Distribution of Heavy Metals in Soil of the Temporary Municipal Solid Waste Landfills in the City of Botosani, Romania

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Abstract. In this study, the potential of soil contamination with heavy metals was evaluated, respectively Cd, Cu, Mn, Ni, Pb and Zn, in the area of the temporary municipal solid waste landfill located in the city of Botosani, Romania. The presence of heavy metals in the investigated area decreased in the sequence (mg/kg): Mn (860) > Zn (93.6) > Ni (48.9) > Cu (30.2) > Pb (20.1) > Cd (0.76), registering a slight increase in the southern part of the deposit as a result of the direction of rainwater flow. The concentrations of heavy metals in the soil in the vicinity of the temporary municipal waste landfill were similar to background levels for agricultural soils in Romania. The quantification of heavy metals in the soil did not show exceedances of the reference concentrations and no environmental pollution with heavy metals was identified.

1. Introduction

The main sources of soil pollution are the storage of solid waste, the large-scale use of fertilizers and pesticides in agriculture [1,2] as well as the atmospheric deposition of toxic substances produced as a result of human activities [3,4,5].

Soil contamination with toxic pollutants such as heavy metals is a global problem [6,7,8,9] that requires the identification of radical and practical solutions to reduce the risks as much as possible [10,11]. Once in the soil, heavy metals cause imbalances in the chemical and biological processes in it, because they reduce biological activity, reduce nitrification processes, and have a toxic effect on plants [12]. Heavy metals from plants are transmitted through food chains to humans [13,14].

Due to their easy and cost-effective operation, landfills are the most widely used method of municipal solid waste disposal in the world [15]. Soil contamination leads to changes in soil fertility and the composition of biocenoses on neighboring lands [16].

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In general, as a result of the lack of facilities and poor exploitation, waste deposits are among the objectives recognized as generators of impact and risk for the environment and human health [15,17]. Very large quantities of waste from cities or industrial waste are stored on the ground, which sometimes end up having direct consequences on human settlements. Each inhabitant of European cities "produces" approximately 1 kg of waste per day [18].

Non-waterproofed urban waste deposits are often the source of contamination of groundwater with nitrates and nitrites, but also with other polluting elements. Both the leachate generated by the deposits and the water flowing down the slopes influence the quality of the surrounding soils, which has consequences on their use. Soil pollution in areas near a landfill and areas contaminated by landfill leachate is a serious concern in municipal solid waste management [19,20].

In Romania, landfill represents the main method of waste disposal, approximately 57% of the total amount of municipal waste is being stored for disposal. One of the pollutants that become an indicator to detect the occurrence of soil contamination is heavy metals like Cd, Cu, Mn, Ni, Pb and Zn contamination in landfill leachate.

In this work, our goal was to identify the heavy metals and their distribution in soil from the area of the temporary municipal solid waste landfill in the city of Botosani, Romania.

2. Materials and Method

2.1. Sampling Locations

In this study, to quantify the impact on the soil generated by the household waste storage activity, soil samples were taken from 12 sampling points, respectively 40 soil samples.

Soil samples were taken from the perimeter of the waste landfill - 4 sampling points, 12 soil samples and from the adjacent land, at different distances from the southern part of the investigated perimeter 8 sampling points, 28 soil samples, in order to identify the area of dispersion of contamination. The location of the soil sampling points is represented in fig. 1.

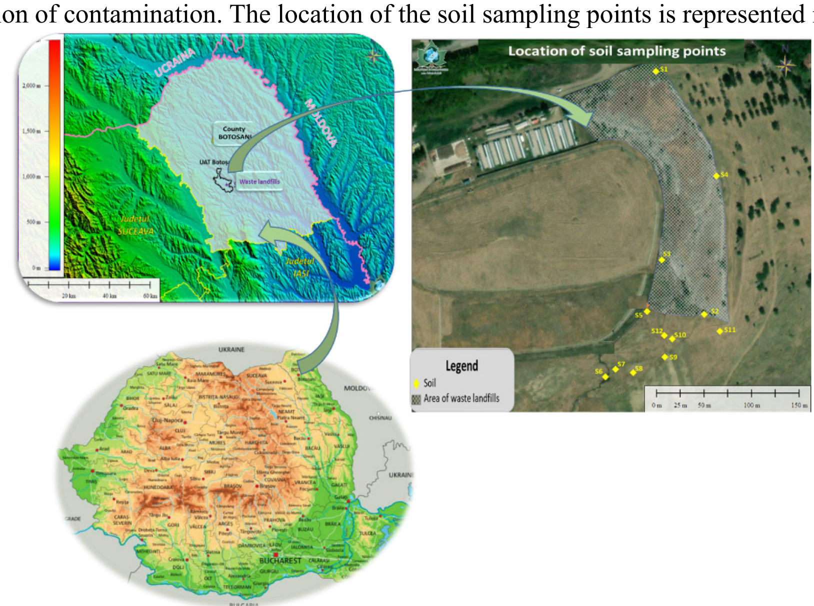

Fig. 1. Location of soil samples taken from the area of the investigated objective

2.2. Methods

The sampling method was based on the provisions of the national standard "Collection of samples for pedological and agrochemical studies" and the recommendations contained in the National Regulations on the assessment of environmental pollution [21].

Soil samples were taken from different depths, namely 10 cm, 30 cm and from 50 to 50 cm to the depth allowed by the lithology of the area of interest, after removing the superficial layer (vegetable soil). All samples were collected in the absence of groundwater.

The samples were taken with the help of a motophoresis and a manual boring, with the collection of sufficient amounts of soil for analysis, which were transferred into labeled plastic containers. The collection tool was cleaned after each sampling, to prevent accidental contact of substances contained in the samples that may alter the results of the analyses.

2.3. Chemical analysis of heavy metals.

The soil samples were dried at room temperature, homogenized, mortared and sieved. An amount of approximately 0.5 g of soil from the 150 μm homogenized fraction was mineralized with Aqua Regia ($HCl:HNO_3$ in a 3:1 ratio) using a microwave digestion method. The content of heavy metals Cu, Cr, Mn, Pb, Ni and Zn were determined by high resolution atomic absorption spectrometry with continuous optical source in flame with HRCSAAS ContrAA 700 Spectrometer.

The following standards were used for the processing and analysis of soil samples: ISO 11464 – Soil quality. Pretreatment of samples for physical-chemical analysis; ISO 11466 – Soil quality. Extraction of soluble trace elements (Cd, Cu, Cr, Mn, Ni, Pb, Zn) in aqua regia; ISO 11047 – Soil quality. Determination of metals from soil extracts in aqua regia – Methods by flame atomic absorption spectrometry and electrothermal atomization.

The interpretation of the results regarding the identification and quantification of heavy metals in the soil samples was carried out on the basis of land use according to Order 756/1997 [22], respectively for sensitive use in the situation where the land is used for residential and recreational areas, for agricultural purposes, as protected areas or sanitary areas with restrictions and less sensitive use in the situation where the land is used for industrial or commercial activities.

3. Results and Discussion

The distribution of the concentration of soil pollutants in the investigated area was carried out by interpolating the values obtained for the investigated pollutants in the 12 sampling points by using the Voxler software, produced by Golden Software. XYZC format input files were created where:

- X and Y represent the coordinates of the sampling points in the reference system Stereo 70/datum Dealul Piscului 1970
- Z represents elevation values considering the depths from which the samples were taken
- Component C contained the concentration values for each of the analyzed analytes.

Using an inverse distance method, a three-dimensional interpolation domain was obtained for each element, whose relative positioning to the warehouse area is shown in Fig. 2.

The classification of the interpolated values (color codes) took into account both the alert threshold values for sensitive uses and the normal values for Cd, Cu, Ni, Pb, Zn and Mn.

Below are the representations of the interpolation results (Fig. 3-8), both in general view and sections across the width of the interpolation domain, located from 20 to 20 m and shown in orange in Fig. 2. The perimeter of the waste dump is also represented.

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Fig. 2. Localization of the three-dimensional interpolation range of element values in soil samples

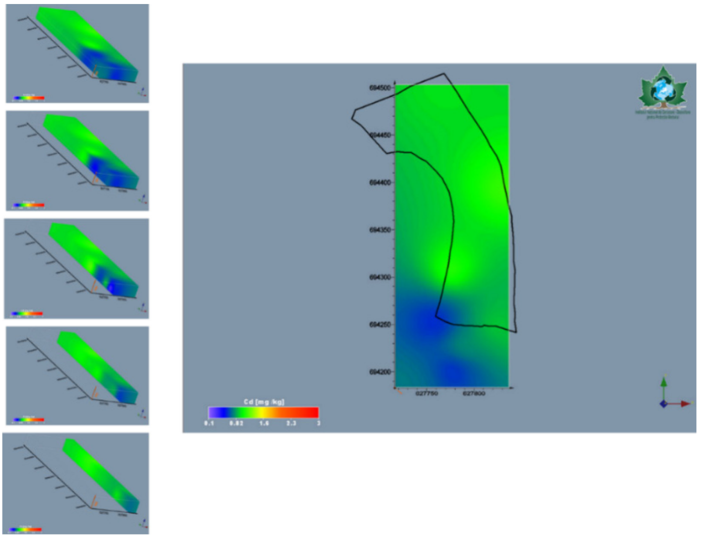

Fig. 3. Distribution of Cadmium concentration (mg/Kg s.u.), waste deposit area

The distribution of cadmium represented in Fig. 3 indicates an accumulation tendency in the area of the landfill, but the concentration value is in the range of normal values in the soil, respectively lower than 1 ppm.

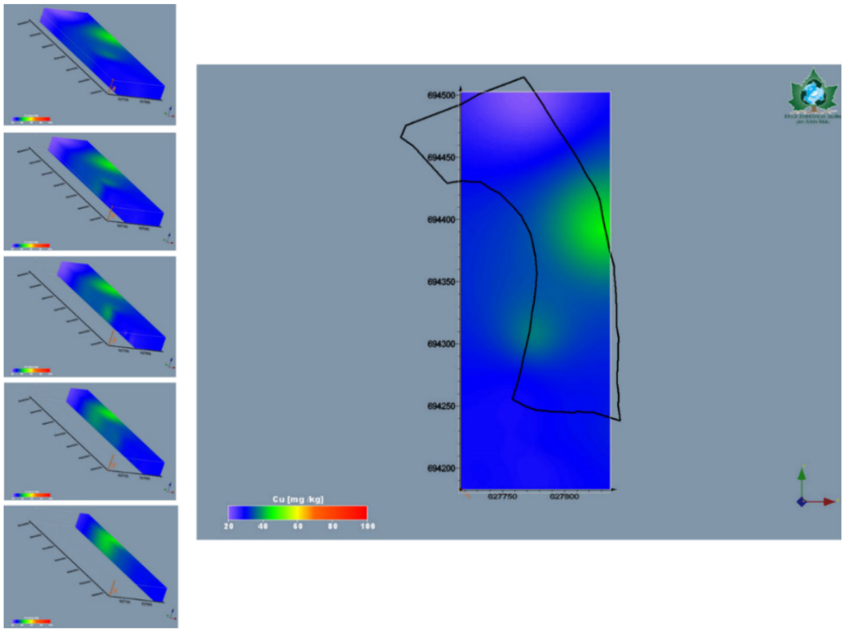

Fig. 4. Distribution of Copper concentration (mg/Kg s.u.), waste deposit area

The distribution of copper shown in Fig. 4 indicates a higher value in the center area of the landfill, respectively 35.6 ppm being close to the level of normal concentration values (22.8 ppm) at its edge.

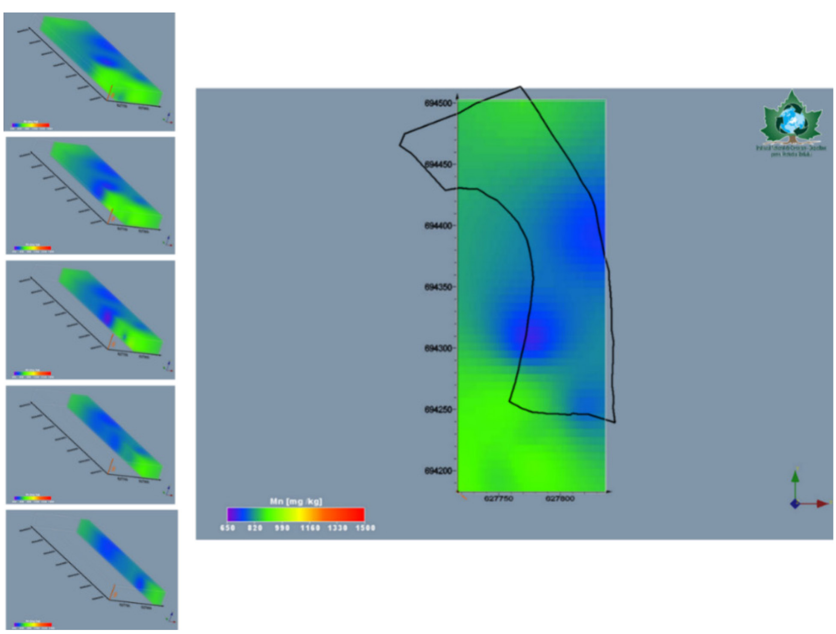

Fig. 5. Distribution of Manganese concentration (mg/Kg s.u.), waste deposit area

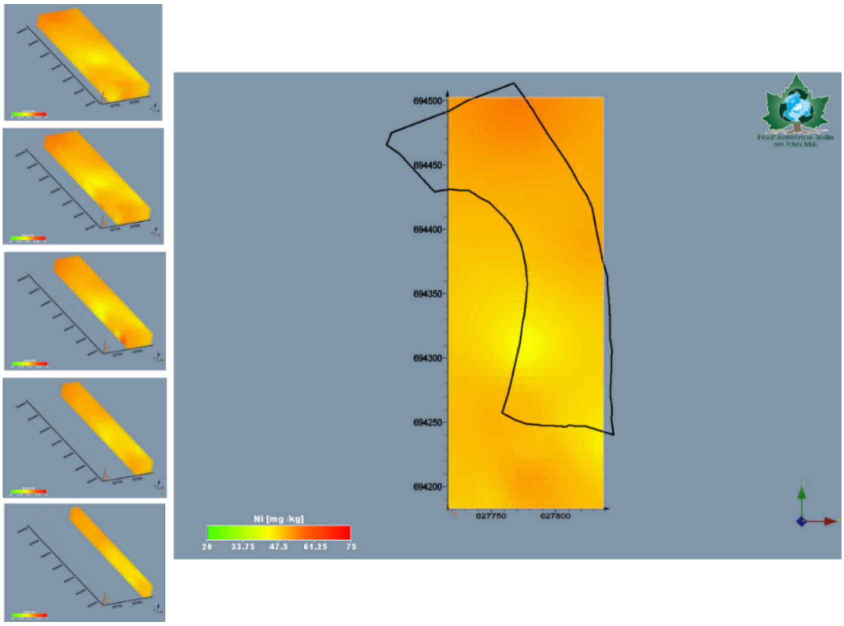

Fig. 6. Distribution of Nickel concentration (mg/Kg s.u.), waste deposit area

Manganese shows a tendency to accumulate in the border area of the landfill (Fig.5), while nickel has a relatively uniform distribution with a slight increase in the northern area of the landfill (Fig.6).

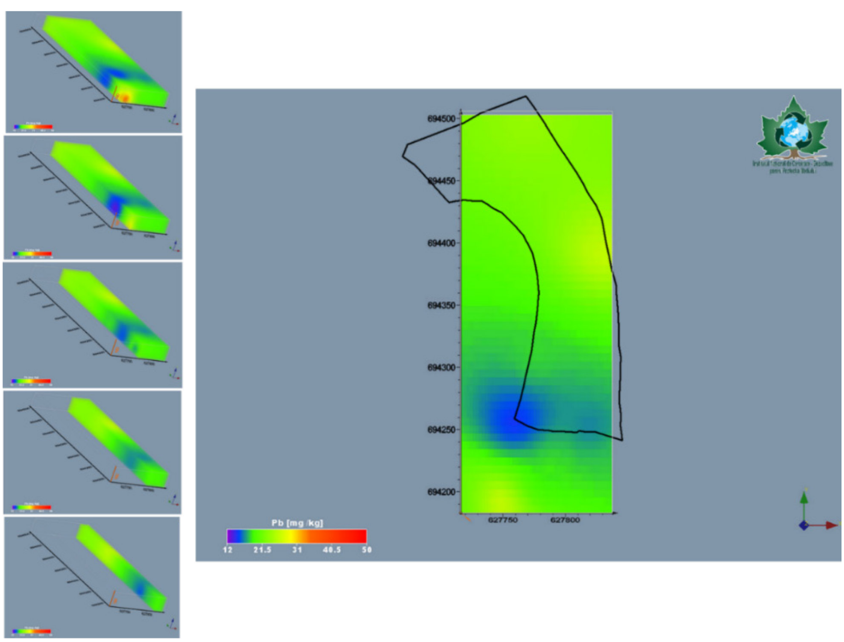

Fig. 7. Distribution of Lead concentration (mg/Kg s.u.), waste deposit area

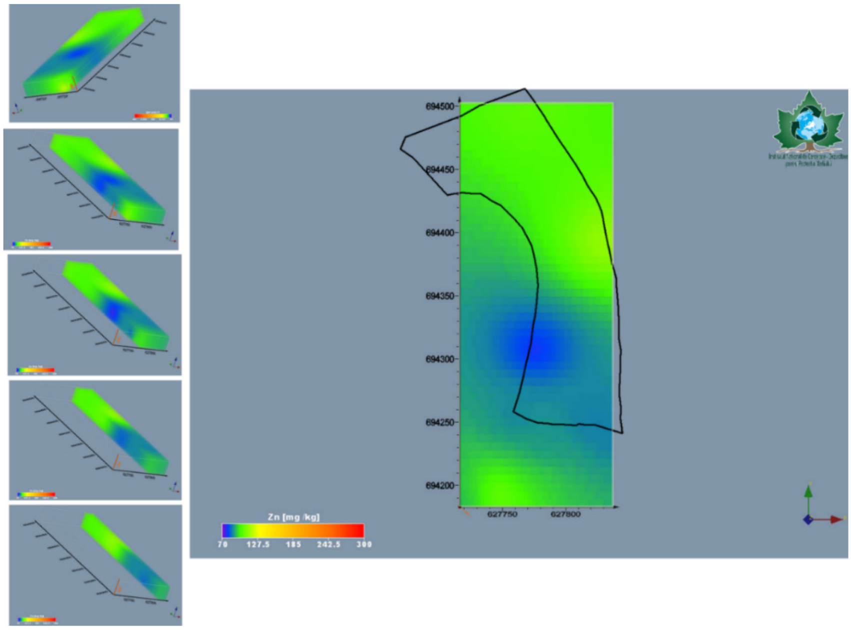

Fig. 8. Distribution of Zinc concentration (mg/Kg s.u.), waste deposit area

The distribution of heavy metals like lead and zinc indicates an accumulation tendency in the northern area towards the center of thel andfill (Fig. 7, Fig 8). The average concentration value is 20.1 ppm for lead and 93.6 ppm for zinc.

The interpretation of the results of the investigations was carried out considering the characterization of the analyzed land as land with less sensitive use for the samples taken from the perimeter of the temporary waste landill (S1, S2, S3, S4) and as land with sensitive use for the samples taken from the area adjacent to its perimeter (between S5 and S12).

- S1
  - The concentration values of zinc, cadmium, copper, manganese, nickel, lead fall within the range of normal values for most of the analyzed samples, with the exception of the concentration values of cadmium, copper and nickel recorded at 0.1 m, of copper and nickel at 0.3 m and of nickel at a depth of 0.5 m, which were below the alert threshold for land with less sensitive use;
- S2
  - The values of the determined metal concentrations fall within the range of normal values;
  - The values of copper, nickel, zinc and manganese concentrations increase slightly with the depth of the analyzed layers, the highest values being determined at a depth of 0.3 m, decreasing at a depth of 0.5 m;
- S3
  - The values of the concentrations of cadmium, copper, nickel, lead and zinc exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with less sensitive use;
- S4
  - The values of the concentrations of cadmium, copper, nickel, lead and zinc exceed the range of normal values in the surface layer, respectively copper and nickel and at the depth of 0.3 m and 0.5 m, the recorded values do not exceed the alert threshold value for lands with less sensitive use;

- S5

- The values of the concentration of cadmium, lead and zinc do not exceed the range of normal values in all the analyzed depth layers;
- The copper and nickel concentration values exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with sensitive use;
- Manganese concentration values vary between the 7 analyzed layers, tending to accumulate at the depth of 1.0 m, 2.0 m and 3.0 m, respectively, where it exceeds the normal value, but does not exceed the alert threshold value for land with sensitive use;

- S6

- The values of the concentration of cadmium and zinc do not exceed the range of normal values in all the analyzed depth layers;
- The copper and nickel concentration values exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with sensitive use;
- Manganese concentration values vary between the 7 analyzed layers, having, the highest value being determined in the sample taken at 2.5 m (1035 ppm) where it exceeds the normal value, but does not exceed the alert threshold value for land with sensitive use;

- S7

- The cadmium concentration values do not exceed the range of normal values in all analyzed depth layers;
- The copper and nickel concentration values exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with sensitive use;
- Manganese concentration values vary between the 3 analyzed layers, exceeding the normal value in the samples taken from 0.5 m (1023 ppm) and from 1.0 m (935 ppm), respectively, but do not exceed the alert threshold value for land with sensible use;
- The values of lead and zinc concentrations slightly exceed the normal values in the soil in the 0.5 m layer, but do not exceed the alert threshold value for land with sensitive use;

- S8

- The values of the concentration of cadmium and lead do not exceed the range of normal values in all the analyzed depth layers;
- The concentration values of copper, manganese and nickel exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with sensitive use;
- The zinc concentration values fall within the range of normal values, except for the sample taken from the 0.5 m layer where the zinc concentration slightly exceeds the normal value in the soil (101.59 ppm);

- S9

- The values of the concentration of cadmium and zinc do not exceed the range of normal values in all the analyzed depth layers;
- The concentration values of copper, manganese and nickel exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with sensitive use;
- Manganese and lead concentration values fall within the range of normal values, except for the sample taken from the 0.5 m layer where the concentration of manganese (1008 ppm) and that of lead (21.29 ppm) slightly exceed the normal value in the soil;

- S10

- Cadmium concentration values do not exceed the range of normal values in all analyzed depth layers

- The copper and nickel concentration values exceed the range of normal values in all analyzed depth layers, but do not exceed the alert threshold value for land with sensitive use;
- Manganese and zinc concentration values fall within the range of normal values, except for the sample taken from the 1.0 m layer where the concentration of manganese (1028 ppm) and that of zinc (117.58 ppm) slightly exceed the normal value in the soil ;
- The lead concentration values exceed the normal values in the soil on the surface, and at a depth of 1.0 m, but do not exceed the alert threshold value for land with sensitive use;

➢ S11 and S12

The samples from these points were taken only from the surface of the soil and the following are found:

- The concentration values of cadmium, manganese and lead do not exceed the range of normal values;
- The copper and nickel concentration values exceed the range of normal values, but do not exceed the alert threshold value for land with sensitive use;
- The zinc concentration value slightly exceeds (105.5 ppm) the normal value in the soil in the sample taken from point S11, but does not exceed the alert threshold value for land with sensitive use;

The presence of heavy metals in the investigated area decreased in the sequence (mg/kg): Mn (860) > Zn (93.6) > Ni (48.9) > Cu (30.2) > Pb (20.1) > Cd (0.76), registering a slight increase in the southern part of the deposit as a result of the direction of rainwater flow. The investigations regarding soil contamination with heavy metals have highlighted the fact that the determined heavy metal content is far below the alert and intervention threshold values for the types of sensitive use imposed by Romanian law [22], being even below or around the value for the normal content in soils, indicated in the same order.

4. Conclusion

The investigations carried out on the impact of the temporary urban waste landfill by contaminating the soil with heavy metals highlighted the fact that the determined heavy metal content is far below the alert and intervention threshold values for the types of sensitive use imposed by the legislation on soil protection, so that it does not influence the quality of the soil, being similar to agricultural land. Heavy metals concentrations did not exceed reference concentrations and did not indicate environmental pollution with heavy metals.

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