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Assessment of heavy metals contents in soil from an industrial plant of southern part of Romania

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Abstract. An investigation of soils is performed in order to establish the impact of heavy metal pollution near an industrial power plant. The use of synthetic products (e.g. pesticides, paints, batteries, industrial waste and land application of industrial or domestic sludge) can result in heavy metal contamination of soils. Heavy metals also occur naturally, but rarely at toxic levels. Soil samples from different depth were drawn. Heavy metals such as Pb, Zn, Cu and Mn were analysed to establish the level of contamination relative to maximum limits enforced by environmental protection agencies. In addition, a measurement for the total organic carbon (TOC) concentration is accomplished.
Key words: Industrial soils, heavy metals, organic carbon.

Rezumat. Studiul s-a realizat în vederea stabilirii impactului poluării cu metale grele asupra unor soluri provenite dintr-o zona industrială. Contaminarea solului cu metale grele poate rezulta în urma unor deversări ale deşeurilor industriale, folosirea unor pesticide şi datorită altor lucrări agricole. Au fost recoltate probe de la diferite adâncimi în vederea monitorizării metalelor grele (Pb, Zn, Cu şi Mn) stabilindu-se nivelul de contaminare al acestora raportat la cel impus de agenţia de protecţie a mediului. Pentru a întregi acest studiu, s-a determinat şi carbonul organic total (TOC) din aceste probe.
Cuvinte cheie: sol contaminat, metale grele, carbon organic.

Introduction. Soil pollution is caused by the presence of man-made organic chemicals or other alteration in the natural ecosystems. This type of contamination arises from the rupture of underground storage tanks, application of pesticides, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides and heavy metals (Fleşeriu 2010; Mathur et al 2010; Coşier & Petrescu-Mag 2008). Chemical and metallurgical industries are the most important sources of heavy metals in soils and sediments (Lokeshwari & Chandrappa 2006). Soil pollution can lead to water pollution if toxic chemicals leach into groundwater or if runoff reaches streams, lakes or oceans (Boukhalfa 2007). The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organisms activity and plant growth (de Vries et al 2007).

Heavy metals and other potentially toxic elements are the most serious soil pollutants. Not unexpectedly, soil contaminants can have significant deleterious consequences for ecosystems. Maximum allowed limits for contaminants are enforced in many countries. Thus, representative soils from Turceni industrial area, sampled from eight (2m, 3.5m, 5.5m, 6.3m, 7.5m, 8.9m, 13m, 14.5m) different depths were selected to be measured. Turceni is a city located in south of Gorj county and came around two industrial projects in the area: Hydropower and Thermal Power Turceni, which form Turceni Energy Complex. The whole activity of small town revolves around them. City Turceni lies largely on the stream of Jiu and Jilt. In terms of climate, the area falls within the specific units southwest climate, a hilly continental climate, with calm winters and cool and dry summers, with sufficient rainfall, but uneven.

Materials and Methods

Instrumental. The pH measurements were done using normal pH-meter. The concentrations of the organic carbon were determined in aqueous solutions and heavy metals (Mn, Cu, Pb and Zn) were determined in aqua regia extractant.

Soil Analysis. For the measurement of TOC in the soil, a paste was prepared by mixing 25 g of the dry soil with 100 mL distilled water. The paste was left to settle for 24 hours. After decantation, a suction pump was used to extract the solution from the paste. The following step was to filter the solution through a 0.45 μm pore diameter membrane filter after the collecting was done. The soil sample solution was analyzed for the total organic carbon using an instrument with NDIR (non dispersive infrared) detector. Carbon in the sample is first converted to CO_2 by oxidation until combustion at 680-1000^{0}C. Sensitive to the absorption frequency of CO_2, the NDIR detector generates in a first step a non-linear signal that is linearized and integrated over the sample analysis time. The resulting area is then compared to stored calibration data and a sample concentration is calculated.

The pH was determined on 1:2.5 (air-dry soil weight:volume of water) soil suspension using a normal pH meter.

Total concentrations of Mn, Cu, Pb and Zn in the soils were analyzed according to aqua regia method. Briefly, 3g of dry soil was weighed in the reaction vessel, 21 mL of HCl followed by 7 mL of HNO_3 was added and left tostand overnight. The suspension was boiled slowly for 2 h under reflux condenser. Total metals concentrations were determined on a Flame Atomic Absorption Spectrometer (Mn) and Grafit Furnace Atomic Absorption Spectrometer (Cu, Pb and Zn).

Instrumental parameters of the atomic absorption spectrophotometer were set according to manufacturer's instructions and for plotting calibration curves specific to each item were analyzed working standard solutions prepared using reference materials Certipur.

Results. The soil condition was assessed both in terms of heavy metal content and the number of carbon compounds, as an indicator of the organic character of the soil.

A large amount of organic or carbon content leads to an increase in growth of microorganisms which contribute to the depletion of oxygen supplies. A possible source of the organic material could be a wastewater treatment plant releasing treated sewage into the soil. The industrial waste effluent may contain carbon compounds with various toxicity levels, reason for monitoring organic levels in both soil and plant effluent.

Regarding heavy metals, the excess accumulation in soils becomes toxic to both people and animals. Due to food chain transfer, an exposure to heavy metals is normally chronic meeting with less cases of acute poisoning through ingestion or dermal contact. The chronic problems associated with long-term heavy metal exposures could be mental lapse caused by lead (Pb) poisoning, headaches, stomachaches, dizziness, vomiting caused by copper (Cu), fatigue, weakness, fever, nausea caused by zinc (Zn), or neurological problems caused by manganese (Mn).

Table 1

Concentrations of heavy metals, pH and organic carbon in industrial soils

Nr.	*Soil sample depth (m)*	*pH (upH)*	*Lead (Pb) (mg/kg)*	*Zinc (Zn) (mg/kg)*	*Cooper (Cu) (mg/kg)*	*Manganese (Mn) (mg/kg)*	*Total organic carbon (TOC) (%)*
1	2	6.82	7.31	26.34	29.92	723.3	1
2	3.5	7.10	7.83	28.17	67.97	951.6	0.85
3	5.5	7.06	11.23	21.54	21.14	877.2	0.81
4	6.3	7.09	6.66	27.3	29.8	733.0	0.79
5	7.5	6.71	7.28	28.02	32.83	421.6	0.72
6	8.9	6.95	9.30	26.12	37.16	394.4	0.7
7	13	6.62	8.5	22.98	23.88	310	0.65
8	14.8	6.59	7.68	22.08	21.5	311.6	0.65

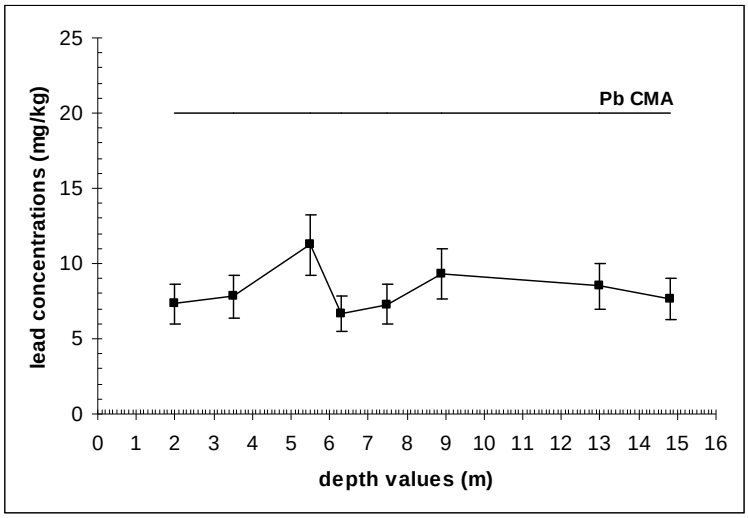

Figure 1. The amount of Pb on different soil depths.

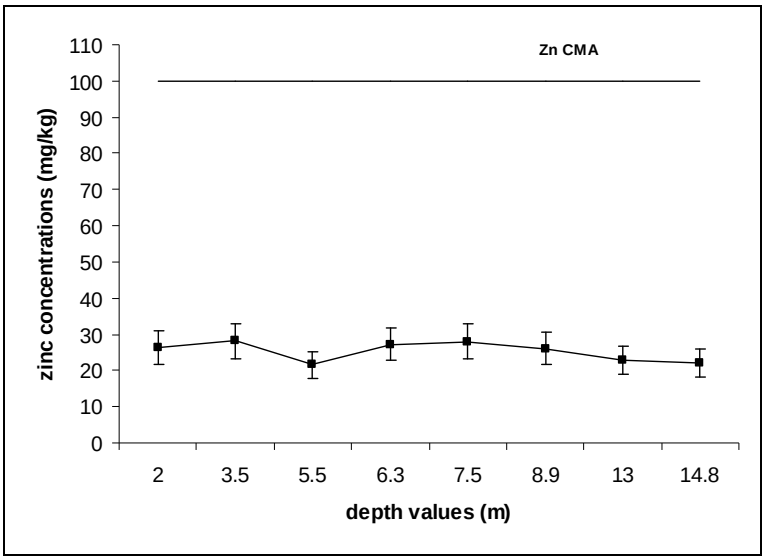

Figure 2. The amount of Zn on different soil depths.

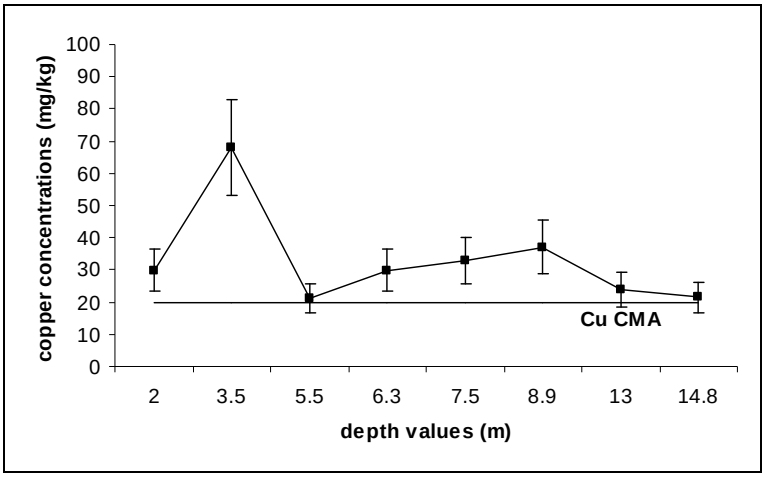

Figure 3. The amount of Cu on different soil depths.

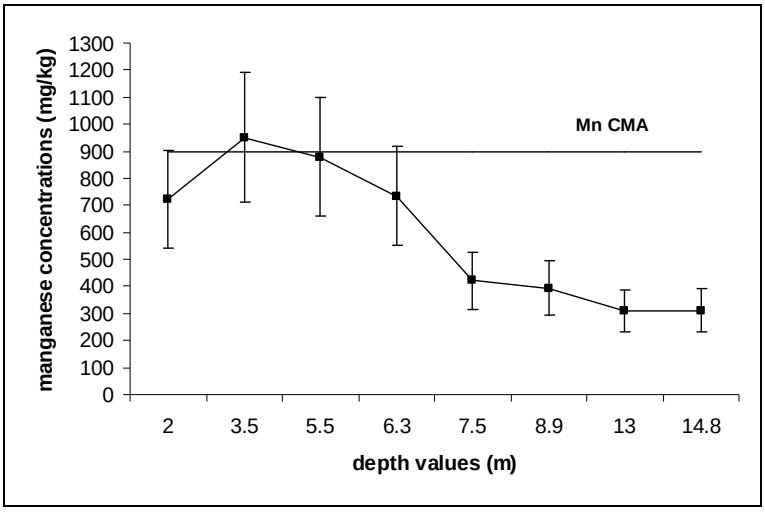

Figure 4. The amount of Mn on different soil depths.

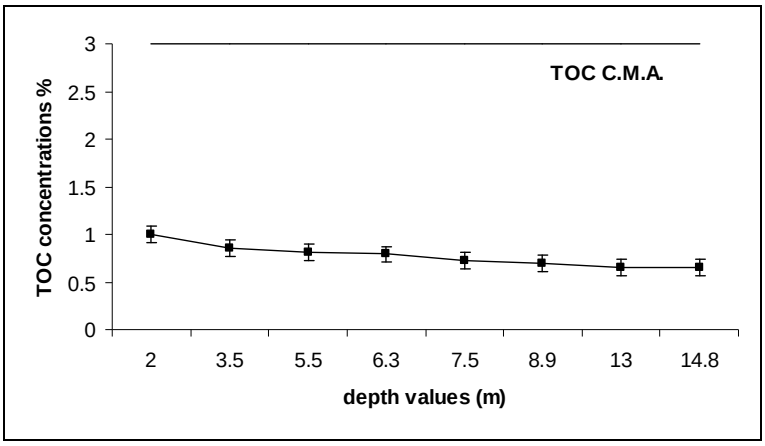

Figure 5. The amount of TOC on different soil depths.

In Figures 1-2, the higher values of concentration of Pb and Zn are at 3.5 m depth, but they did not exceed the limited values recommended by the Order no.756/1997. In Figure 3, all the concentrations of Cu for all depths values exceed the recommended limits from Order no. 756/1997 and in Figure 4 it is observed that only at 3.5 m depth the values of Mn concentration exceed the recommended limits.

In the present case, the heavy metals concentrations are higher at 3.5 m depth. No values of TOC concentrations exceed the admissible limits (see Figure 5).

Discussion. In 2008, the European Commission ranked the 30's largest emitters of the UE, the Turceni Energy Complex being on position 29, after SIDEX Galati who was ranked on 28's position. Because of that, in July 2009, a soils sampling program from industrial area of Turceni started. The pollutants concentrations monitoring from soils, at different depths values, is part from an environmental protection program that will be completed with a data base. This area was chosen because a significant number of industries discharge their wastewater in nearby water bodies or directly in the soil without any treatment. Soils were taken from different depths to estimate the level of contamination.

Conclusions. The heavy metals concentration in soils of the measured area Turceni did not exceed the limited values recommended by the standards for soils. In all of the investigated locations, the study found that concentrations decreased with increasing of soils depth. The results indicate that there is not real environmental risk of contamination from area Turceni. Load of metals is generally not critical, although the continuous exposure to heavy metals does require attention. The pH values of soils are generally

situated between 6.25 and 8.24, due to their buffering quality. The presence of Cu, Mn, Pb, and Zn was determined in most of the investigated areas. TOC is a highly sensitive, non-specific measurement of all organics present in a sample. It, therefore, can be used to regulate the organic chemical discharge to the environment in an industrial plant. In addition, low TOC can confirm the absence of potentially harmful organic chemicals in water discharged in soils from an industrial plant. This monitoring is effective and inexpensive and may encourage polluting industries to be more environment-protective and carefully with all rumors because cost a lot and affect the Romanian industry image.

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