

# Carcinogenic risk evaluation for human health risk assessment from soils contaminated with heavy metals

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**Abstract** Human activities have progressively increased in recent years. Consequently, significant environment deterioration resulted. Soils have a particularly varied vulnerability to heavy metal pollution, especially in the vicinity of industrial areas. Heavy metal contamination of soil may induce risks and hazards to humans and the ecosystem, while toxic metals in soil can severely inhibit the biodegradation of organic contaminants. This paper is focused on human health risk assessment from extremely contaminated soil with heavy metals, mainly with carcinogenic elements. The study refers to an agricultural area in the vicinity of an old metallurgical processing industrial facility. The contaminants evaluated in the present paper are beryllium (Be), cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb). Contamination level is pointed out through laboratory analysis results of soil samples taken from 0–0.2 m, 0.2–0.4 m soil layers and up to 2.1 m soil depth. Some heavy metal concentrations (Cd, Cr and Pb) exceed the intervention thresholds for sensitive areas, as they are stipulated in the national regulation in Romania.

The identified average concentration levels of Cd, Cr<sup>VI</sup> and Pb in the first layer of the investigated land are 23.83, 7.71 and 704.22 mg/kg<sub>d.w.</sub>, respectively. The results show that the potential risk of human health is relevant (higher than the acceptable one after World Health Organization) and a possible solution for the remediation should become a major concern for the investigated area.

**Keywords** Exposure · Metals · Risk assessment · Soil pollution

## Introduction

Metal presence in the environment occurs in both natural and anthropogenic forms. Contaminated ecosystems have impacts on plants, microorganisms, aquatic organisms and life support functions such as immobilization, mineralization and nitrification, and in this way, the human health and the health of the ecosystem are negatively influenced (Mani and Kumar 2014).

Soil, a non-renewable resource, acting as an interface between ground, air and water, facing nowadays a complex pollution generated by human activities, which implied notable contributions to the increase in environmental metal concentration (Granero and Domingo 2002). Events diversity and situations are characteristic of the chemical elements on interaction with different components of soil or environmental elements. Increasing the capacity of metal migration and propensity for sudden chemical combinations may increase their toxicity affecting the food chain, which invariably ends in man.

While usually natural forms are present at relative low concentrations, in recent years a number of anthropogenic sources have an important impact. Industry and the vehicle

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exhausts are the major role for soil pollution via particulate matters containing heavy metals, producing soil pollution both in depth and on the surface. Last decades studies revealed, also, that heavy metals in soils are associated with the quality of agricultural products in the rural areas (Wu et al. 2010).

The investigated area considered in the present study has a relatively central position region of Romania, being the valley of a river corridor. The research was conducted between 2011 and 2014, and the soil samples were collected in autumn 2001. The concentration level of Be, Cd, Cr (total), Cr(VI), Ni, Pb in agricultural soil near the Sometra metallurgical plant was analyzed, the most important factory for processing of nonferrous ores in Romania. The industrial unit is located in Copsa Mica, in the valley of Târnavă Mare River, in north of Sibiu, 33 km east of Blaj and 12 km southwest of Medias. Here, there are various economic resources. Even that the most important chemical and metallurgical centers in the country are in the adjacent area, the agriculture is a concern of the inhabitants also. Potential risk to human health in such areas should be correlated with the up taken of pollutants not only by inhalation (air borne particles) (Wang et al. 2013; Chen et al. 2013; Wilcke et al. 1998), but also by up taken through the food chain (Khan et al. 2008; Zhuang et al. 2009).

Since 2008, air quality monitoring was carried out in this region by means of the automatic air quality monitoring, local network which consists of 4 automatic stations. According to the 2008–2009 Regional Environmental Protection Agency (REPA) reports, the assessment of the air quality data found that the particulate matter (PM<sub>10</sub>) and Pb concentration values in ambient air exceed the allowed limits established by Order 592/2002 (which are 50 µg/m<sup>3</sup> for PM<sub>10</sub>, respectively, 0.5 µg/m<sup>3</sup> for Pb). Following these findings, the Romanian National Environmental Protection Agency (NEPA) started the development of the program for air quality management.

Even that concerning heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V and Zn are required in minute quantities by organisms (excessive amounts of these elements can become harmful), other heavy metals (Pb, Cd, Hg and As) do not have any beneficial effect on organisms and they are very harmful to both plants and animals (Chibuikie and Obiora 2014). Therefore, this research focuses on study of Be, Cd, Cr (total), Cr(VI), Ni, Pb concentration levels in the soil from this interest rural–urban area. The human health risk posed by exposure of the inhabitants to heavy metals contaminated soil is evaluated since risk assessment through different methods is an important tool for identification and management of toxic metals (Rahib et al. 2015). The potentially toxic heavy metals are analyzed in order to protect receptors located in both polluted zone and

background parts (Liu et al. 2006; Sun et al. 2010; Zheng et al. 2010). The present research has a significant practical importance with regard to monitoring the safety of agricultural activities and human life quality in the studied area, near a metallurgical plant. Results indicate that the metallurgical plant caused great influence on the soil quality and there is a great need for implementation of remediation strategy of the contaminated sites. Consequently, it should be given proper attention in order not to increase the present level of metals in the area. The study and its results are of great importance for the development of a proper management of the contaminated sites; it can also serve as complementary tool for the development of prevention strategies. The value of the work is given by the fact that human health risk from contaminated soils with Be, Cd, Cr, Ni and Pb was assessed since exposure to these soils through different exposure pathways could be regarded as a potential health hazard.

## Materials and methods

For the characterization of the investigated area from Central Romania in terms of the inorganic persistent substances (heavy metals), an area of 4000 m<sup>2</sup> has been chosen.

### Samples collection

Soil sampling was performed under the provisions of STAS 7184-1:84 (STAS 7184/1 1984) and ISO 11074:2015 (ISO 11074 2015). Thus, according to selected surface (4000 m<sup>2</sup> from a batch of 1.89 ha), has been established a sampling spot grid of which soil was sampled at different depths (0–0.2, 0.2–0.4 and up to 2.1 m).

The area from which the samples were collected was historically used for agricultural purposes. The texture of the sediments ranged from sandy to loamy type. Soil samples were collected from twelve different points (hereafter referred to as P1–P12). The samples were air-dried and stored at low temperature (4–5 °C), preserved by cooling prior to work-up and analysis (Cocârţă et al. 2012).

### Analytical procedure

A special attention has been focused on samples preparation stage, being known that correctness in respecting the analytical procedure is essential for the quantitative analysis results. Average samples were obtained (method of the quarters for specific chemical analyses) from shredding material, carefully avoiding contamination. Then, soil samples have undergone the following operations: dried in oven (3 h at 105 °C), smashed and sieved, being brought to



a particle size less than 0.02 mm. Soil samples were brought in aqua regia solution (Novaes dos Santos and Alleoni 2013) according to the SR ISO 11466:1999 method (SR ISO 11466 1999). Prepared samples were stored in the 100-mL capacity polyethylene containers. The soil samples were bring with aqua regia at room temperature for 16 h in order to allow slow oxidation of organic matter in soil. The pH of the soil samples was between 7 (the minim pH of the soil samples) and 7.88 (the maximum value of soil sample pH). Even that the pH of soil samples was different, the working pH for all samples was 2.

According to the standardized methods specifications, the obtained extract, as previously described, was used for determination of heavy metals by the following atomic absorption spectrometry techniques: (1) flame detection—Cd, Ni, Cr, Pb, (2) electrothermic—Be and (3) UV–Vis spectrometry—Cr(VI) determination (Scancar et al. 2000). Quantitative chemical analysis was performed using Shimadzu AA-6300 Spectrophotometer, for determination of Be, Cd, Ni, Cr, Pb in soil samples, and Shimadzu UV-1700 UV–Vis Spectrophotometer for Cr<sup>VI</sup>. Analytical determination of heavy metal elements was performed following the analysis methods presented in Table 1, even that recent studies evidenced new methods for determination of heavy metal ions (Gupta et al. 2013a, b; Yola et al. 2012, 2014). Working parameters related to the flame atomic absorption spectrometric determination (FAAS) equipment that was used are synthesized in Table 2.

The hexavalent chromium (Cr(VI)) determination was realized by 1,5-difenylicarbazine (DPC) in line with SR ISO 11083/98. The soil was analyzed the second day after the sample collection in order to prevent and/or minimize any conversion of hexavalent chromium to the trivalent state. The soil sample was extracted in aqua regia according to SR EN ISO 15587-1:2002 and analyzed by the difenylicarbazine colorimetric method. The complexation-reagent solution was formed by 1 g 1,5-difenylicarbazine in 100 mL acetone resulting in this way a red–violet complex at pH = 2 whose absorbance was measured at 540 nm. The amount of each soil sample has more than 1 g of dry weight (between 1.1 and 1.5 g of dry weight), and 3 replicates for each sample were worked. The complexation

time was 15 min, and the pH during complexation was 2. The sample alkalification was done by adding 15 mL of NaOH 0.1 mol/L. Phosphoric acid was used for pH control.

### Data analysis

In force thresholds established by the Romanian national legislation on the assessment of environmental pollution (specified in Order 756/1997, chapter III “Regulations concerning the pollution of soils”), is considered for this research results discussion (MO 1997).

Order 756/1997 establishes the alert and intervention threshold concentrations of pollutants in soils, in correlation with the specific purpose of land use. Table 3 presents the selection of alert and intervention thresholds concentrations for the research-targeted heavy metals.

### Human exposure and health risk assessment methodology

The exposure is the amount of pollutant absorbed by the human body through different pathways (inhalation, ingestion, dermal contact), the latter leading the contaminant to the exposed subject (multiple impact pathways). Rather, exposure assessment identifies the situations that lead to the exposure and calculate the absorbed dose by an exposed organism or estimated the emissions in a particular environmental sector, like soil, in the present study. The dose absorbed by a subject represents the amount of pollutant that may be correlated with the effects posed on the human health, it is of course referring to unit human body weight and unit time, being expressed based on available toxicological data. To the extent that these data are referring to the dose effectively absorbed by the target organ, the dose is considered equally with the exposure. In the case these refer to the extern dose, the dose is calculated multiplying the exposure with a bioavailability factor relating to the exposure pathways (e.g., pulmonary bioavailability, gastrointestinal or dermal). From the quantity point of view, the exposure estimations is performed using both a) information on concentrations level of pollutant from different environmental compartments (air, water, food chain) and b) time information on the presence of subjects in different locations where they are subject of exposure and the extent in which the pollutant effectively reach the subject.

Concerning soil pollution, human risk assessment could be an important tool for decision-making factors in order to identify the best solution for the contaminated soil management. At international level, the first methodology for human risk assessment due to exposure to contaminated soils was developed in 1989 by the Environmental

**Table 1** Standardized methods for determination of heavy metals

Pollutant	Analytical method
Beryllium	SR EN ISO 15586:2004
Cadmium	SR ISO 11047/1999
Chromium—total	SR ISO 11047/1999
Chromium (VI)	SR ISO 11083:1998
Nickel	SR ISO 11047/1999
Lead	SR ISO 11047/1999

**Table 2** Spectral parameters for FAAS determination of metals by the use of AAS-6300 spectrometer

Pollutant	Wavelength (nm)	Detection limit (mg/l)	Type of flame	Lanthanum chloride	Background correction
Beryllium	234.9	0.0003	Oxidizing air/acetylene	No	Zeeman
Cadmium	228.8	0.005	Oxidizing air/acetylene	No	Deuterium
Chromium	357.9	0.01	Reducing air/acetylene	Yes	Halogen
Nickel	232.0	0.02	Oxidizing air/acetylene	No	Deuterium
Lead	217.0	0.05	Oxidizing air/acetylene	No	Deuterium

**Table 3** Establish reference legislative limit values for heavy metals (mg/kg dry weight)

Heavy metal	Reference values according to the Romanian Ord. 756/1997				
	Normal values	Alert threshold depending on land use		Alert threshold depending on land use	
		Sensitive areas	Less sensitive areas	Sensitive areas	Less sensitive areas
Beryllium	1	2	7.5	5	15
Cadmium	1	3	5	5	10
Chromium (total)	30	100	300	300	600
Chromium (VI)	1	4	10	10	20
Nickel	20	75	200	150	500
Lead	20	50	250	100	1.000

Protection Agency of the United States of America (US EPA)—Risk Assessment Guidance for Superfund (US EPA 1989). Subsequently, due to the increase in concern related to the issue of contaminated soils, other methodologies were developed, such as CSOIL developed in the Netherlands, RBECA developed in Italy and CLEA developed in Great Britain. However, all these methodologies are based on the principles developed by the US EPA methodology. In Romania, there are no data, expertise and regulation for the development of human health risk assessments concerning soil pollution (Dumitrescu et al. 2012). As heavy metals are a worldwide pollution problem (are indestructible and most of them have toxic effects on living organisms when they exceed a certain concentration), monitoring these metals is important for safety assessment of the environment and human health in particular (Batayneh 2012).

Related to the present research, human health risk assessment to Be, Cd, Cr<sup>VI</sup>, Ni and Pb is evaluated based on soil contamination. In order to evaluate risk, heavy metal concentrations for both layers are considered. Two main exposure pathways have been selected due to the site-specific land uses and the feature of metals: dermal contact and ingestion of both soil and home-produced vegetables. For the characterization of potential carcinogenic effects, the average daily dose and individual risk are calculated with the following equations (US EPA 1997):

- Exposure through dermal contact

$$I_1 = [\text{CS} \times \text{CF} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}] / [\text{BW} \times \text{AT}] \quad (1)$$

The exposure through dermal contact  $I_1$  is calculated taking into account the chemical concentration in soil (CS), the conversion factor (CF), the skin surface area available for contact (SA), the absorption factor (ABS), the exposure frequency (EF), the exposure duration (ED), the body weight (BW) and the mean time (AT).

- Soil ingestion

$$I_2 = [\text{CS} \times \text{CF} \times \text{IR} \times \text{FI} / \text{BW}] \times [\text{EF} \times \text{ED} / \text{AT}] \quad (2)$$

For the calculation of the exposure through soil ingestion  $I_2$ , data related to the ingestion rate (IR) and fraction ingested from contaminated source (FI) are considered.

- Food ingestion

$$I_3 = [\text{CF} \times \text{IR} \times \text{FI} \times \text{EF} \times \text{ED}] / [\text{BW} \times \text{AT}] \quad (3)$$

$$\text{CF} = C_{\text{dep}} \times \text{GRAF} + C_{\text{trans}} \quad (3.1.)$$

$$C_{\text{dep}} = 0; \quad C_{\text{trans}} = C_s \times \text{UF} \quad (3.2.)$$

The exposure through food ingestion is calculated in this paper taking into account: ingestion of vegetables  $I_3$



considering data related to ingestion rate (IR) and fraction ingested from the contaminated source (FI). Heavy metals concentration in vegetables is estimated considering the concentration due to the direct deposition of contaminants is zero, and the concentration due to translation from the roots is based on root uptake factor (UF) and concentration of contaminant in soil (Cs). It was assumed that 100 % of the territory is dedicated to the cultivation of crops (corn), this being the real context. Concerning diet, 10 % of the corn is used from the contaminated area. These are assumed percentages, considering the local context.

- Carcinogenic risk

$$\text{IndividualRisk} = I \times \text{SF} \quad (4)$$

where  $I$  = chronic daily intake (mg/kg/day) and SF = slope factor (mg/kg/day).

In case the risk is determined by several pollutants, the risk is calculated as the sum of the risk generated by each pollutant for each exposure pathway:

$$\text{Risk}_{\text{Total}} = \sum \text{Risk}_i \quad (5)$$

where  $\text{Risk}_i$  is the estimated risk of each substance.

- Total exposure

$$\begin{aligned} \text{CancerRisk} = & \text{Risk}_{\text{Total}}(\text{exposurepathway1}) \\ & + \text{Risk}_{\text{Total}}(\text{exposurepathway2}) + \dots \\ & + \text{Risk}_{\text{Total}}(\text{exposurepathwayi}) \end{aligned} \quad (6)$$

## Results and discussion

### Experimental data

Heavy metals in soil are involved in a series of complex chemical and biological interactions that include oxidation-reduction, precipitation and solubilization, volatilization, bioaccumulation and bio-percolation.

Mineralogical composition of soils and its variation differentiate the behavior of heavy metals. Organic materials, clay minerals and amorphous oxides of Fe, Mn and Al play a major role in the adsorption of heavy metals. Speciation of heavy metals in soil solution depends largely on their adsorption on the surface of the soil components and/or precipitation as a separate phase (Choi 2006).

One of the most important factors controlling the immobilization (adsorption) and mobility of heavy metals in soils is pH; low pH associated with low water hardness can lead to increased metals toxicity as a result of their increasing mobility. Aging is a factor which affects also the mobility of metals in soils and plants. As a result of

chemical processes, metal mobility can decrease over time, with or without reducing the total concentration of metal. The degree of aging of metal depends on the following factors: temperature, drying and soaks, pH, total concentration as well as total concentration of the metal (Sposito 1989).

The present research targets the concentration levels of each metal, i.e., Be, Cd, total Cr and  $\text{Cr}^{\text{VI}}$ , Ni and Pb, in twelve points on two soil layers (0–0.2 and 0.2–0.4 m) and in depth up to 2.1 m. Figure 1 presents concentration levels found in both soil layers for all five metals.

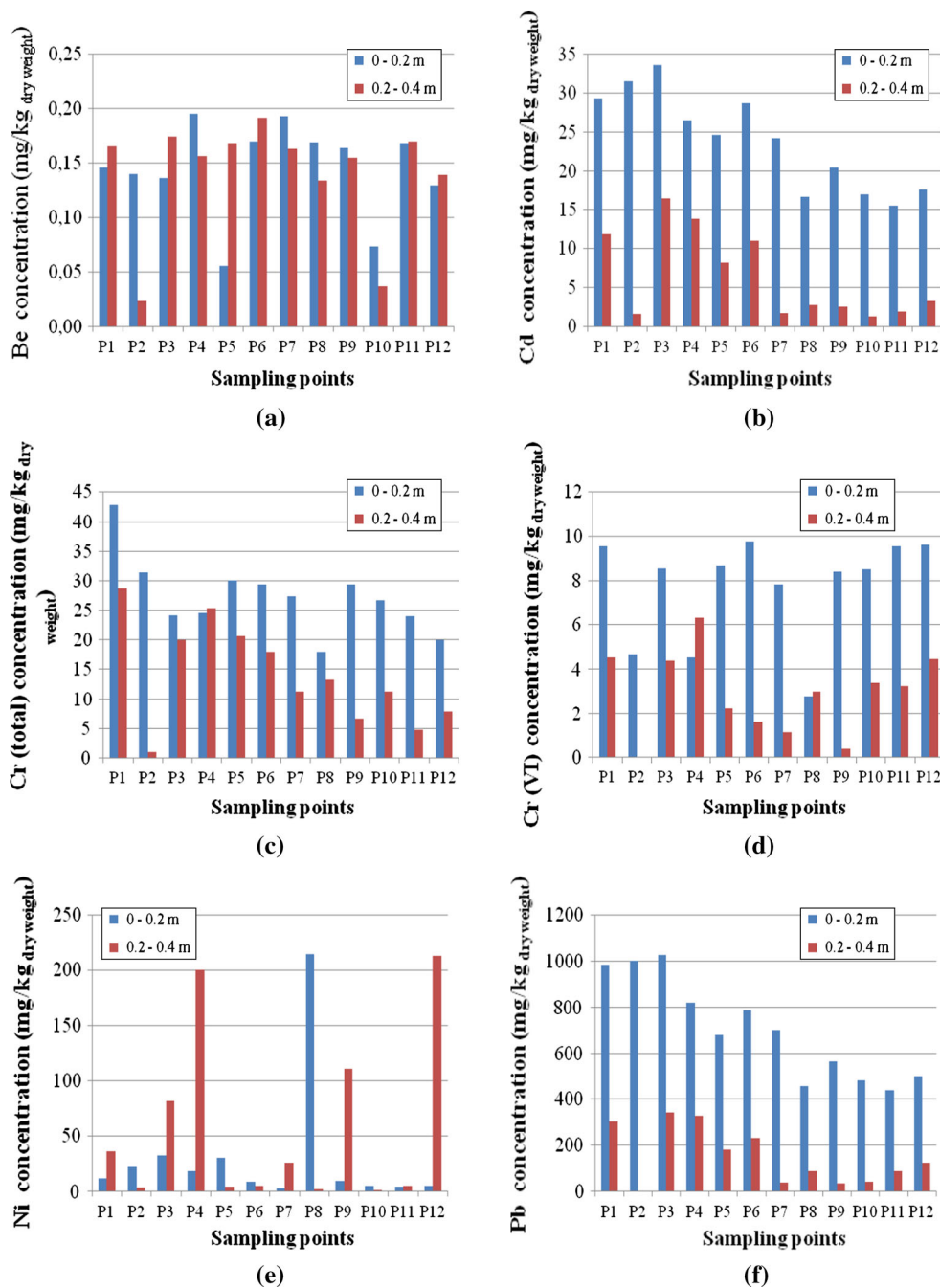
Figure 1 reveals visible quantitative evolution between soil layers:

- Be concentration is almost the same for both soil layers (0–0.2 and 0.2–0.4 m). Only for 3 sampling points, P2, P5 and P10, results show big variation of Be concentrations between these two layers. The rest of sampling points presents an average load of 0.15 mg Be/kg<sub>d.w.</sub>, which is beyond the norm of alert threshold for sensitive use. The maximum concentration value, almost ten times less than the alert threshold for sensitive use, was obtained in both soil layers, but in different location (0.195 mg Be/kg<sub>d.w.</sub> in P4 and 0.191 mg/kg<sub>d.w.</sub> in P6).
- Cd concentrations have a net difference between the surface and the bottom soil layer, being almost 3 times bigger in surface layer. The intervention threshold limit established by Romanian law of 5 mg/kg<sub>d.w.</sub> is much exceeded for all surface layer sampling points. Even if for the 0.2–0.4 m soil layer depth the concentration values strongly decreased in comparison with surface soil layer, there are some points (P1, P3, P4, P5 and P6) which still exceed the intervention threshold limit.
- Cr(total) concentrations are less the limits set in the Romanian legislation, the maximum concentration itself being far below the alert threshold of 100 mg/kg<sub>d.w.</sub>, although the Cr(VI) speciation exceeds the alert threshold limits for sensitive areas established by legislation at 4 mg/kg<sub>d.w.</sub> in all surface points. Even for beneath soil layer Cr(VI) resulted data are in 4 sampling points bigger than this limit too. This fact indicates a chronic pollution of the area generated by a persistent discharging in the environment.
- Ni concentrations exceed the sensitive areas alert threshold limit of 75 mg/kg<sub>d.w.</sub> in one surface soil layer point (P8) and in 4 bottom soil layer points (P3, P4, P9 and P12), but all concentrations are less than the threshold of intervention for sensitive areas.
- All Pb concentrations exceed both the alert (50 mg/kg<sub>d.w.</sub>) and intervention alert (100 mg/kg<sub>d.w.</sub>) thresholds





**Fig. 1** Concentrations variation in 0–0.2 and 0.2–0.4 m soil layers for: **a** Be; **b** Cd; **c** Cr—total and VI; and **d** Ni and **e** Pb

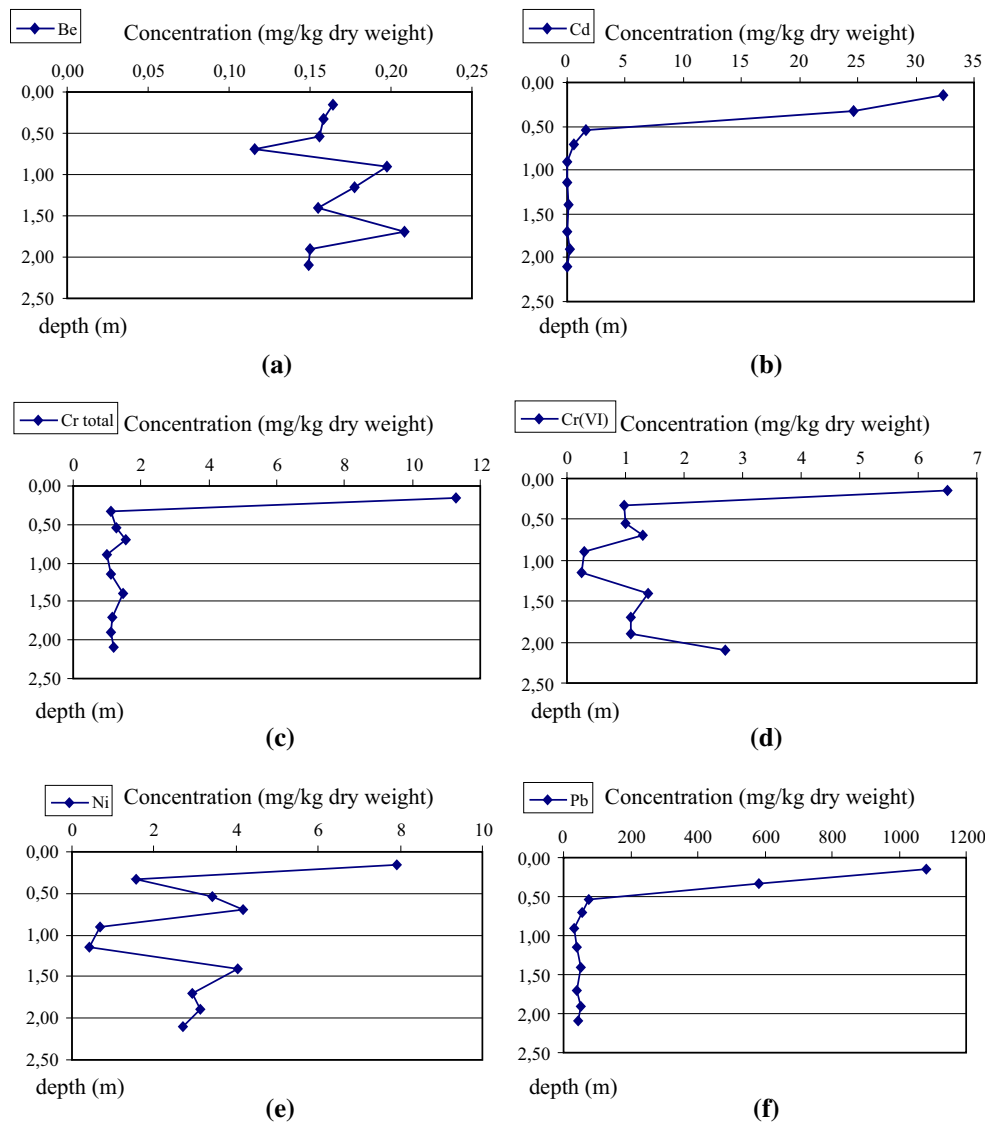


for sensitive areas. For the surface soil layer, Pb concentrations are 8–20 times bigger than the alert limit for sensitive areas. General tendency of Pb concentration is to decrease with soil layer depth, but only for bottom soil layer the concentration values falls under the alert threshold. The existence of an old Pb pollution factor in this area it is more than evident.

The heavy metal concentrations indicate that both soil layers present a complex pollution. All five measured

metals have significant concentration levels which concerns the health of population from the area. For some of considered heavy metals, Cd, Cr(VI), Ni and Pb, the pollution tends to become chronically. Therefore, taking into consideration higher concentration values obtained for 0–0.4 m soil depth, it was evaluated also the in depth variation of all five studied metals concentrations up to 2.1 m.

Figure 2 presents in depth average results variation of heavy metal concentrations.



**Fig. 2** In-depth soil average concentrations for: **a** Be; **b** Cd; **c** Cr total and VI; **d** Ni; and **e** Pb

Figure 2 shows clearly the followings findings:

- except Cd, all other 4 heavy metals are present in all soil samples, up to 2.1 m depth;
- even if soil depth increases, the Be and Ni concentrations do not decrease drastically and vary around an average value of 0.25 mg/kg<sub>d.w.</sub> for Be, and, respectively, 2 mg/kg<sub>d.w.</sub> for Ni;
- Cr total and Cr(VI) have the same variation profile. Cr(VI) concentrations represent almost a half from the total Cr concentrations values. Below 0.5 m soil depth, all Cr(VI) concentration values are less than 4 mg/kg<sub>d.w.</sub> (alert limit for sensitive areas);
- Cd and Pb concentrations decrease drastically in depth soil to small values;

- all studied heavy metals present for 2.1 m depth soil sample concentrations below the allowed limits established for sensitive areas, which indicate that the pollution found for surface soil layers do not strongly leached to the underground waters;
- this research results should be an alarm trigger and intend to be a base for helping authorities further environmental protection program development for this area.

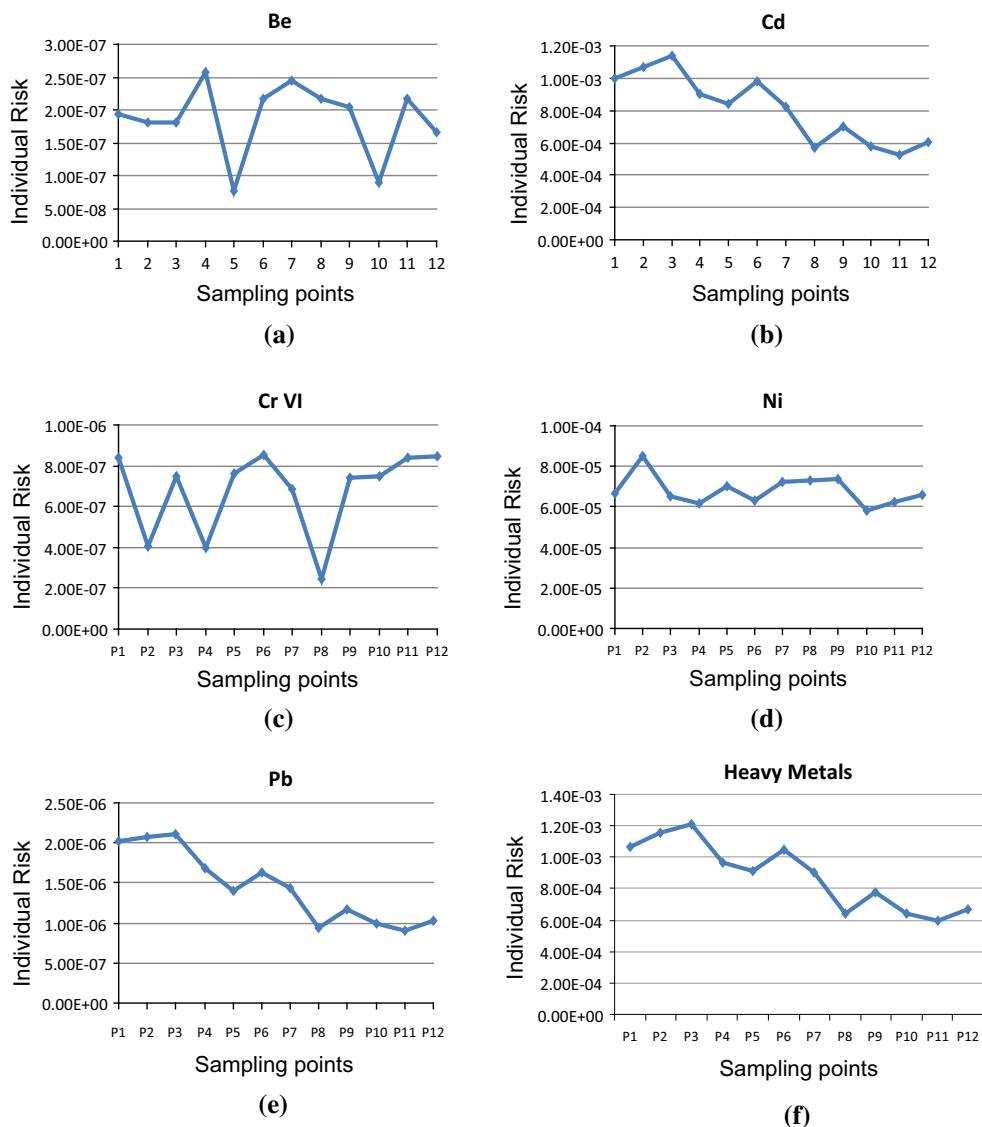
**Exposure assessment and risk characterization**

Potential human health risk of Be, Cd, Cr<sup>VI</sup>, Ni and Pb in sandy to loamy soil used in agriculture from Central

Romania is analyzed by the method of risk assessment based on dose–effect relationships. Concerning to the estimated individual risk, taking into consideration the heavy metal concentrations from the first layer (0–0.2 m), the main results are presented in Fig. 3.

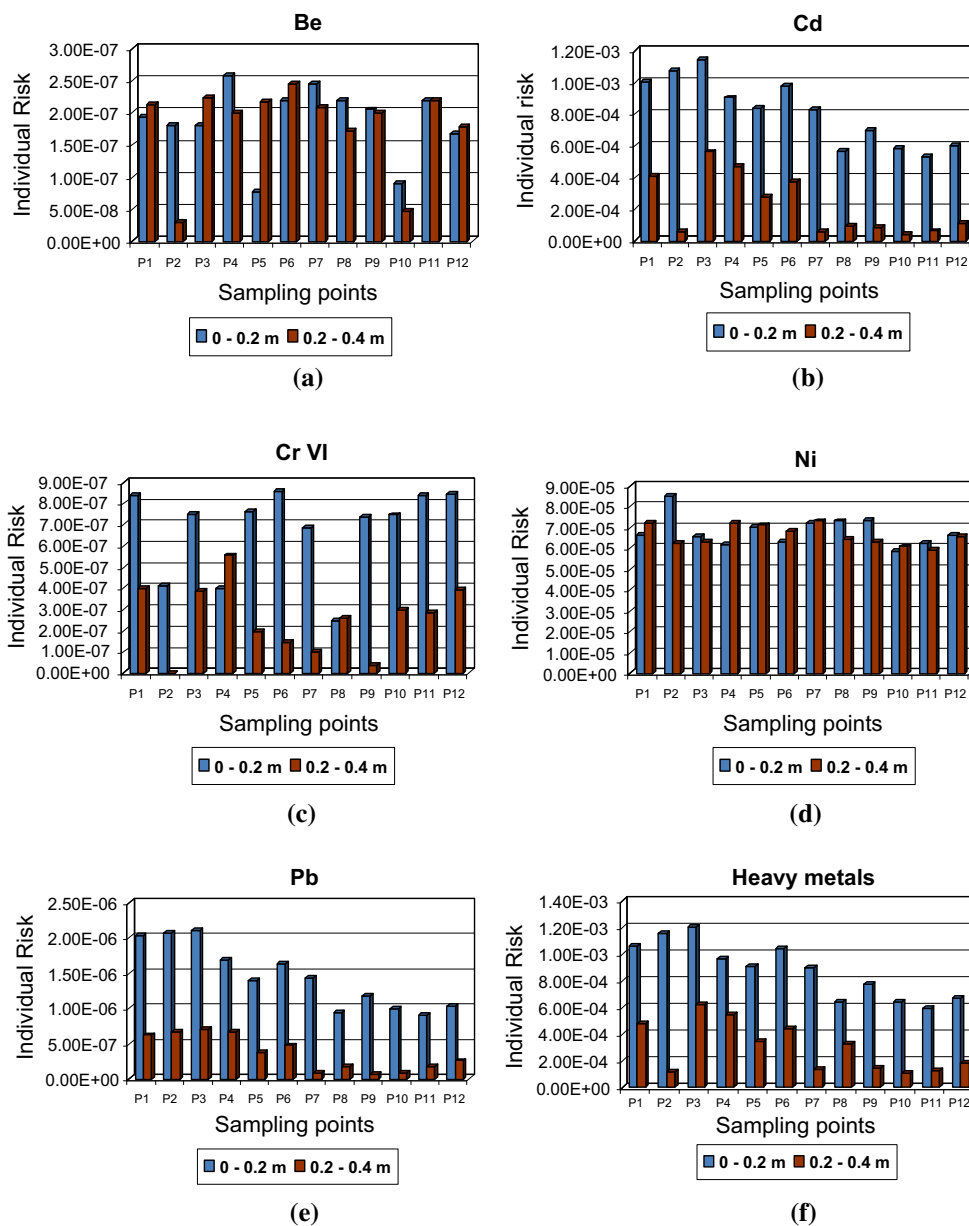
As it can be observed in Fig. 4, the associated individual risks of the first layer concerning metals such as Cd, Ni and Pb are higher than  $10^{-6}$  which means one case of cancer over one million of exposed people (World Health Organization) (Dumitrescu et al. 2012). Even that Pb concentration is 8–20 times bigger than the alert limit for sensitive

use, the highest individual risk was obtained related to Cd level of concentration in soil. This result was also evidenced by Ye et al. (2015): the evaluation of the ecological risk showed that Cd, Hg and As had relatively high ecological risk index, especially the ecological risk of Cd should be paid attention to. This is explained by the fact that Cd carcinogenicity is higher than the carcinogenicity of Pb or Ni. Slope factors for the assessed elements considering the ingestion pathway are illustrated in Table 4. Heavy metal levels of concentration in soil, linked to the pollutant carcinogenicity, are decisive factors concerning



**Fig. 3** Human health individual risk of: **a** Be; **b** Cd; **c** Cr<sup>VI</sup>; **d** Ni; **e** Pb; and **f** all five metals





**Fig. 4** Individual risk variation in 0–0.2 and 0.2–0.4 m soil layers for: **a** Be; **b** Cd; **c** Cr<sup>VI</sup>; **d** Ni; **e** Pb; and **f** all five metals

**Table 4** Heavy metal concentration levels, slope factors and estimated individual risks

	Heavy metals average concentration in first layer (mg/kg <sub>d,w</sub> )	Slope factor (mg/kg/day)	Individual risk
Beryllium	0.15	$1.5 \times 10^{+1}$	$1.87 \times 10^{-7}$
Cadmium	23.83	$1.5 \times 10^{+1}$	$8.10 \times 10^{-4}$
Chromium (VI)	7.71	$4.20 \times 10^{-1}$	$6.76 \times 10^{-7}$
Nickel	50.68	$9.10 \times 10^{-1}$	$6.82 \times 10^{-5}$
Lead	704.22	$8.50 \times 10^{-3}$	$1.45 \times 10^{-6}$

**Table 5** Basic statistics for the surface soil layer data (all concentrations in mg/kg dry weight)

Variable	Symbol	<i>N</i>	Mean	Min	Max	SD
Surface soil layer (0–0.2 m)						
Beryllium	Be	12	0.15	0.06	0.20	0.04
Cadmium	Cd	12	23.83	15	34	6.28
Total chromium	Cr <sup>tot</sup>	12	27.29	18	43	6.35
Hexavalent chromium	Cr <sup>VI</sup>	12	7.71	3	10	2.36
Nickel	Ni	12	30.29	4	215	58.89
Lead	Pb	12	704.22	440	1.026	220.47
Surface soil layer (0.2–0.4 m)						
Beryllium	Be	12	0.14	0.02	0.19	0.05
Cadmium	Cd	12	6.35	1	16	5.57
Total chromium	Cr <sup>tot</sup>	12	14.05	1	29	8.53
Hexavalent chromium	Cr <sup>VI</sup>	12	2.89	n.d.	6	1.89
Nickel	Ni	12	57.34	1	215	78.50
Lead	Pb	12	149.63	n.d.	343	123.52

the risk acceptability related to the investigated area. In this way, Fig. 3b, d and e illustrates risks over the acceptable one of  $10^{-6}$ . The average of individual risks of every single element is following the same trend as its slope factors and not the pollutant concentration level as it can be observed in Table 4. Excepting Ni, generally, the highest risk from soil heavy metals contamination is observed in the first layer (Fig. 4) where for the same pollutant, were observed two concentration levels linked to the soil layers: 0–0.2 and 0.2–0.4 m.

The number of replicates (*N*) while calculating the average concentration is 12 because in the investigated area, the soil samples were carried out from 12 points. Descriptive statistics like mean, standard deviation (SD) and range of metals concentration are illustrated in Table 5. SD was derived applying the equation from the package of Microsoft Office Excel 2007.

## Conclusion

The research indicates that both soil layers, 0–0.2 and 0.2–0.4 m depth, present a complex pollution.

All analyzed heavy metals (Be, Cd, Cr total and Cr(VI), Ni, Pb) have significant concentration levels which concerns the health of the population from the area (especially concerning Cd, Ni and Pb elements). For some of the analyzed heavy metals, Cd, Cr(VI), Ni and Pb, the pollution tends to become chronic. Except Cd, the other studied metals (Be, Cr total and Cr(VI), Ni, Pb) are present in all

the soil samples, up to 2.1 m depth. Cd and Pb concentrations decrease drastically in the soil samples. Be and Ni concentrations do not decrease drastically with soil depth. Below 0.5 m soil depth, all studied heavy metal concentrations are below the Romanian legislative allowed limits for sensitive areas, but they are still being detected.

The research indicates that the pollution found for surface soil layers does not strongly leach to the underground waters. The outcome of the risk assessment has indicated that contamination with heavy metals as Cd, Ni and Pb in the investigated area poses a potential health risk to the inhabitants. The individual risk estimated for the analyzed area of interest ( $10^{-4}$  compared to the acceptable one) leads to the necessity of intervention actions. The results of such an analysis are an essential element for the decision-making factors in terms of the management of contaminated sites. The obtained results illustrated that the heavy metals pollution in soil, particularly Cd, Ni and Pb, may cause an unacceptable risk to human health especially if the contaminated land surrounding the metallurgical plants is used for agriculture (sensitive use as in our case study). On the other hand, in order to reduce the health risk, decreasing or avoiding the consumption of homegrown vegetables is desirable.

The research results should be an alarm trigger and is intended to be a base for helping authorities in further development of environmental protection program for this area. Furthermore, using risk assessment as a tool in order to identify the most appropriate solution for the management of contaminated sites could be another important use



of risk assessment. The obtained results across the present research work could be a reference for future contamination assessment.

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