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Original Article

Heavy Metal Contamination of Soil in Copşa Mică Area

MUNTEAN Edward, Nicoleta MUNTEAN, Marcel DUDA

University of Agricultural Science and Veterinary Medicine Cluj-Napoca, Mănăştur Street, no. 3 - 5
400372 Cluj-Napoca, Romania

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Abstract

Copşa Mică was one of the most polluted areas in Romania, well known also in Europe for its status. The heavy metal pollution was due to a factory for processing non-ferrous ores (S.C. Sometra S.A.), largely responsible for the most health problems of the local population due to its emissions of sulphur dioxide, solid particles in suspension and heavy metals. Soil contamination occurred, representing a high risk for environment and human health, in relation with the contaminated land use for agriculture. The situation changed after Sometra applied some measures for pollution's reduction and after the official closure of the factory in 2009, hence it is important to find out which are the actual levels of contamination, especially on surfaces used for agriculture. In this research, the distribution of four heavy metals of high concern for environment and human health (Pb, Cu, Cd and Zn) was measured in several sites located in Copşa Mică area during 2009 and 2011, continuing a previous research. These heavy metals were determined using atomic absorption spectrophotometry, their measurement being performed using a Shimadzu AA-6300 double beam atomic absorption spectrophotometer, with both flame atomization and graphite furnace. The obtained data revealed the following ranges for the studied elements: 8.02 – 110.65 µg/kg for lead, 22.51 - 179.15 mg/kg for copper, 0.06 – 3.19 µg/kg for cadmium and 38.16 – 1842.11 mg/kg for zinc. The maximum lead concentrations were recorded in samples originating from Micasasa and Agarbiciu, while those for cadmium, zinc and copper were recorded in Copşa Mică.

Keywords: cadmium, copper, lead, zinc, soil, AAS.

1. Introduction

Industrial pollution is a major factor causing degradation of the environment, affecting the public health as well; the presence of heavy metals in polluted areas can induce a potential toxic risk as they may contaminate the environmental compartments (water, soil, air) and many of them have bio-accumulation capacity in plants [8, 11, 12, 16, 18, 23 - 25) and in animal tissues [3, 22].

Heavy metal contamination of soils occurs mainly due to industrial activities; these pollutants are persistent in soil and pose a long-term risk to ground water quality and ecosystem functioning [3, 5, 9].

Soil contamination with heavy metals presents a high risk for human and animal health mainly due to agricultural activities, because plants are able to accumulate these pollutants from soil and thus they pass on animals and humans [11].

Heavy metals could have a negative influence on plant development, affecting processes such as photosynthesis, gaseous exchange or absorption, determining a reduction in plant growth, dry matter accumulation and yield [4].

Heavy metals may affect severely the human health causing neurological disorders, low birth weight, spontaneous abortion, damaging internal organs, slowing the organism's growth and development and in extreme cases they may even cause death [5, 6, 9].

Heavy metals represent a major threat for the development of the human embryo, for newborn and children. Children are among the most affected, as

*Corresponding author
Tel +40754074375; Fax +40264593792
email:edimuntean@yahoo.com

they may accumulate higher doses of heavy metals via food ingestion because they consume higher food amounts than adults, related to their own weight [10]; their exposure to some heavy metals may cause anemia, learning difficulties, may affect memory and the nervous system and even lead to behavior deviations such as increasing hyperactivity [28].

In Romania there are three areas highly polluted with heavy metals because of non-ferrous ores extraction and metallurgical processing, extensively monitored during the last decades: Copşa Mică [5, 21], Zlatna [15, 19, 20] and Baia Mare [13, 14], all located in Transylvania.

From these, Copşa Mică was one of the most polluted areas in Romania, well known also in Europe for the ecological lack of balance induced by the non-ferrous metallurgy [5, 17, 20].

The heavy metal pollution in this area is due to a factory for processing non-ferrous ores (S.C. Sometra S.A.), largely responsible for the most health problems of the local population due to its emissions of sulphur dioxide, solid particles in suspension and heavy metals [21, 23, 24].

As a consequence, soil contamination occurred, thus causing a high risk for environment and human health, in relation with the contaminated land used for agriculture [20, 21].

More than that, because of its position along the Târnava Mare River, the transport of pollutants was favored by the existing air currents, the contaminated surface being quite large [1, 5, 7].

Previous studies showed that the accumulation of the pollutants in the soil in the Copsa Mică area determines the acidification of soils and a reduction of the nutritive element contents, the decrease of the quality of the organic matter, the modification of the microbiological activity, the destruction of the soil structure [2].

In most of the former studies, atomic absorption spectroscopy was used for the determination of heavy metals [16, 17, 22, 24]; during the last years multielemental techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [14, 20] or inductively coupled plasma mass spectrometry (ICP-MS) [14], as well as non-destructive analytical techniques, such as X ray fluorescence [5] or neutron activation analysis [20] were employed for the same scope.

The purpose of this paper is to find out the levels of soil contamination on agricultural soils after the official polluting plant closure in 2009.

2. Material and method

2.1. Chemicals

Nitric acid and hydrofluoric acid were from Merck, while cadmium, lead, zinc and copper standards for atomic absorption spectroscopy were from Fluka, containing all 1000 mg/L metal in nitric acid. Ultrapure water with a specific resistance of 18.2 MΩ. cm was utilized, being obtained from a Direct Q 3UV Smart (Millipore).

2.2. Sampling & sample preparation

Soil samples were collected from two horizons (0-20 cm and 20-40 cm deep) and stored in polyethylene bags; sampling locations and the distances from Sometra were given in table 1. The samples were labeled, sealed and transported to the laboratory where they were dried, crushed, cleaned from extraneous material and sifted through a 2 mm mesh sieve then milled, according to ISO 11464 [27]. An aliquot of each sample was then treated with 3 mL of HNO_3 65% and 3 mL of HF 40%; wet digestion using a Berghoff Microwave Digestion System MWS-3+ was used.

Table 1. Sampling sites

Sampling site	Coordinates		Distance from Sometra plant [km]
Copşa Mică	$46^0$06’50.27” N	$24^0$13’38.24” E	0.1
Agarbiciu	$46^0$03’36.21” N	$24^0$10’49.28” E	7.4
Micasasa	$46^0$05’05.97” N	$24^0$05’10.45” E	11.0
Seica Mare	$46^0$01’51.36” N	$24^0$09’38.88” E	11.0
Valea Lunga	$46^0$06’52.93” N	$24^0$02’20.17” E	15.0

2.3. Atomic absorption analysis

Measurements were performed using an AA-6300 Shimadzu double beam atomic absorption spectrophotometer (Shimadzu Corporation, Japan), with both flame and graphite furnace atomization, equipped with deuterium lamp for background correction and hollow-cathode lamps for each of the studied elements, as well as with an ASC-6100F autosampler, data acquisition and processing software. Calibration curves were prepared using five concentrations, the linear correlation coefficients obtained ranging between 0.9780 - 0.9983. The standard operation conditions were those recommended for each metal in the instrument’s method. All measurements were carried out in triplicates.

2.3. Data analysis

Instrument control, data acquisition and chromatographic data analysis were accomplished using WizAArd software (Shimadzu Corporation, Japan); the data matrix was processed in Excel 2003 (Microsoft, USA), then principal component analysis (PCA) was performed using MatLab (The Mathworks, USA) after mean center preprocessing.

3. Results and Discussion

The mean values of the obtained data are presented in table 2; comparing the values recorded during 2009 (from which those related with Cd and Pb were reported by Muntean et al., in 2010) with those from 2011, a decrease of concentrations in soil is obvious for all monitored heavy metals.

This is a consequence of ceasing Sometra's plant activity (hence, the lack of inputs in the soil system for new amounts of contaminants) and of levigation.

Table 2. Mean values for the heavy metal concentrations recorded in Copşa Mică area

Sampling sites	Cd (µg/ kg)		Pb (µg/ kg)		Zn (mg/ kg)		Cu (mg/ kg)	
	2009	2011	2009	2011	2009	2011	2009	2011
Copşa Mică - s	3.19	2.35	45.51	31.94	1842.11	1195.36	179.15	151.64
Copşa Mică - d	2.31	1.63	63.29	33.17	609.44	472.19	135.27	104.75
Seica Mare - s	2.02	1.57	21.58	16.79	614.69	537.49	34.15	24.06
Seica Mare - d	0.45	0.32	12.73	10.22	285.48	210.65	50.26	27.66
Micasasa - s	0.94	0.69	70.48	54.83	1131.16	891.21	124.35	91.68
Micasasa - d	1.42	0.48	105.23	52.09	872.31	641.49	51.28	30.91
Agarbiciu - s	0.39	0.25	110.65	85.75	1271.16	960.56	109.36	70.98
Agarbiciu - d	0.56	0.22	65.97	46.27	592.75	449.12	73.01	55.42
Valea Lunga - s	0.18	0.14	16.35	12.63	163.52	125.84	47.58	32.36
Valea Lunga - d	0.11	0.06	10.39	8.02	70.2	38.16	35.12	22.51

Note: s: 0 – 20 cm horizon; d: 20 – 40 cm horizon

For cadmium, the highest concentration was recorded in Copşa Mică, the sampling site being close to Sometra; only the value recorded in 2009 in the 0 - 20 cm horizon was higher than the warning threshold, which is 3 mg/ kg [26]. Lead soil contamination in 2009 was maximal in Agirbiciu and Micasasa, exceeding not only the warning threshold (50 mg/ kg), but also the intervention threshold of 100 mg/ kg [26]; the lead levels decreased in 2011, but they were still over the warning threshold for both locations. The concentrations recorded for zinc were the highest ones, with a maximum of 1842.11 mg/ kg for Copşa Mică, most of them exceeding the intervention threshold (200 mg/ kg). Despite the values from 2011 are lower, this threshold is still overreached [26].

Copper concentrations were all lower than the intervention threshold (200 mg/ kg), three sites exceeding however the warning threshold of 100 mg/ kg [26] in 2009: Copşa Mică, Micasasa and Agarbiciu. From these, only Copşa Mică exceeded the warning threshold in 2011. PCA analysis of data originating from 2009 surface samples lead to a model with two principal components (PC) that explains 95.63% of data variability; the corresponding biplot (fig. 1) reveals similar loadings of zinc and copper on the first PC and hence their similar contaminant behavior in the studied soils.

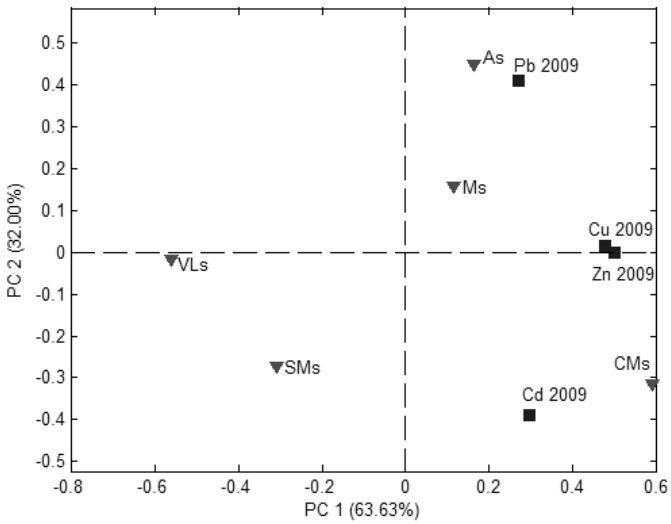

Figure 1. Biplot for 2009 data. Sampling site's codes are: VLs – Valea Lunga, CMs – Copşa Mică , As – Agirbiciu, SMs- Seica Mare, Ms – Micasasa

The highest loading on PC1 corresponding to Copşa Mică (CMs) is related with the maximum contamination with cadmium, copper and zinc (CMs - the most contaminated site), the lowest loading corresponding to Valea Lunga (VLs - the least contaminated site), while PC2 describes mainly the lead contamination, Agirbiciu and Micasasa (As and Ms) being the most contaminated sites with this metal.

Heavy metal contamination of the studied sites depends not only of the contamination source, but also of the soil characteristics and meteorological factors; despite the pollution source was closed few years ago, the studied soils are still contaminated with relatively high concentrations of cadmium, lead, zinc and copper.

4. Conclusions

Despite the obvious decrease of the concentrations for all the considered heavy metals during the studied period, soil pollution with cadmium, lead, zinc and copper in Copşa Mică area keeps up at relatively high levels, in some cases exceeding the warning threshold limits and even the intervention threshold limits imposed by the Decree 756/ 1997 [26].

Hence, the obtained results showed that soil contamination in the studied area is significant, needing soil remediation solutions.

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