Journal of Young Scientist, Volume V, 2017
ISSN 2344 - 1283; ISSN CD-ROM 2344 - 1291; ISSN Online 2344 - 1305; ISSN-L 2344 – 1283

MONITORING OF HEAVY METAL FROM SOILS ON THE INDUSTRIAL PLATFORM FROM BUCHAREST, ROMANIA

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Abstract

The aim of this study was to determine the content of heavy metal from different profile of soil from the industrial platform situated in the southern part of Bucharest, in order to identify the risk of contamination with his chemical element in this area. Samples (0-0.05 and 0.20-0.025 m depth) were taken directly from four points situated in the proximity of some of the Bucharestrepresentative industrial centres with anonferrousactivity (manufacture of basic iron and steel and of ferrous-alloys; manufacture of basic precious and other non-ferrous metals), as required by law.All analyses were performed in the Pollution Control Department, Water, Soil, Wastes Pollution Control Laboratory from National Research and Development Institute for Industrial Ecology, Bucharest, Romania, in accreditation system according to (SR EN ISO 17025/2005) referential standard.
The results display that there is a constant risk of contamination with the following heavy metals: Nickel (all four locations) and Lead, Copper, Chromium (total) and Zinc (in at least three locations).

Key words: heavy metal, contamination, industrial platform, Bucharest.

INTRODUCTION

One of the chemical elements which represent a risk of soil contamination is those which make part from the group of heavy metals.
The term contamination is different from pollution and implies that the concentration of heavy metal is higher than would naturally occur, but does not necessarily mean that the chemical element is causing any harm. Polluted also refers to a situation in which the concentration of a heavy metal is higher than would naturally occur but also indicates that the substance is causing harm of some type. Therefore a soil could be contaminated but not polluted. The source of heavy metal comesfrom both the natural environment (there are occasionally sourceswho don´t cause pollution) and especially from anthropogenic activities (e.g. industrial field).
Intensive human activities have resulted in over-accumulation of heavy metals in soilscausing environmental pollution (Luo et al., 2009).
Over the last few decades, the anthropogenic inputs of several heavy metals into soils have exceeded the natural heavy metal components of the Earth´s crust (Facchinelli et. al., 2001). Facchinelli et al. (2001) analyzed the effects of anthropogenic and natural influences on the heavy metal concentrations of cultivated soils in the Piedmont (northwest Italy) using multivariate statistic and geostatistical approaches. They found that the Cr, Co and Ni concentrations were mainly controlled by the parent rocks, whereas Cu together with Zn and Pb alone were controlled by anthropogenic activities.
Other authors revealed that the As and Ni concentrations in the topsoil mainly originated from the soil parent materials and the Cd, Zn, Cu, Pb and Cr concentrations largely originated from anthropogenic sources (Hu and Cheng, 2013).Soil heavy metal concentrations are dynamic; they are in a state of change with a variety of natural and anthropogenic sources (or”input pathways”), as well as output pathways (Xia et.al., 2014).

Among the various anthropogenic sources we can include the following activities: current and/or historical industrialization, urbanism and intensive chemical use in agriculture.

In agricultural soils, the accumulation of heavy metals is a growing public concern because it threatens environmental health; elevated heavy metal uptake by crops may also affect food quality and security (Harmanescu et al., 2011; Wu et al., 2015).Heavy metals can be accumulated in agricultural soils from industrial emissions, disposal of high metal wastes and sewage sludge and agricultural sources, such as livestock manure, inorganic fertilizers, agrochemicals, pesticides (Hu and Cheng, 2013; Khan et al., 2008; Mohammed et al., 2011).

Considering that soil is animmense „crucible"/melting pot that brings together in timeubiquitous heavy metals, their accumulation in soils is now one of the issues that concern public opinion because it is the main cause of diseases. According to the Center for Disease Control (CDC) the USA incidence of autism spectrum disorders rose 2.2 timesin the year 2010 compared to 2000 (Wingate et.al., 2014).

In the UK a five-fold increase in autism in the 1990's, reached a plateau in the 2000's up to 2010 (Taylor et al., 2013). One of the important causes of this increase is environmental influence, including many candidates. Many chemical classes or specific chemicals related to autism have been reviewed by Rossignol or Sealey and C.J. Carter or R.A. Blizard (Rossignol et.al. 2014; Sealey et. al., 2016). The first two of them are pesticides and heavy metals (cadmium, lead, arsenic, manganese, or mercury). Soil heavy metal pollution has become an important environmental issue (Tchounwou et al., 2012). Therefore, an important prerequisite in the control and remediation of heavy metal contaminated soils is to determine the source of contamination (Lin et al., 2010; Zhang et al., 2009b).

In Romania, there are four important laws which define the legal frame regarding soil pollution (OM 756/1997, OM 184/1997, HG 1403/2007 and HG 1408/2007). Our country, as an EU Member State, has implemented national Pollutant Release and Transfer Register establishing the European Pollutant Release and Transfer Register (Regulation E-PRTR). This institutes a register of emissions and transfers of pollutants at Community level (hereinafter "the European PRTR/E-PRTR) as a publicly accessible electronic database in order to let them the opportunity to participate at the environmental decision making and help prevent and reduce environmental pollution.

E-PRTR covers 28 EU Member States, Iceland, Liechtenstein, Norway, Serbia and Switzerland; contains annual data reported by more than 30,000 industrial facilities and refers to 91 pollutants falling under seven groupswhich includes heavy metals.One type of data to be reported annually by each industrial facility for which the applicable thresholds are exceeded are the releases to air, water and land of any of the 91 E-PRTR pollutants.

The E-PRTR data for Bucharest-Ilfov and for industrial activity revealed that this area didn´t have soil pollution with heavy metal, in the period 2007-2014. On the other side, the E-PRTR provides data regarding the pollution with heavy metals in water and air (Table 1).

Table 1.E-PRTRdata regarding the pollution with heavy metals in water and air

Year	Sector of activity	Types of pollutions with heavy metal (Kg)	
		air	Water
2014	waste and waste water management	-	Cr (360), Cu (460), Ni (1270)
2013	production and processing of metals	-	Cr (128)
	waste and waste water management	-	Cr (269), Cu (209), Ni (1070)
2012	energy	Cd (11.4), Hg (12)	-
2011	energy	Cd (31.2), Hg (31.9)	-
2010	energy	Cd (46), Hg (48)	-
2009	energy	Cd (94.6), Hg (96.7)	-
2008	energy	Cd (31.3), Hg (32.3)	-
2007	energy	Cd (73), Hg (76)	-

In the period 2013-2014, the sources of pollution water with heavy metals were the sectors of waste and waste water management and the production and processing of metals.

The largest amount of heavy metal that polluted water was: Nickel (2340 Kg), Copper (669) and Chromium (629).

MATERIALS AND METHODS

This study was conducted in the industrial platform situated in the southern part of Bucharest, the capital of Romania (Figure 1). The main industries in the area include manufacture of basic iron and steel and of ferrous-alloys and manufacture of basic precious and other non-ferrous metals.
The industrial complex has developedits activity since 60´s.

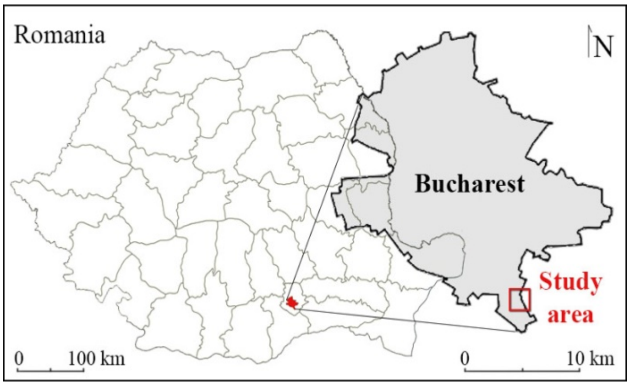

Figure 1. The location of study area

The samples were taken in a plain area, from four locations where there are potential sources of heavy metal (Table 2).

Table 2. Details of sampling points

Locations	Point Number	Coordinates	The smell of the probe	Depth (m)	Presence/ absent of groundwater
1.	1-1	44.35°N 26.14°E	no smell	0-0,05	absent
	1-2		no smell	0,20-0,25	absent
2.	2´-1	44.35°N 26.15°E	no smell	0-0,05	absent
	2´-2		no smell	0,20-0,25	absent
3.	3´-1	44.36°N 26.14°E	No smell	0-0,05	absent
	3´-2		No smell	0,20-0,25	absent
4.	4´-1	44.36°N 26.14°E	No smell	0-0,05	absent
	4´-2		No smell	0,20-0,25	absent

We analysed an area of about 1000 square meters and in order to know the actual quality of soil we sampled eight soil profiles (0-0.05 and 0.20-0.25 m) - one soil sample was collected from each layer of the profile of soil (fig. 2).

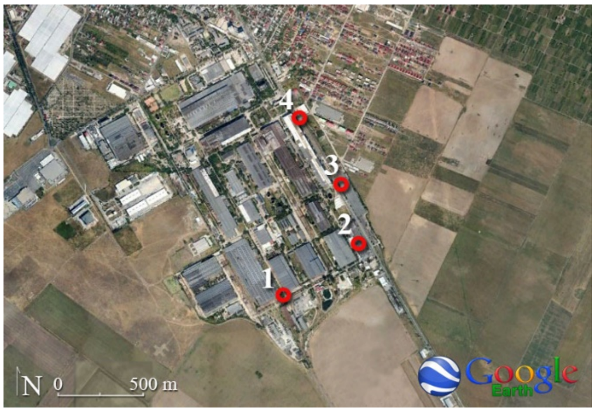

Figure 2. Locations of samples in the industrial platform

The first two locations of the samples were collected directly from the industrial platform (fig 3) and another two samples from the proximity of the Nonferrous Centre (fig. 4).

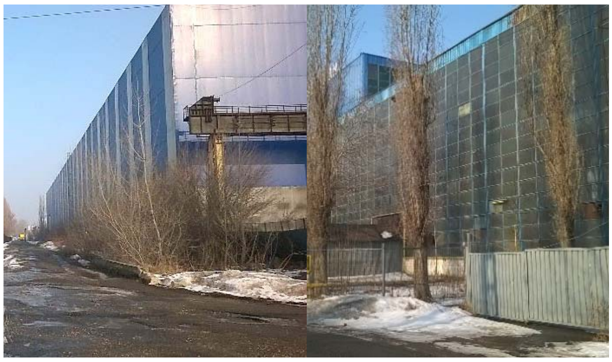

Figure 3. Picture of the first two locations

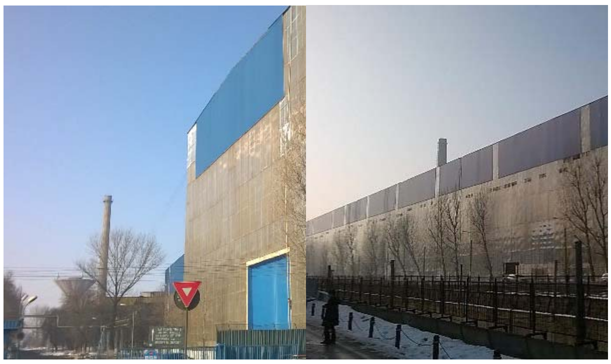

Figure 4. Picture of the second two locations

Sample preparation

All eight soil samples were air-dried at room temperature (24 hours), crushed and retained

the particle dimensions less than 150 µm. Around two grams of sample were dissolved in aqua regia (a mixture of suprapure acids HCI 30% and HNO3 65% in the ratio 21 to 7 mL). The mixture was mineralized on sand bath until complete dissolution.
After cooling, the samples were filtered on paper filter (porosity less than 45 µm) in a 50 mL volumetric flask and filled with ultrapure water.
The heavy metal content in the samples was determined by inductively coupled plasma optical emission spectrometry.
A calibration curve in the range of 0.5-2.5 mg/L (Arsenic/As, Cadmium/Cd, Chromium/Cr, Copper/Cu, Manganese/Mn, Molybdenum/Mo, Nickel/Ni, Lead/Pb and Zinc/Zn) was performed using a Certified Reference Material solution (100 mg/L Multi Element Standard Solution, Certipur, Merck).
The quality control of the data was carried out according to Quality Control Standards 21A, 100mg/L, produced by PerkinElmer.
A reagent blank in order to estimate the metal contents from acids was prepared.
All analyses were performed in the Pollution Control Department, Water, Soil, Wastes Pollution Control Laboratory from National Research and Development Institute for Industrial Ecology, Bucharest, Romania, in accreditation system according to (SR EN ISO 17025/2005) referential standard.

Equipment

Analytical technique used for determination of Arsenic/As, Cadmium/Cd, Chromium/Cr, Copper/Cu, Manganese/Mn, Molybdenum/Mo, Nickel/Ni, Lead/Pb and Zinc/Zn from soil samples was inductively coupled plasma optical emission spectrometry performed using a Perkin Elmer Optima 5300 DV ICPEOS Spectrometer.
All the chemicals were of analytical reagent grade (Merck quality).

Figure 5. Picture of Perkin Elmer Optima 5300 DV ICPEOS Spectrometer

RESULTS AND DISCUSSIONS

For an actualand accurate review of the risk of contamination with heavy metalsfrom one of the industrial platform from Bucharest, we selected four points from this area.
Therefore we calculated the values of concentrations ofsome heavy metal from two profile of soil(0-0.05 and0.20-0.25 m) and compared it with references value,accordingtoRomanian law(Table 3).
Also, we analysed the variation of pH values sampled from those four locations and two profile of soil. We determined that pH are weakbasic, values are ranging between 7,3-7,7 (Table 3).
The Arsenic/As contentwas over the normal value from the samples soils where we had a pH at 7.3-7.4. We can appreciate that in theindustrial area (location one and two) we have a risk of soil contamination with Arsenic, especially in the soils profiles from the surface (0-0.05 m depth).
The Cadmium /Cd content exceeded normal value in soil samplesfrom location number three situated in the proximity of industrial platform. Therefore, we identified that there is a risk of soil contamination with Cadmium. Also, the content of Cd exceeded in samples belonging to first location (0.05 m depth).
The Cobalt/Co and Chromium (VI) contents from all soil samples were below normal values of heavy metal under the Romanian law.
The Chromium/Cr (Total) andCopper/Cu contents were over normal value in soil samples from the industrial platform (location 1, 2 and 3). Therefore, there is a risk of soil

contamination with Chromium (total) and Copper.

The manganese/Mn and Molybden/Mo contents were over normal value in soil sample where we had a pH at 7.3.In those two locations there is a risk of contamination with this heavy metals.

The Molybden/Mo content was at alert levels in the soils samples from the fourth location (0-0.05 m depth).

The Nickel/Ni content exceeded normal value in all soil samples from industrial platform and therefore, there is a risk of contamination with this heavy metal.

The Lead/Pb content was at alert levels in the soil sample from the first location (at 0-0.05 m depth). Also, it exceeded the normal values in soil from three locations fromindustrial platform and therefore represents a risk of contamination.

The Zinc/Zn content was over the normal value in the soil samples from three locations from industrial platform (at 0-0.05 m depth) where there is a risk of contamination with this heavy metal.

Table 3. The heavy metals content from soil samples and pH value

Soil Profile	The chemical element – Heavy metal											pH
	Arsenic (As)	Cadmium (Cd)	Cobalt (Co)	Chromium (Cr) Total	Chromium (Cr) Cr (VI)	Copper (Cu)	Manganese (Mn)	Molybdenum (Mo)	Nickel (Ni)	Lead (Pb)	Zinc (Zn)	
	Mg kg⁻¹ dm (dry matter)											
Location 1.												
1-1	6.06	1.38	12.8	90.1	<0.5*	61.2	1019	13.9	70.0	449	345	7.3
1-2	5.91	0.30	11.7	41.6	<0.5	22.9	707	1.97	36.9	22.8	56.6	7.4
*Quantification limit of the applied analytical method												
Location 2.												
2'-1	5.38	0.98	11.9	112	<0.5	50.8	1078	3.94	47.8	44.9	207	7.3
2'-2	3.54	0.45	11.9	245	<0.5	39.2	853	1.69	42.6	35.3	86.3	7.7
Location 3.												
3'-1	4.07	1.23	8.82	37.7	<0.5	54.1	649	<0.03	31.1	181	180	7.7
3'-2	4.26	1.07	7.71	49.9	<0.5	51.9	582	0.57	30.1	218	208	7.5
Location 4.												
4'-1	1.44	0.14	4.27	29.3	<0.5	12.6	207	15.0	83.6	13.8	45.8	7.7
4'-2	2.96	0.26	5.60	17.3	<0.5	27.1	309	0.20	21.4	20.7	78.6	7.5

Color legend for soils less sensible (industrial area) according to MO756/1997

Color / Heavy Metal	Arsenic (As)	Cadmium (Cd)	Cobalt (Co)	Chromium (Cr) Total	Chromium (Cr) Cr (VI)	Copper (Cu)	Manganese (Mn)	Molybdenum (Mo)	Nickel (Ni)	Lead (Pb)	Zinc (Zn)
Normal values (Mg kg⁻¹ dm (dry matter)	5	1	15	30	1	20	900	2	20	20	100
Over normal Values (Mg kg⁻¹ dm (dry matter)	5<x<25	1<x<5	15<x<100	30<x<300	1<x<10	20<x<250	900<x<2000	2<x<15	20<x<200	20<x<250	100<x<700
Alert thresholds (Mg kg⁻¹ dm (dry matter)	25	5	100	300	10	250	2000	15	200	250	700
Action levels (Mg kg⁻¹ dm (dry matter)	50	10	250	600	20	500	4000	40	500	1000	1500

CONCLUSIONS

After the determination of the content of heavy metal in soils samples from an industrial area we highlight the following:

- in all four locations of the industrial platform there is a constant risk of contamination of the soil with Ni. This result confirms the E-PRTR data for Bucharest-Ilfov which revealed that, in 2013-2014, the largest amount of heavy metal that polluted water was Nickel (2340 Kg). The source of this pollution was the sector of waste and waste water management which represent one of the actual and important cause of contamination of soil;
- in addition, in three locations of the industrial platform there is another constant risk of contamination of the soil with Pb, Cu, Cr (total), and Zn. The risk of contamination with Cu and Cr confirm the E-PRTR data for Bucharest-Ilfov which revealed that, in 2013-2014, two of the heavy metals that polluted water were Copper (669 Kg) and Chromium (629Kg). Thesource of the pollution with Cr was the sector ofproduction and processing of metals which is on the industrial platform that we studied. In addition to E-PRTR data we discovered in soil two new heavy metal: (Pb and Zn).

It is possible that the content of Cr, Co and Ni were mainly controlled by the parent rocks, whereas Cu together with Zn and Pb alone were controlled by anthropogenic activities.

- the pH value (7.3) determined the contamination of soil from location 1 and 2 with As, Mn and Mo;
- the more contaminated soils with heavy metals, especially Pb were in the location 1 which is in the proximity of agricultural soil (e.g. greenhouse);
- a certain situation which occurred is a high degree contamination of soil possibly because there is a particular source of pollution with the Pb (locations 1) and Mo (location 4).

With this actual data about the content of Ni, Cr, Cu, Pb, Zn, As, Mn and Mo in soil from industrial platform from the southern part of Bucharest I hope to prevent the pollution of soil with heavy metals, accordingly to the EU principle”it is better to prevent than to mend after”.

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