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Study of urban soil collected from a future residential complex area from Galati, Romania

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Abstract
In this paper, soil samples collected from an area where a real estate will develop were studied. The study presents a qualitative and quantitative XRF analysis of samples from an oil factory, Prutul S.A. and old industrial establishment, S.C. Intfor S.A. To assess the level of pollution there were calculated by using Microsoft Excel: total contamination index (HC), Saet summary index after the hazard index (ZC), total pollution index (ZCT) and ecological risk factor (ER). The conclusion for location Prutul S.A. is that the majority of the samples had concentrations below the limits proposed by legislation. In this case, the exceptions are the elements Cr, Ni, and As. Regarding S.C. Intfor S.A., due to the main area of activity, a significant amount of Zn was present, directly affecting the environmental health. Moreover, the presence of Hg, Pb, Cu, Cr, As, V, etc., makes from location F a highly polluted place.

Keywords: soil analysis, oil factory, old industrial establishment, XRF.

1. INTRODUCTION

The soil monitoring is important regardless of the type of activity carried out on it. In general, agricultural soil is less contaminated than the soils from urban areas, where heavy metals are prevalent due to traffic, industrialization and rapid urbanization. Heavy metals are natural constituents of the Earth's crust. However, due to the increasing level and diversity of human activities, they often exist in concentrations that exceed the legal limits [1]. In urban areas, atmospheric depositions are found to be the main source of heavy metal accumulation. As a fingerprint of urban pollution are Pb, Cu, Zn and Cd from different car parts and from different types of industries. Due to their toxicity, that can produce serious health risks, all the uptake pathways for the population must be taking into account [2].

2. EXPERIMENTAL

In cases where the location of the real estate development used to be in industrial areas for production or hazardous material/substance storage, specific soil or groundwater analyses are necessary. If the analyses are according to the legislation, the real estate development proceeds. If they exceed the legal limits, soil remediation is recommended.

The primary objective of this work was to determine the level of soil pollution, the possible effects of pollution on human health and the environment, and, last but not least, to provide viable alternatives for the restoration of contaminated soil. This work has focused on studying soil quality by collecting samples from different areas, with a focus on the activities that have taken place or are currently taking place in the area were a new real estate will develop.

Site description

Prutul S.A.

Prutul S.A. factory is located within city limits in Galați, and it uses approximately 900 tons of seeds per day during its 330 days of operation per year. It is one of the leading producers of vegetable oil in Romania, been established in the year 1992, with CAEN 1041 that corresponds to the manufacturing of oils and fats.

The samples were collected on November 2002, near the oil factory, from surface (0 cm) and a depth of 10 cm, as can be seen in **Figure 1**. The locations were named as A, B, C and D.

Sampling area	Sample name	Depth (cm)	Latitudine (N)	Longitudine (E)
Prut S.A.	A	0	45°26′28"	28°03′40"
		10		
	B	0	45°26′25 "	28°03′46 "
		10		
	C	0	45° 25′26"	28° 03′41"
		10		
	D	0	45° 26′26"	28° 03′46"
		10		
S.C. Intfor S.A.	E	0	45° 26′11"	28 °04′08"
		10		
	F	0	45° 26′11"	28 °04′12"
		10		
	G	0	45° 26′11"	28 °04′07"
		10		
	H	0	45° 26′10"	28 °04′10"
		10		

Figure 1. Coordinates and satellite images of the sampling locations

S.C. Intfor S.A.

S.C. Intfor S.A. was established following the former Laminorul de Tablă in Galați, founded in the year 1990. In terms of its business activities, the company was involved in galvanizing steel, manufacturing ducts, metal structures, reinforcing PVC joinery, as well as producing cold-rolled pipes and profiles.

The samples were collected on November 2002, from surface (0 cm) and a depth of 10 cm, as can be seen in **Figure 1**. The locations were named as E, F, G and H.

Method of analysis

For analysis, the soil samples were left to dry in the laboratory by exposing to open air. The next step involved removing debris such as stones, glass, plastic, and vegetation from the samples. To pass through a 250 µm sieve, the dried soil was finely ground using a mortar and pestle. Following these steps, the soil was encapsulated using special capsules designed for ED-XRF analysis. The capsule assembly included elements specified in the working protocols, such as films to support the sample, Mylar X-Ray Film, and Millipore filter paper [3].

Due to the fact that conventional methods for determining concentrations are costly and involve long and complicated sample preparation protocols, it was used the portable XRF device, which represented an optimal alternative. This is because the results are obtained fast and efficient, especially in terms of costs. Additionally, this method is non-destructive, sensitive, multi-elemental, and precise, used in a wide range of analyses and studies, starting from art up to industrial applications. The analyses are performed on samples that do not require digestion or additional preparation, and the results provide a large number of elements with concentrations determined in a relatively short time [3].

3. RESULTS AND DISCUSSION

The soil of cities and industrial areas is usually contaminated with many specific elements, which subsequently necessitates the characterization of heavy metal pollution. To assess the degree of soil pollution with heavy metals, it is recommended to calculate equations that relate the concentrations of normal soil elements to those that have been determined. With the help of the results, a classification of soil pollution can be carried out. It starts with the total contamination index (HC), as presented in **equation (1)** [4, 5]:

$$HC=\sum Kk_i \text{ , where } Kk_i = \frac{c_i}{c_{ib}} \quad (1)$$

$\mathbf{C_i}$ is the element concentration in the sample and $\mathbf{C_{ib}}$ is the background elemental concentration that in this case was the normal concentration presented in the Romanian legislation [6].

The total contamination index does not differentiate heavy metals based on their harmful effects on the environment. Therefore, it is recommended to determine the Saet summary index after the hazard index (ZC) as presented by **equation (2)**:

$$ZC=\sum Kk_i - (n-1) \quad (2)$$

Here, 'n' represents the number of elements that where considered. If ZC is greater than 16, there is no hazard. If 16 < ZC < 32, there is a moderate hazard. If 32 < ZC < 128, there is a hazard. ZC greater than 128 indicates extreme hazard.

According to the state standard GOST 17.4.102-83, heavy metals and metalloids are classified into three hazard classes. The first class with high hazard includes the elements: As, Cd, Hg, Se, Pb, Zn; the second class with moderate hazard includes: B, Co, Ni, Mo, Cu, Sb, and Cr; the third class with low hazard includes: Ba, V, W, Mn, and Cr.

The toxicity of these elements has been determined separately, considering their toxicity classes. Thus, the total pollution index (ZCT) is calculated while taking into account the correction factors for the toxicity of the elements, as presented in **equation (3)**:

$$ZCT = 1.5ZC_{C(1)} + 1ZC_{C(2)} + 0.5ZC_{C(3)} \quad (3)$$

Here, $ZC_{C(1)}$, $ZC_{C(2)}$, and $ZC_{C(3)}$ represent the hazard index for the first, second, and third classes of hazard, respectively, and 1.5, 1, and 0.5 are the corresponding correction factors for their toxicity.

In addition, the ecological risk factor, ER, has been determined, which is used to quantitatively express the potential ecological risk of a contaminant. This concept was initially suggested by Hakanson in 1980. ER reflects the biota's stability against the potential toxicity of substances and demonstrates that this is derived from heavy metals. It is calculated using the following **equation (4)**:

$$ER = T_r \cdot C_f \quad (4)$$

In this equation, Tr is the toxic response factor for a specific substance with a concentration Cf. For As, Cr, and Ni, the values of Tr were 10, 2, and 6, respectively, and these are used for Prutul S.A. For S.C. Intfor S.A., the values used were 2, 5, and 1 for Cr, Pb, and Zn, as indicated in the study by Li et al. [7].

The calculation involves summing the products of Tr and (Cf / Cf_{ref}) for each substance. If ER is less than 40, there is a low ecological potential. If ER is found between 40 and 80, the ecological potential is moderate. For ER values between 80 and 160, there is a significant ecological potential. ER values between 160 and 320 indicate a high ecological potential. If ER is equal to or greater than 320, the ecological potential is very high. These thresholds are used to categorize the ecological risk associated with the contaminants [8, 9, 10]. It's mentioned that all these equations have been calculated using the Microsoft Excel application.

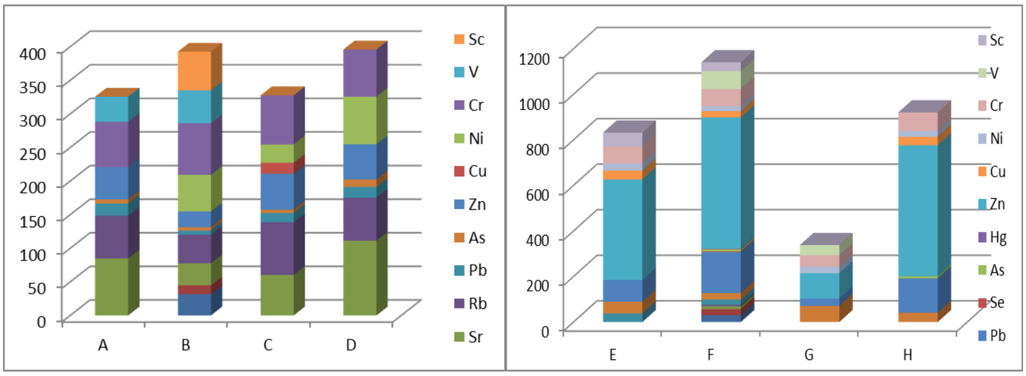

Figure 2. The total elemental concentrations for Prutul S.A. (A, B, C and D) and S.C. Intfor S.A. (E, F, G and H)

Prutul S.A.

The study of heavy metals is important to provide a basis for planning a strategy to improve environmental quality and achieve sustainable urban development [11]. Samples labeled from A to D were collected from the four cardinal points around Prutul S.A. Each sample was analyzed three times, and the average of the obtained values was calculated. In this work, the focus is on understanding how pollution in the top 10 cm of soil can influence the quality of life and the environment. An average of the concentrations obtained from the surface and 10 cm depth was taken into account. Attention was directed towards As, Cr, and Ni because they showed the most repeated deviations from normal values.

For Prutul S.A., after calculating the total contamination index, ZC, its value indicates that there is no hazard. This information is presented in **Table 1**.

Tabel 1. The total pollution index (ZCT) for Prutul S.A.

Kki	**As**	**Cr**	**Ni**	**ZC**	**ZCT**
A	1.20	2.25	nd	1.45	4.05
B	0.97	2.56	2.73	4.25	6.73
C	0.93	2.44	1.36	2.73	5.20
D	2.19	2.34	3.55	6.08	9.18
				14.51	25.16

The total pollution index (ZCT) has been calculated, taking into account the correction factors for the toxicity of the elements, and it is presented in **Table 1** in the last column. After this correction, it can be observed that the location of Prutul S.A. is characterized by a situation of moderate hazard. This suggests that, when considering the toxicity of the elements, the ecological risk at **Prutul S.A.** is in a moderate range.

The ecological risk factor (ER), calculated and presented in **Table 2**, indicates a moderate ecological potential for As at locations A, B, and C. A significant ecological potential is observed for As at location D and for Cr at all locations. Ni presents a high ecological potential at location C and a very high ecological potential at the other locations.

Regarding the potential ecological risk index (RI), location A has a moderate ecological potential, locations B and C have a significant ecological potential, and location D has a very high ecological potential. These conclusions can also be observed in **Figure 2**, where the summed concentrations of the elements obtained in the XRF analysis are graphically represented.

Table 2. The ecological risk factor (ER) and the potential ecological risk index (RI) for Prutul S.A.

ER	As	Cr	Ni	RI
A	59.90	135.22	nd	195.12
B	48.30	153.34	327.05	528.68
C	46.65	146.30	163.05	356.00
D	109.65	140.35	421.05	671.05

S.C. INTFOR S.A.

Table 3. The total pollution index (ZCT) for S.C. INTFOR S.A.

Kki	Cr	Pb	Zn	ZC	ZCT
E	2,49	4,75	4,42	9,66	16,24
F	2,55	9,00	5,75	15,31	24,69
G	1,67	1,61	1,12	2,39	5,75
H	2,74	7,53	5,75	14,02	22,67
				41.38	69.35

The total pollution index (ZCT) has been calculated, taking into account the correction factors for the toxicity of the elements, and it is presented in **Table 3**, the last column. After this correction, it can be observed that there is a hazard.

The ecological risk factor (ER), calculated and presented in **Table 4**, indicates a significant ecological potential for Cr at locations E, F, and G, as well as for Zn at location G. A high ecological potential is observed for Cr at location H and for Pb at location G. A very high ecological potential is associated with the elements Pb and Zn at locations E, F, and H.

This information suggests that the locations E, F, G, and H exhibit significant ecological risks and potential pollution, particularly for Cr, Pb, and Zn. The correction for toxicity factors highlights these risks.

Table 4. The ecological risk factor (ER) and the potential ecological risk index (RI) for S.C. INTFOR S.A.

ER	Cr	Pb	Zn	RI
E	149,69	474,74	441,79	1066,21
F	153,08	900,28	575,41	1628,76
G	100,05	160,56	111,81	372,43
H	164,50	753,04	575,26	1492,79

Regarding the potential ecological risk index (RI), it shows a significant ecological potential for location G, and locations E, F, and H exhibit a very high ecological potential. These conclusions are also reflected in **Figure 2**, where the summed concentrations of elements obtained from the XRF analysis are graphically represented.

Among all the locations, G is the least affected by pollution, while F is the most affected. This information provides a clear indication of the varying degrees of ecological risk and pollution among the different sites.

4. CONCLUSIONS

In conclusion, regarding the location Prutul S.A., it can be observed that the majority of the samples had concentrations below the limits proposed by legislation. Exceptions are the elements Cr, Ni, and As. Location D stands out as a potential source of pollution due to anthropogenic activities. On the other hand, locations A, B, and C show a predominantly increasing trend in concentration values, likely attributed to either the parent material or historical pollution. The non-uniformity of the results suggests intense human activity on the soil. Location D, which is near a waste disposal area, may be a source of contamination. In the other areas, various reconstruction and consolidation activities have taken place, leading to soil mixing and, consequently, the dispersion of soil elements.

Location F presents a clear anthropogenic enrichment trend. This is a due to the fact that this location is very close to one of the production halls of S.C. Intfor S.A., a company engaged in producing metallic profiles and galvanizing steel. It is not uncommon for industrial processes, such as galvanization, to involve various elements, and these processes can lead to the release of certain metals into the environment, contributing to localized pollution. This information underscores the importance of assessing and mitigating the environmental impact of industrial activities on nearby areas. Due to the main area of activity in this area, a significant amount of Zn is present, directly affecting the environmental health. Moreover, the presence of Hg, Pb, Cu, Cr, As, V, etc., makes location F highly polluted, with an ecological risk factor of 1629, considered very high. In practical terms, this ecological risk factor is at least 8 times higher than the value at location A (195), which was the lowest. Additionally, a portion of the Pb concentration may originate from the heavy traffic on the road artery near locations E, F, and H. In conclusion, regarding the location of S.C. Intfor S.A., it can be observed that the majority of the samples showed concentrations below the limits proposed by legislation, with the exception of the elements Cr, Cu, Pb, As, and Zn. However, the presence of elements such as Sb, Sn, Cd, Ag, Se, Ag, Hg, and V at location F deviated from this pattern. These findings suggest that there may be pollution at location F due to human activities. In contrast, locations H, in most cases, exhibit a trend of increasing concentrations with depth, which can be attributed to either the parent material or past pollution.

After analyzing the concentration of heavy metal elements, it is recommended that any remediation efforts take into account several important factors such as: speed and efficiency, cost-effectiveness, suitability for the type of pollution and land use after remediation.

In this context, it is recommended to use in situ physical remediation methods, which are suitable for light pollution and, particularly, for stable pollutants. Two methods can be employed, which can be combined for optimal effectiveness:

- covering contaminated soil with uncontaminated soil: this involves placing a layer of uncontaminated soil with a thickness of 40-70 cm over the contaminated soil to prevent the transfer of contaminants from the soil to plants. Over time, potential issues may arise due to natural soil mixing by earthworms or field mice. To prevent such situations and to monitor the treatment's effectiveness, it is recommended to drill monitoring wells to regularly check the quality of water.
- sealing the area with an asphalt layer: this method involves sealing the area with a layer of asphalt, commonly used as a base for structures like roads, parking lots, or buildings. Typically, a layer of asphalt with a minimum thickness of 10 cm and a maximum of 20 cm is recommended. It is crucial in this case to design and implement an effective rainwater drainage system [12].

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