fauna, has been the subject of extensive scientific research. In 2019, Fundeni had a recorded population of 846 inhabitants [4].

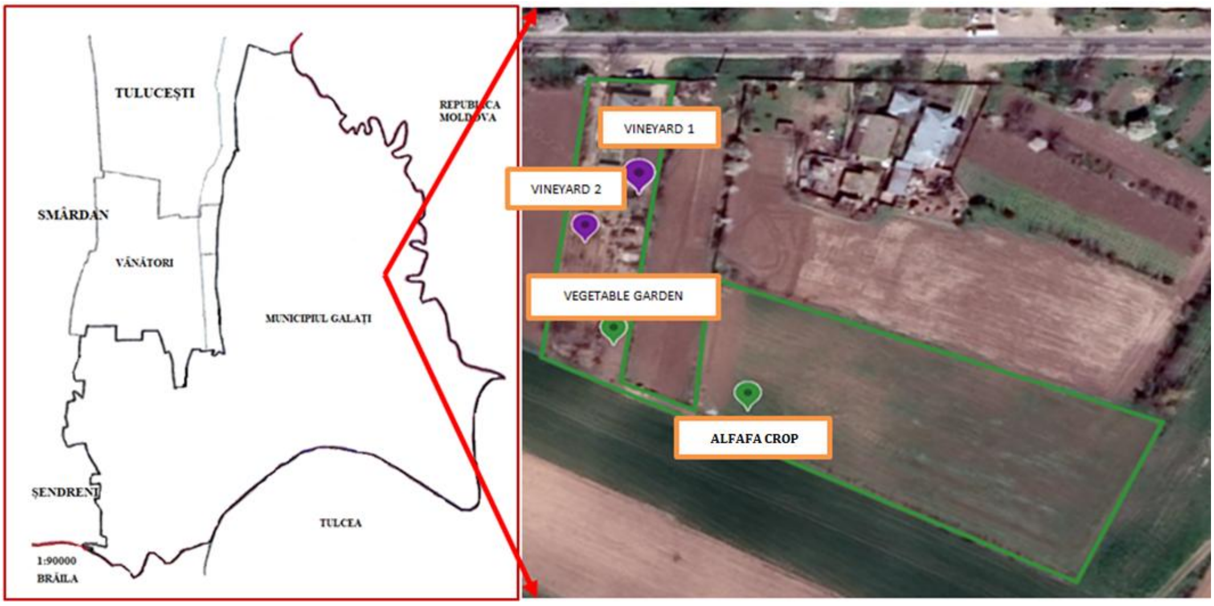

Figure 1. Area of the vegetable garden, the alfalfa crop, and the two vineyard locations [adapted from Google Earth]

Regarding the economic activity of Fundeni commune, various economic agents operate within its territory, including commercial companies, family associations, and authorized individuals. Their main areas of activity include trade, public food services, agriculture, construction, milling, dairy processing, and bakery production.

In terms of agricultural activity, the administrative territory of Fundeni commune covers a total area of 4,231 hectares. Of this, 3,179 hectares are agricultural land, distributed as follows: 2,699 hectares of arable land, 374 hectares of pastures and meadows, and 106 hectares of vineyards and orchards. The main cultivated crops include maize, barley, sunflower, alfalfa, and wheat.

The non-agricultural land, totaling 1,052 hectares, is divided as follows: 503 hectares of forests, 250 hectares of water bodies, 61.61 hectares of roads, 231.39 hectares of built-up areas, and 6 hectares of non-productive land [4, 5].

Regarding the soil samples studied in this paper, they were collected from the surface, at a depth of 5 cm and 30 cm, weighing approximately 0.5 kg. Representative samples were taken from the area of a vegetable garden, an alfalfa field, and two vineyard sites. These locations were selected with the aim of studying how agricultural practices influence soil quality and, ultimately, the quality of the crops that grow and develop in these areas. Figure 1 shows the locations on the map, generated using Google Earth.

For the analysis, the soil samples were brought to the INPOLDE center laboratories, "Dunărea de Jos" University of Galati, being left to dry, and any stones and vegetation residues were removed from the mass. The soil was finely ground and passed through a 250 μm sieve. After preparation, the soil was encapsulated using capsules for XRF analysis. For the creation of the capsules, Mylar X-Ray Film was used to support the sample, and Millipore filter paper was employed.

After the capsules were labeled, they were analyzed for heavy metal content at the European Excellence Center for Environment within the Faculty of Sciences and Environment, "Dunărea de Jos" University of Galati, using a portable Elvatech XRF device.

3. RESULTS AND DISCUSSION

To assess the degree of soil pollution, simple evaluation indices were used. Among these are: the enrichment factor (EF), the integrated pollution index (IPI), the migration index (MI), and the ecological potential risk (Ei and RI).

Enrichment factor (EF) is calculated to obtain information regarding anthropogenic pollution. It is determined by dividing the measured concentration of elements by the concentration of the same element at the European level, as presented in equation (1). The European averages proposed by Salminen [6,7,8] were taken into account for the European average in the case where the normal value declared in Romanian legislation was not identified.

$$\mathrm{EF} = \frac{C_{\mathrm{obtained}}}{C_{\mathrm{normal\_value}}} \tag{1}$$

If the result is lower than 0, pollution is not considered present. If the value is in the range 0 – 1, the soil is classified as unpolluted to slightly polluted; between 1 and 2, it is moderately polluted; between 2 and 3, it is moderately to heavily polluted; between 3 and 4, it is heavily polluted; between 4 and 5, it is heavily to extremely polluted; and if the value > 5, the soil is considered extremely polluted.

The integrated pollution index (IPI) is defined as the average value of the enrichment factors of contaminants in a sample. If the IPI value is ≤1, pollution is considered low; if 1 < IPI ≤ 2, pollution is moderate; and if IPI > 2, pollution is high [8].

The migration index (MI) is calculated to assess the mobility degree of elements using equation (2) [8].

$$\mathrm{MI} = \sum_{i=1}^{n} \left(\frac{C}{C_T}\right) d \tag{2}$$

where: n represents the number of sample layers, C is the concentration of the contaminant in layer n, C_T is the total concentration across all layers, and d represents the depth of the layer.

In this case, *n* is equal to 3, with values varying between 0.3, 5 and 30. This factor can range from 1, if the element is entirely accumulated in the first centimeter, to a maximum of 30 if it is accumulated in the last 30 centimeters. The migration potential is classified into four categories based on the obtained values: class A (<5), very low; class B (5–10), moderate; class C (10–20), high; class D (>20), very high [7,8].

The potential ecological risk index (RI) was calculated to assess the ecological risk by evaluating the impact of heavy metals in vegetables. RI was determined using equation (3) [8]:

$$\mathrm{RI} = \sum E_i = \sum T_i \cdot \frac{C_i}{B_i} \tag{3}$$

where: C_i represents the determined concentration of the element in the soil sample, B_i is the background concentration, T_i is the toxicity coefficient and E_i is the total ecological risk index [8].

Since values for T_i were only identified for specific elements, the values of T_i for the following chemical elements were considered in this study: Zn = 1, Cr = 2, Cu = 5, Pb = 5, Ni = 5, As = 10, Cd = 30, and Hg = 40 [8].

The E_i values are classified as follows: if $E_i < 40$ there is a low risk, $40 \leq E_i < 80$ for a moderate risk, $80 \leq E_i < 160$ represents a high risk, if $160 \leq E_i < 320$ is a higher risk and a severe risk is represented for $E_i > 320$.

The RI values are classified as follows: if $RI < 138$ is presented a low risk, $138 \leq RI < 276$ is a moderate risk, $276 \leq RI < 552$ is a high risk and if $RI \geq 552$ then is a severe risk [8].

Table 1. Enrichment factor (EF) and integrated pollution index values (IPI) for samples collected from vegetable garden and alfalfa crop

EF		Cr	Ni	Cu	Zn	As	Rb	Sr	Mo	Cd	Sn	Sb	Pb
Vegetable garden	0	1.30	2.39	2.23	1.44	0.85	0.74	0.55	8.50	13	1.30	-	0.58
	5	1.40	2.56	2.46	1.40	1.28	0.75	0.58	-	19	1.35	-	0.58
	30	-	2.44	2.46	1.42	1.71	0.67	0.49	2.25	-	1.15	6.40	0.58
IPI		1.30	2.50	2.40	1.40	1.30	0.70	0.50	3.60	16	1.30	2.10	0.60
Alfalfa crop	0	0.80	3	2.46	1.27	0.85	0.79	0.52	7.50	13	1.90	8.20	0.58
	5	0.70	2.94	2	1.21	1.71	0.73	0.46	9	8	-	8.80	0.58
	30	1	2.56	2.54	1.23	1	0.73	0.50	9	-	1.30	9.20	0.58
IPI		0.80	2.80	2.30	1.20	1.20	0.70	0.50	8.50	10.50	1.10	8.70	0.60

Table 2. Migration index (MI) for samples collected from vegetable garden and alfalfa crop

MI	Cr	Ni	Cu	Zn	As	Br	Rb	Sr	Zr	Mo	Cd	Sn	Sb	Pb
Vegetable garden	2.81	11.75	12.14	11.75	15.07	11.34	11.15	10.98	10.92	15.57	3.09	10.96	30	2.65
Alfalfa crop	13.78	10.86	12.41	11.68	10.87	14.24	11.41	11.76	11.26	12.44	2.09	12.37	12.31	14.16

Table 3. Potential Ecological Risk Index (RI) and total ecological risk index (E_i) for samples collected from vegetable garden and alfalfa crop

E_i	Depth (cm)	Cr	Ni	Cu	Zn	As	Cd	Pb
Vegetable garden	0	5	10.75	7.25	0.75	12	390	3.25
	5	5.73	11.5	8	0.73	18	570	3.25
	30	-	11	8	0.74	24	-	-
RI		10.73	33.25	23.25	2.22	54	960	6.5
Alfalfa crop	0	3.07	13.5	8	0.66	12	390	-
	5	2.80	13.25	6.5	0.63	24	240	3.5
	30	4.07	11.5	8.25	0.64	14	0	5.65
RI		9.93	38.25	22.75	1.93	50	630	9.15

The concentrations of heavy metals in the studied gardens for chromium (Cr) ranged from 42 mg kg^{-1} to 86 mg kg^{-1}, exceeding the legal limits in all locations except for the vegetable garden at a depth of 30 cm.

Although these concentrations are high, they do not exceed the alert threshold for less sensitive areas, which is 100 mg kg^{-1}. It was observed that in the vegetable garden, the maximum concentration was found at a depth of 5 cm, whereas in the alfalfa cultivation area, concentrations increased with depth. Changes in redox conditions, as well as other soil properties related to flooding or irrigation, can alter pH levels, potentially enabling the transition of Cr from its stable form (Cr III) to its more mobile and toxic form (Cr IV). For this reason, frequent monitoring of Cr concentrations is recommended.

According to the calculated equations, values presented in Tables 1–3, the enrichment factor (EF) values for Cr in the vegetable garden ranged between 1.30 and 1.40, and integrated pollution index (IPI) was 1.3. In the alfalfa cultivation area, the EF values ranged between 0.70 and 1, with an IPI of 0.8. Thus, in the first case, EF classifies the soil as moderately polluted, which is confirmed by the IPI value. In the alfalfa-growing soil, the EF indicates that the soil is unpolluted to slightly polluted, and the IPI, being below 1, confirms low pollution levels. Regarding the migration index (MI) values, the vegetable garden had a value of 2.81, classifying it in Class A with low migration potential, whereas in the alfalfa field, Cr showed a high migration potential.

As for the ecological risk assessment of heavy metals in plants, both ecological risk index (Ei) and potential ecological risk index (RI) indicated a low risk.

The concentrations of nickel (Ni) ranged from a minimum of 43 mg kg^{-1} to a maximum of 54 mg kg^{-1}, exceeding the normal values established by legislation in all locations. The Ni values were nearly identical at both the surface and deeper layers, indicating that its primary source is the parent material. Although the concentrations are elevated, they do not exceed the alert threshold for less sensitive areas, which is 75 mg kg^{-1}. In Romania, concentration limits are regulated by Order No. 756/1997, issued by the Ministry of Waters, Forests, and Environmental Protection. Similar to Cr, the highest Ni concentration in the vegetable garden was found at a depth of 5 cm, suggesting a correlation between these elements. In contrast, in the alfalfa cultivation area, Ni concentrations decreased with depth, indicating a potential anthropogenic pollution source. According to the calculated equations in the vegetable garden, the enrichment factor (EF) for Ni ranged between 2.39 and 2.56, with an integrated pollution index (IPI) of 2.5. In the alfalfa cultivation area, the EF ranged between 2.56 and 3, with an IPI of 2.8. Thus, in the first case, EF classifies the soil as moderately to heavily polluted, while IPI categorizes the pollution level as high. Similarly, for the alfalfa field, both EF and IPI indicate that the soil is moderately to heavily pollute. Regarding the migration index (MI) in the vegetable garden, it was 11.75, classifying it in Class C with high migration potential. In the alfalfa field, MI was 10.86, also indicating high migration potential for Ni. For the ecological risk assessment of heavy metals in plants, both the ecological risk index (Ei) and the potential ecological risk index (RI) for Ni indicated a low ecological risk.

The concentrations of copper (Cu) ranged from a minimum of 26 mg kg^{-1} to a maximum of 33 mg kg^{-1}, slightly exceeding the normal values (20 mg kg^{-1}) established by legislation in all locations. Cu concentrations were nearly identical at both the surface and deeper layers, indicating that its primary source is the parent material. Although these concentrations are elevated, they do not exceed the alert threshold for less sensitive areas, which is 100 mg kg^{-1}. In both cases, concentrations increase with depth, suggesting possible accumulation over time. In agriculture, Cu can originate from various sources, including pesticides, treatments, and manure applications.

According to the calculated equations in the vegetable garden case, the enrichment factor (EF) for Cu ranged between 2.23 and 2.46, with an integrated pollution index (IPI) of 2.4. In the alfalfa cultivation area, the EF ranged between 2.46 and 2.54, with an IPI of 2.3. Thus, in both cases, EF classifies the soil as moderately to heavily polluted, while IPI categorizes the pollution level as high. Regarding the migration index (MI) in the vegetable garden, MI was 12.14, classifying it in class C with high migration potential. In the alfalfa field, MI was 12.41, also indicating high migration potential for Cu. For the ecological risk assessment of heavy metals in plants, both the ecological risk index (Ei) and the potential ecological risk index (RI) for Cu indicated a low ecological risk.

The concentrations of zinc (Zn) in the vegetable garden soil at different depths (0, 5, 30 cm) were 75, 73, and 74 mg kg^{-1}, respectively. In the soil where alfalfa was cultivated, the concentrations were 66, 63, and 64 mg kg^{-1} at the same depths. The legal threshold for zinc is 100 mg kg^{-1}, which, as observed, was not exceeded in either case. The Zn concentrations were nearly the same at both the surface and deeper layers, indicating that the source of Zn is the parent material. According to the calculated equations in the vegetable garden, the enrichment factor (EF) for Zn ranged between 1.40

and 1.44, with an integrated pollution index (IPI) of 1.4. In the alfalfa cultivation area, the EF ranged between 1.21 and 1.27, with an IPI of 1.2. Thus, in both cases, the EF indicates that the soil is polluted, with IPI categorizing the pollution level as moderate. Regarding the migration index (MI) in the vegetable garden, MI was 11.75, classifying it in class C with high migration potential. In the alfalfa field, MI was 11.68, indicating that Zn also has a high migration potential in this soil. For the ecological risk assessment of heavy metals in plants, both the ecological risk index (Ei) and the potential ecological risk index (RI) for Zn indicated the lowest risk among all the metals studied.

The concentrations of arsenic (As) in the vegetable garden soil at different depths (0, 5, 30 cm) were 6, 9, and 12 mg kg^{-1}, respectively. In the soil where alfalfa was cultivated, the concentrations were 6, 12, and 7 mg kg^{-1} at the same depths. The legal limit for arsenic is 5 mg kg^{-1}, which, as shown, was exceeded in all cases. However, the alert threshold for sensitive areas was not surpassed. The concentration values for As in the vegetable garden soil show an increasing trend, suggesting a possible enrichment from the parental material. According to the calculated equations in the vegetable garden, the enrichment factor (EF) for As ranged between 0.85 and 1.71, with an integrated pollution index (IPI) of 1.3. In the alfalfa cultivation area, the EF ranged between 0.85 and 1.71, with an IPI of 1.2. Thus, in both cases, the soil is classified as lightly to moderately polluted. Regarding the migration index (MI) in the vegetable garden, it was 15.07, placing it in class C with high migration potential. In the alfalfa field, MI was 10.87, indicating that As also has a high migration potential here. For the ecological risk assessment of heavy metals in plants, both the ecological risk index (Ei) and the potential ecological risk index (RI) for As indicated a low ecological risk.

Silver (Ag) in the soil reduces its fertility, enters the food chain by being absorbed by plants, and can infiltrate the groundwater. Particles deposited on the surface of plant cells can inhibit the growth of plants such as radishes, lettuce, and Brussels sprouts However, for arugula crops, it was demonstrated its beneficial presence in the soil [9]. In this study, the Ag concentrations were below the detection limit of the used XRF device, as indicated in other studies conducted in Galati region, around the Steel Complex and the Prut River [10,11].

The concentrations of lead (Pb) in the garden soil at depths of 0, 5, and 30 cm were 13, 13, and 0 mg kg^{-1}, respectively. In the soil where alfalfa was grown, the concentrations at the same depths were 16, 0, and 14 mg kg^{-1}. The legal limit for Pb is 20 mg kg^{-1}, and, as it can be seen, this limit was not exceeded in any case. According to the calculated equations, the EF values for Pb in the garden soil were 0.58, with an IPI of 0.6. For the alfalfa crop, the EF values were identical to those of the garden soil. Thus, in both cases, the soil is lightly to moderately polluted. The MI value for the garden soil was 2.65, classifying it in class A (MI<5) with a very low potential for migration. For the soil where the alfalfa crop grows, the MI value was 14.16, indicating a high potential for Pb migration. Regarding the values that characterize the ecological risk of heavy metals in plants, both the Ei and RI for Pb indicated a low risk. Lead is a common contaminant in urban areas due to its use as an additive in gasoline and paint, as well as in other sources. Lead additives were first added to gasoline in Australia from 1932 to 2002 and in Romania until 2005, following the implementation of the European Union directive 98/70/EC issued in 1998 [12, 13]. In paint, lead is found in the form of lead chromate in chrome yellow, lead oxide for red lead, and lead carbonate for white lead [2]. Lead in the soil typically shows the following pattern: the highest concentrations are found in older areas, while lower concentrations are found in more recently developed areas, due to its stability in the soil. This pattern has been observed in America (Indianapolis, Indiana), Australia (Sydney), and England (London). In contrast to the permissible concentrations in our region, Australia permits lead concentrations of 300 mg kg^{-1} for residential areas and gardens, and 600 mg kg^{-1} in parks and playgrounds. Lower permissible concentrations are in California (80 mg kg^{-1} in residential areas), Canada (70 mg kg^{-1} in agricultural areas and 140 mg kg^{-1} in residential areas), Norway (100 mg kg^{-1} in parks, schools, playgrounds), and England (80 mg kg^{-1} in agricultural areas, 200 mg kg^{-1} in residential areas). Worldwide, there is no consensus on lead concentration limits, but the limits are generally higher than the concentrations found in the Earth's crust (10–23 mg kg^{-1}) [1]. In most locations, the concentrations decreased with depth, reflecting an enrichment of the upper layer with heavy metals. Additionally, the affinity of heavy metals for organic matter is well-known, which leads to their accumulation in the upper layers of soil.

The concentrations of cadmium (Cd) were 13, 19, and 0 mg kg^{-1} in the soil samples taken from the vegetable garden at depths of (0, 5, 30 cm), while for the alfalfa crop, the values were 16, 0, and 14 mg kg^{-1}. According to legislation, the normal value for cadmium is 1 mg kg^{-1}, which, as observed, was exceeded in all cases, except for the sample collected from the vegetable garden at 30 cm and from the alfalfa crop at a depth of 5 cm. The determined concentrations exceeded the alert threshold for sensitive areas (3 mg kg^{-1}) as well as the intervention threshold for sensitive areas (5 mg kg^{-1}). In most locations, the intervention threshold for less sensitive areas (10 mg kg^{-1}) was also exceeded. The values of Cd concentrations, in both cases, showed a decreasing trend, indicating potential anthropogenic pollution or an affinity for the organic material present. According to the calculated equations, the EF values for cadmium in the case of the vegetable garden ranged from 13 to 19, with an IPI of 16. For the alfalfa crop, EF values ranged from 8 to 13, with an IPI of 10.5. Thus, according to the EF values, the soil is extremely polluted with cadmium. The MI value for the vegetable garden is 3.09, and it is classified in class A with a very low migration potential. For the soil taken from the alfalfa crop, its MI value is 2.09, indicating that cadmium has a very low migration potential. Regarding the values that characterize the ecological risk of heavy metals in plants, both Ei and RI for Cd showed very high values. Thus, Ei ranged from 390 to 570 for the vegetable garden, and RI had a value of 960. These values characterize the soil as having a severe ecological risk of cadmium in vegetables. For the alfalfa crop, Ei values ranged from 240 to 390 with an RI of 630, values indicating that the taken soil presents a severe ecological risk of cadmium in the alfalfa crop. Furthermore, among metals, Cd and Zn are known to be mobile in soil and to migrate, polluting the groundwater unless retained by the clays in the upper layer.

In conclusion, regarding the vegetable garden and the location where alfalfa is cultivated, it can be observed that most of the samples had concentrations below the legislative limits. Exceptions were observed for the elements: Cr, Ni, Cu, As, and Cd. It can be noted that the concentrations of elements such as Cr (in the vegetable garden), Ni (in the alfalfa crop), and Cd (in both cases) were higher in the upper layer, indicating possible pollution due to anthropogenic activities, combined with an affinity for the organic material present. On the other hand, elements like Cr (in the alfalfa crop) and Cu (in both cases), due to their trends, presented enrichment from the parental material. Additionally, there are elements that show very similar concentrations across the three depths, such as Ni (in the vegetable garden) and Cu (in the alfalfa crop).

Therefore, in addition to the concentration of elements in the soil, it is also necessary to determine the bioaccumulation factor and the translocation factor from roots to other parts of the plants. These factors vary significantly depending on the species, type of heavy metals, and their interactions. Thus, selecting appropriate plants is crucial for human health. Generally, plants with large leaves, such as those belonging to the species *Brassica oleracea*, accumulate heavy metals in their edible parts, while the species *Lactuca sativa* also shows a high absorption capacity for various heavy metals [14].

Influence of Vineyards on Soil and Heavy Metal Concentrations

In general, sun-exposed slopes are often occupied by vineyards, which induce changes in both soil morphology and heavy metal concentrations, particularly copper (Cu), due to the use of copper sulfate for spraying. It has been observed that intensive cultivation of vineyards nearly doubled copper concentrations compared to those inherited from the parental material. As a result, copper is largely unstable and, therefore, available to plants. Heavy metals from anthropogenic sources represent the available fraction under environmental conditions. This fraction can be transported into plants via the root system and accumulate in various parts, including the grapes. The final consequence is an increase in heavy metal concentrations in wine. Continuous consumption of wine with high Cu concentrations can lead to chronic poisoning, as it has a high absorption rate at the gastrointestinal level (Cu 45-98 %, depending on the wine type) [15].

For this reason, soil samples were collected from two vineyard locations (vineyard 1 and vineyard 2) that have been cultivated for at least 23 years.

Soil quality influences vineyard growth and grape ripening by affecting soil temperature, water reserve, and mineral content. Limited water resources affect the size of grape berries, which are the basis for quality wine production. In addition to nutrients, the grapevine also absorbs nitrogen, which influences vigor, berry size, and grape composition. Ideally, vineyards are planted in areas where soil temperature, water retention capacity, and available nitrogen are optimal for the type of wine to be produced. Additionally, factors such as terrain, fertilization, and local agricultural activities are taken into consideration. The composition of the grapes depends on the climate, and the sugar content in the berries depends on the soil where the crop is located, mineral concentrations, and water content. Soil quality is often influenced by human activity, particularly through the addition of copper to protect crops from downy mildew. It has been proven that soil mineral reserves (N, P, Mg, K, Ca, Fe, B, Mn, Zn) do not directly affect wine quality. An exception is phosphorus, either from the parental material of the soil or from excessive fertilization, which can lead to an increase in the pH of must and wine. Although many famous vineyards are developed on soils rich in limestone, calcium is not mandatory for a high-quality vineyard soil, as many other renowned vineyards are developed on acidic soils with low calcium concentrations. The positive effects of calcium are indirect [16].

4. CONCLUSIONS

Soil samples were collected from a vegetable garden, an alfalfa field, and two vineyards located in Fundeni Commune, Galati County, and were subjected to both qualitative and quantitative analyses to determine heavy metal concentrations. The final results indicated exceedances of normal concentrations in the soil for elements such as Cr, Ni, Cu, As, and Cd in the vegetable garden soil. For the vegetable garden soil, the values also exceeded the alert threshold for sensitive areas and even the intervention threshold for Cd.

For the vineyard locations, the metals that exceeded normal values were Cr, Ni, Cu, Zn, As, and Cd. Moreover, Cd also exceeded the alert threshold for sensitive areas and, in several places, even the intervention threshold.

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