# Horizontal and vertical variability of heavy metals in the soil of a polluted area

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**ABSTRACT**

The Příbram region belongs to the most polluted areas in the Czech Republic. Atmospheric deposition of potentially toxic elements from lead smelter represents the main source of contamination in this region. In this study, the most polluted location intensively used for agriculture situated northeast from the source of contamination was investigated. The individual sampling points were positioned by GPS and representative samples were taken from 0–60 cm split into three 20 cm layers. In the soil samples total Pb and Cd contents, plant available contents of these toxic elements and soil pH were determined. The total Cd content at the investigated site reached up to 13 mg/kg and Pb up to 2500 mg/kg in the top layer. The concentration of both elements decreases with depth and in the 40–60 cm layer the maximum content of only 6 mg Cd/kg and 400 mg Pb/kg was found. The plant available the content of Pb and Cd in the soil is related to the pH value. The correlation coefficient of exponential regression for Cd is –0.799 and for Pb is –0.787. The obtained data was processed by Surfer 7 software resulting in digital maps of horizontal and vertical contamination of this location. This observation confirmed the airborne source of soil contamination. However, some of the individual sampling points suggested local geogenic contamination of the soil where more detailed further research is required.

**Keywords:** potentially toxic elements; cadmium; lead; spatial variability; soil; polluted area Příbram

Human activity causes undesirable enrichment of soil by trace elements, with an effect on geogenic content. Trace elements can enter into soil from mineral and organic fertilizers, waste (sewage sludge, etc.); air pollutants and irrigation water (Lombi et al. 2001). The so-called old load of urban soils in cities and in areas of mining and processing of mineral resources (mainly metals) are still a serious problem (Ross 1994).

The stability of elements in the soil is high in contrary to other components of the environment (atmosphere, water), causing long-time or even permanent pollution (Kozák 1991). The total contents and potential mobility of these elements depends on chemical and physical properties of both the soil and the elements and the content is gradually decreased by leaching, plant uptake, erosion and evaporation. Spontaneous degradation is very limited by long half-time (Pb 740–5900 years, Cd 13–1100 years). A significant factor affecting he behaviour of the elements in the soil is their sorption (Kabata-Pendias and Pendias 1986). The pH of the soil influences the solubility and availability for plants most significantly (Tlustoš et al. 1995, Hooda and Alloway 1996, Krebs and Gupta 1998, Podlešáková et al. 1998). The majority of ion fractions start getting mobile with decreasing pH (Wenzel et al. 1999).

The metals in the soil can occur in water-soluble fraction, exchangeable, bound to carbonates, bound on oxides and hydroxides of Fe and Mn, bound to soil organic matter and bound to structural matrix of minerals (residual) (Tessier et al. 1979). The most readily available to the plant were water-soluble and exchangeable fractions. The other forms except residual ones are potentially available and changing soil properties (Makovníková 2000) can increase their mobility.

The region of Příbram belongs to the most damaged areas in the Czech Republic. The main source of Pb contamination was the atmospheric deposition of trace elements by galenite mining followed by ore smelting and lead processing. Mining and metallurgical activities in this area led to enhancement of As, Cd and Zn contents in soil, due to the high content of trace elements in parent rock. The higher content of Pb in the air and the accumulation of trace elements in the soil and plants have a negative influence on the quality and quantity of agricultural production (Vrubel et al. 1996). With greater distance from the source of contamination the concentration of elements in soil decreases. The zone of maximum contamination is up to 1.5 km from the chimney of the smelter (Vrubel et al. 1996). Rieuwerts and Farao (1996) and Borůvka et al. (1996) noted extremely high contamination in this region, too.

When investigating spatial variability of soil properties and soil contamination, it is important to approach separately the parts of the area with

different size and relative homogeneous character of the property under consideration, but not the whole area. With the help of modern technology it is possible to quantify the variability with sufficient accuracy. For exact determination of the location we used a Global Position System (GPS), followed by Geographic Information System (GIS) technology were used. The technology is able to transform obtained data into various information layers. By the ESRI definition GIS represents an organised collection of hardware, software and geographical data, proposed to effective obtaining, saving, modifying, analysing and imaging all forms of geographical information. These systems can be used for determining the range and variability of contamination of the area by trace elements. Output is a digital map of horizontal and vertical characterisation of the contamination. This information allows us to determine the range and intensity of contamination and to suggest the most suitable way for contamination removal or restriction of trace elements uptake by agricultural plants on arable land with the respect to defined areas.

GIS is used for determining the vertical and horizontal contamination in polluted areas more often. Hellawell et al. (2001) used GIS to determine the range of soil contamination by chloride solvent and to suggest an optimal and beneficial remediation technology. They used an irregular triangular grid. This system was also used for the detection of magnesium oxides emission effects on changes of pH and for depicting spatial distribution of pH values (Machin and Navas 2000). Facchinelli et al. (2001) used GIS to map contamination by Cr, Co, Ni, Cu, Zn and Pb in Piedmont (NW Italy).

The aim of this study was to determine and to depict in the form of digital maps the spatial variability of soil contamination by Cd and Pb in the locality of the greatest influence of emissions from Kovohutě Příbram stack. And to determine locations with other than emission contamination and then afterwards to specify the relation between available content of trace elements and soil pH.

## MATERIAL AND METHODS

The investigation was focused on the most emission-damaged part of Příbram region to characterize effects of airborne Cd and Pb soil pollution. This part is due to dominant south-western airflow located in the northeast from the source of contamination – Kovohutě chimney (Vrubel et al. 1996). This area is characterised as mildly warm, mildly wet till wet highlands. The dominant soil type is Cambisols, less frequently Fluvisols and Gleysols (Vrubel et al. 1996). Investigated area is mainly used for agriculture. About 60% of samples were taken from arable soil and 40% from grassland.

46 soil samples were collected from an area of 4 km². Positions of samples were irregular and were accurately localized by Garmin GPS II receiver. Most of the samples were from arable land. Locations with high probability of secondary contamination from smelter waste were excluded. Irregularity of sampling positions is proved by greater importance of determining of the range of contamination than of using geometrically regular grid.

The digital map (Figure 1) with latitude and longitude on axes shows the spatial distribution of 46 sampling points. The cross represents the location of source of contamination (chimney). Due to vicinity of the stack (Huťský woodlet and city border) it was impossible to obtain samples in the
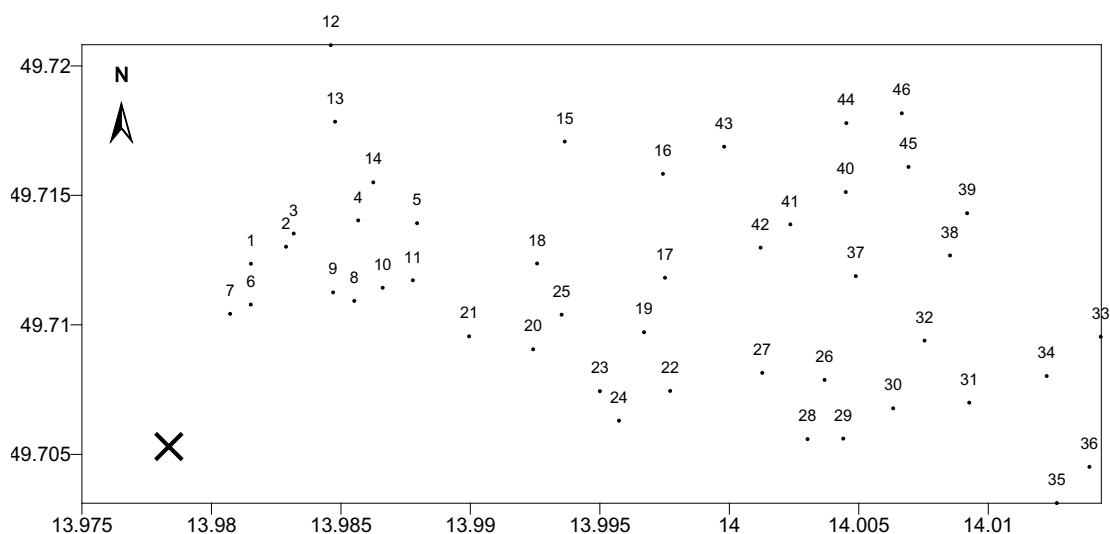


Figure 1. Soil sampling points (× – source of contamination, x axis – longitude, y axis – latitude)
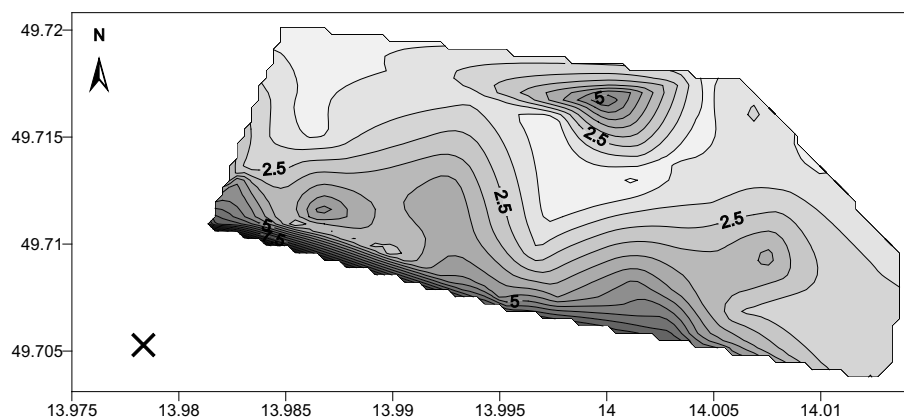
Figure 2. Total content Cd in soil (ppm) – A-layer 0–20 cm (× – source of contamination, x axis – longitude, y axis – latitude)
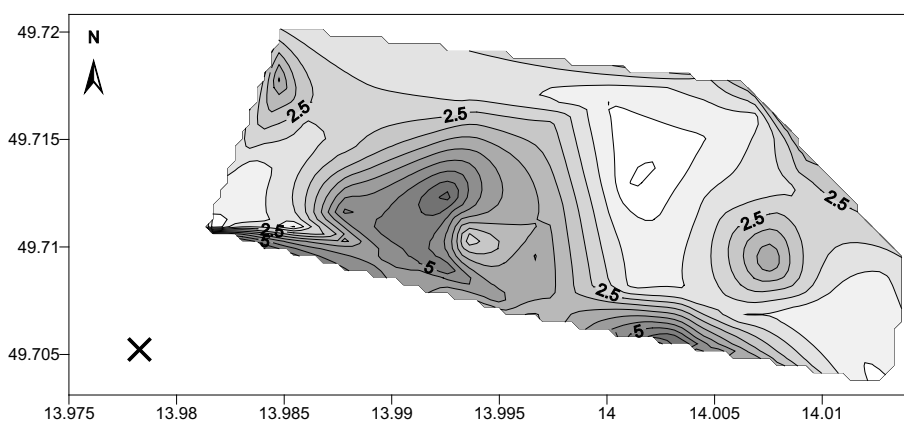


Figure 3. Total content Cd in soil (ppm) – B-layer 20–40 cm (× – source of contamination, x axis – longitude, y axis – latitude)
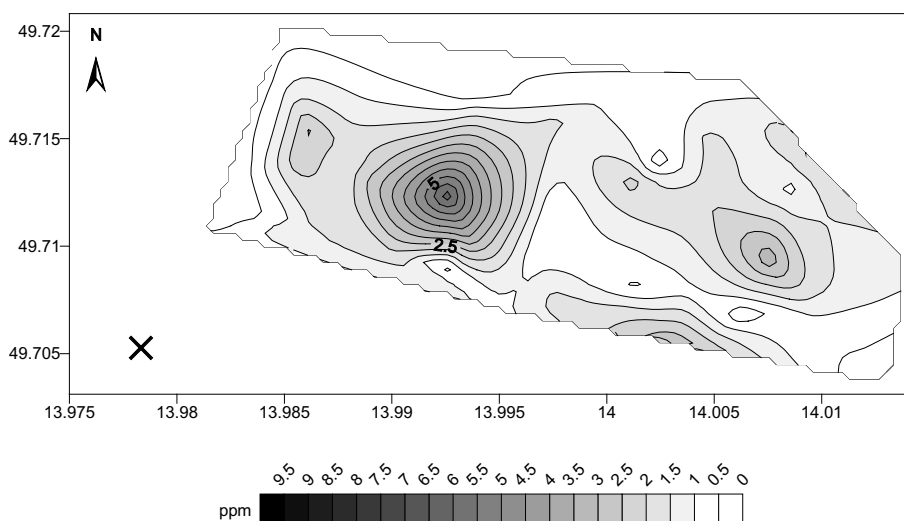


Figure 4. Total content Cd in soil (ppm) – C-layer 40–60 cm (× – source of contamination, x axis – longitude, y axis – latitude)

very neighbourhood of contamination source. The closest point is the one of number 7. The distance is about 400 m from the chimney.

Mean soil sample is the sum of 8 samplings from the circle of 6 m radius. Samples were taken mainly from arable land down to depth of 60 cm split into
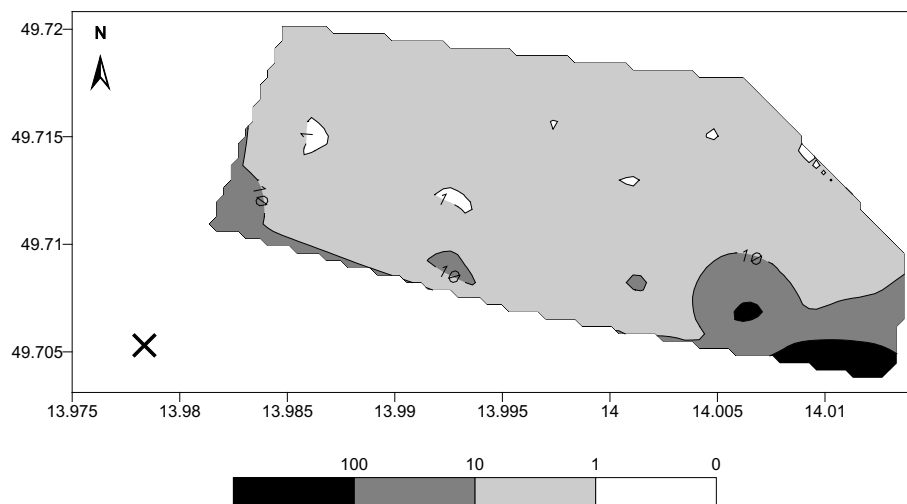
Figure 5. Ratio of the Cd contents in A- and C-layer (× – source of contamination, x axis – longitude, y axis – latitude)

3 layers of soil profile (A-layer = 0–20 cm, B-layer = 20–40 cm, C-layer = 40–60 cm). The individual layers were evaluated separately.

After drying and homogenisation of samples the pH value in 0.01 mol/l CaCl$_2$ extract in ratio 1:10 (w/v) (Page et al. 1982) was determined. Total element concentrations in soil were determined separately in digests obtained by two-step decomposition as follows: 0.5 g of sample was decomposed by dry ashing in a mixture of oxidizing gases (O$_2$ + O$_3$ + NO$_x$) in Apion Dry Mode Mineralizer (Tessek, CZ) at 400°C for 10 h; the ash was then decomposed in a mixture of HNO$_3$ + HF, evaporated to dryness at 160°C and dissolved in diluted *aqua regia* (Száková et al. 2000). The plant available contents of Pb and Cd were determined in 1 mol/l NH$_4$NO$_3$ extract in ratio 1:2.5 (w/v) for A-layer (Pruess et al. 1991). Inductively coupled plasma optical emission spectrometry (Vista Pro, Varian, Australia) was applied for determination of Cd and Pb in both soil digests and extracts.
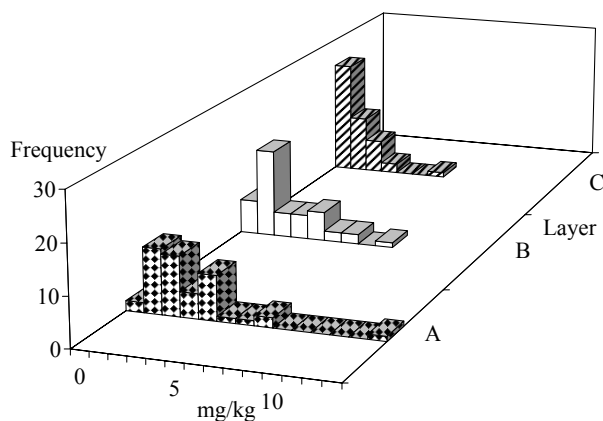
Quality of soil analyses was controlled by reference material RM 7001 Light Sandy Soil with certified contents of Cd 0.32 ± 0.05 mg/kg, Pb 43.8 ± 3.7 mg/kg and obtained Cd 0.33 ± 0.02 mg/kg and Pb 40.2 ± 3.4 mg/kg.

Obtained data were processed by Surfer 7 (Golden Software 1999) to contour digital maps. Natural Neighbor method was used. The maps represent vertical changes of pH values in different parts of the area, vertical and horizontal distribution of Pb and Cd contamination. Input data were divided into intervals. Intervals for pH values were 0.2 unit wide, 0.5 mg/kg for Cd content and 100 mg/kg for Pb content due to large range of values. Division by isolines is better for visual consideration of variability by size, shape and distribution of areas of the same values.

**RESULTS AND DISCUSION**

Cadmium concentrations in individual layers depicted by isolines and colors are presented in Figures 2–4. Total Cd content in soil varied from 13.1 mg/kg in A-layer to 0.01 mg/kg in C-layer. Surprisingly, the Cd contents did not decrease regularly with the distance from the chimney but a strip of higher contents occurred (Figure 2). This strip contains the sampling locations 6, 7, 24 and 28, where the total content was higher than 6 mg/kg. For the other locations the content decreases with distance from the contamination source, with exception of location 43, where the Cd content 5.8 mg/kg was measured regardless of the concentrations about 1 mg/kg in surrounding locations. This abnormality will be investigated in detail in further research. The trend of contamination in transitional B-layer is depicted in Figure 3. It is apparent that from Figure 4 (C-layer) the Cd concentration decreases



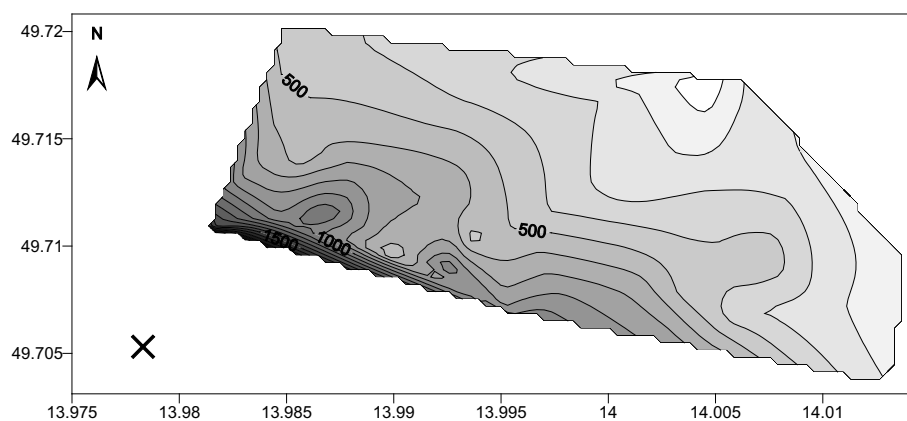Figure 6. Frequency histograms of Cd distribution in A-, B-, C-layers

Figure 7. Total content Pb in soil (ppm) – A-layer 0–20 cm (× – source of contamination, x axis – longitude, y axis – latitude)
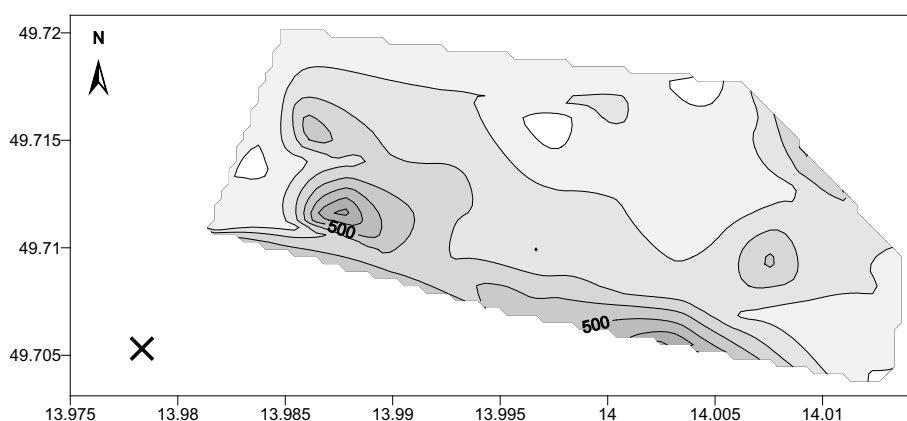


Figure 8. Total content Pb in soil (ppm) – B-layer 20–40 cm (× – source of contamination, x axis – longitude, y axis – latitude)
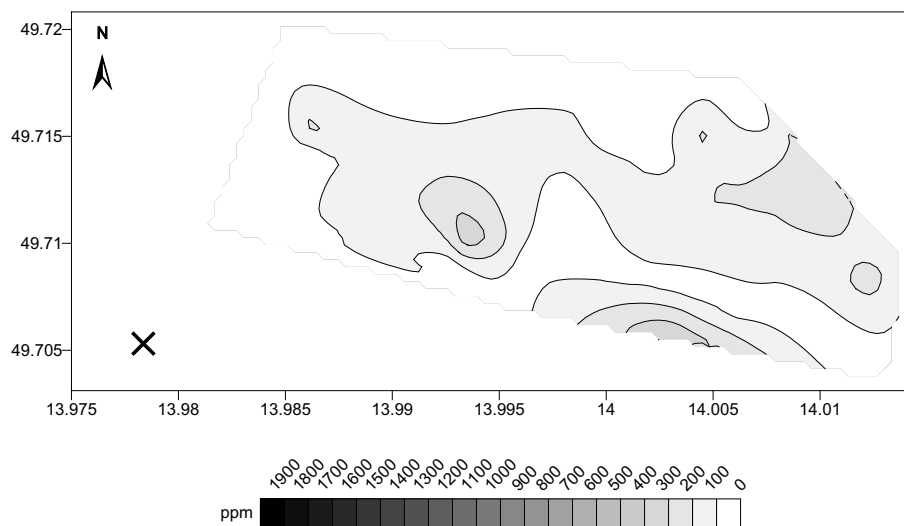


Figure 9. Total content Pb in soil (ppm) – C-layer 40–60 cm (× – source of contamination, x axis – longitude, y axis – latitude)

with depth. Total contents are lower in C-layer than in A-layer, but there are also some exceptions – they could be seen from the map from the ratio of A-layer and C-layer content (Figure 5). It is mainly location 14, where the Cd concentration raised from 1.02 mg/kg in A-layer to 2.59 mg/kg in C-layer, then location 42 (from 0.9 to 2.21), location 18, where the concentration in C-layer is
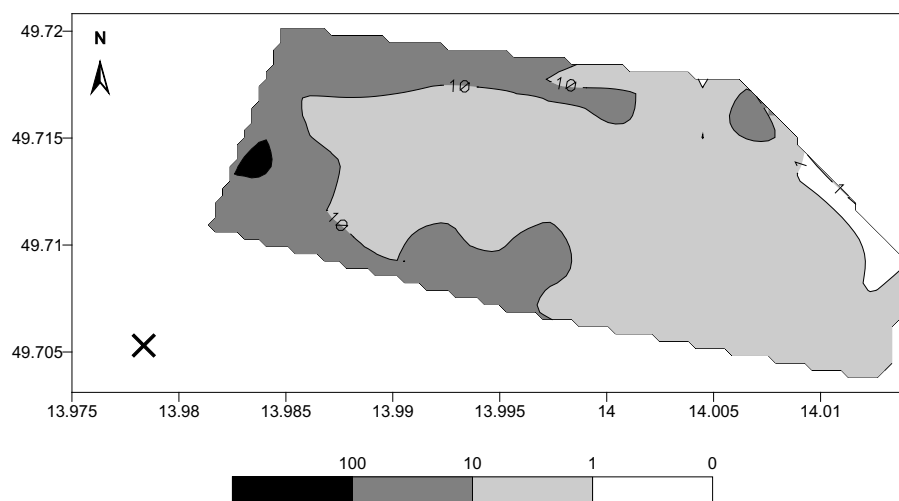
Figure 10. Ratio of the Pb contents in A- and C-layer  (× – source of contamination, x axis – longitude, y axis – latitude)

twofold higher than the concentration in A-layer (6.34 mg/kg), in vicinity of points 16 and 39, where the ratio is about 0.6, and a small increase is in location 40. These locations indicate a high local geogenic contamination requiring further detailed investigation.

Frequency histograms of Cd contents in 3 layers of soil profile (Figure 6) indicated that concentrations above 5.0 mg/kg do not occur in C-layer (except in problematic spot 18) and most often the values are up to 1 mg/kg. In the A-layer the maximum content was 13 mg/kg and most often the values were between 2 and 5 mg/kg. The decrease in total Cd contents with soil profile depth indicates that the surface character of soil contamination is influenced by air pollution.

Figures 7–9 show soil contamination by Pb. Concentrations in the A-layer (Figure 7) reached values above 1000 mg/kg not only in locations 1, 6 and 7 in vicinity of the contamination source, but also in locations 10, 11, 20 and 24. In the A-layer the total Pb contents range from 116 to 2538 mg/kg.
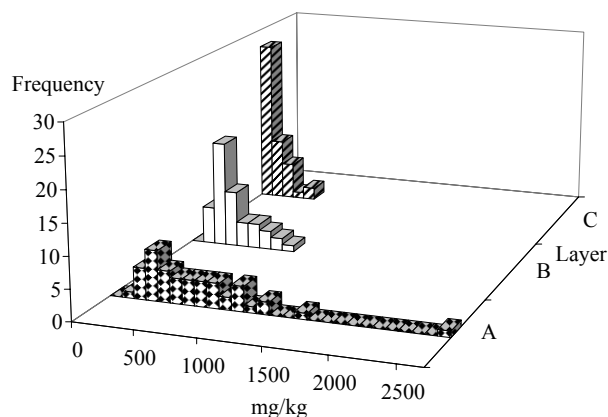


Figure 11. Frequency histograms of Pb distribution in A-, B-, C-layers

Figure 8 shows the contamination in the B-layer. The contents decrease with the depth – in the C-layer (Figure 9) the values were in the range of 4.3–411 mg/kg. Due to very low mobility of Pb this decrease is more considerable then Cd, but also with exceptions in locations 33, 34 and 39 in the C-layer. The ratio of contents was about 0.8 there (Figure 10). In location 44 the contents raised from 12.7 mg/kg in A-layer to 41.9 mg/kg in C-layer. These sampling points suggested local geogenic contamination similarly as in the case of Cd.

Histograms of Pb contents (Figure 11) show concentrations above 1000 mg/kg in the A-layer, usually in the range of 300–1100 mg/kg, while in the C-layer the maximum concentrations are up to 500 mg/kg, with the mean value of less than 100 mg/kg.

Vrubel et al. (1996) noted concentrations in the scale of percentage of permissible pollution limit. Each interval was made in a specific colour. The results are maps with colour distinguished by the concentration of the element under consideration in arable land in top A-layer. These concentrations do not follow the border of individual fields. For example field No. 2162 showed Pb content in the range from 350 to 700 mg/kg. Our investigations confirmed lower contents (160 mg/kg). Therefore, it is not suitable to deal with a whole piece of land, but with parts of relatively homogeneous character of studied property.

There are horizontal and vertical changes in pH values of the soil in Figures 12–14. These values range from 4.4 to 7.25. In the A-layer (Figure 12) there are apparent localities with values differing very much from surroundings. Around points 9, 12, 17, 18 and 32 the pH value was as high as 7, on the other hand in points 3, 5, 7, 24, 28, 35, 42 and 46 the maximum value was 5.5. From the histogram (Figure 15) the most frequent values in interval 6–6.8
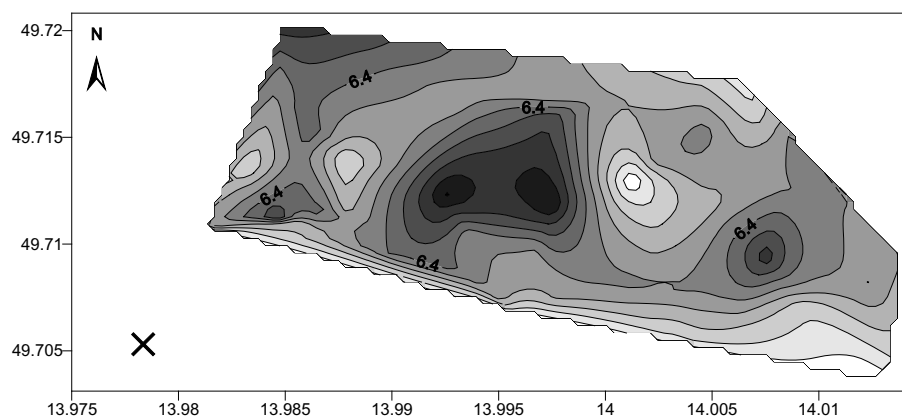
Figure 12. Soil pH – A-layer 0–20 cm (× – source of contamination, x axis – longitude, y axis – latitude)
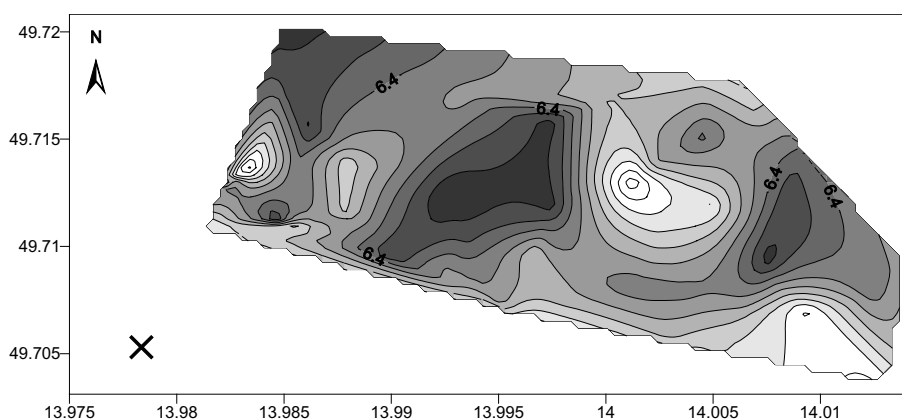


Figure 13. Soil pH – B-layer 20–40 cm (× – source of contamination, x axis – longitude, y axis – latitude)
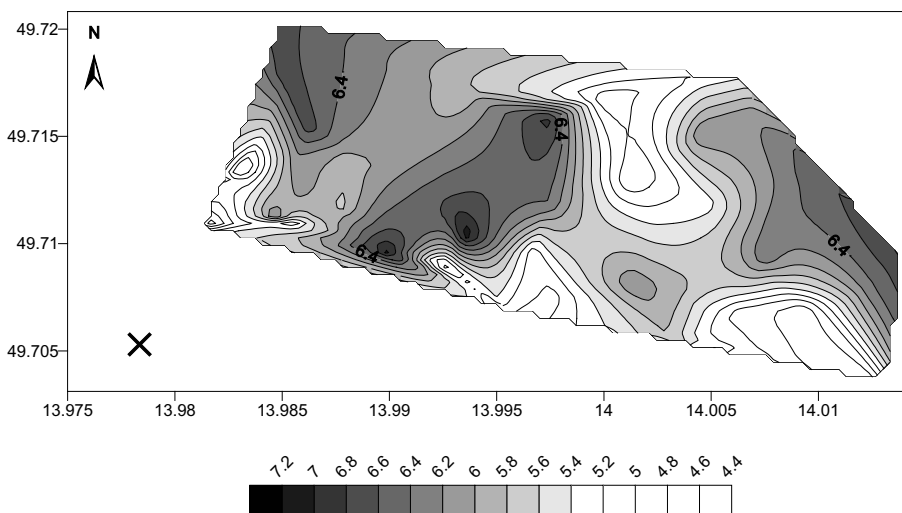


Figure 14. Soil pH – C-layer 40–60 cm (× – source of contamination, x axis – longitude, y axis – latitude)

are seen in this layer. The changes of pH values in the B-layer are in Figure 13. Figure 14 shows pH values in the C-layer. For most individual spots the pH values did not change markedly with depth.

The plant available content of Pb and Cd in soil is related to pH value. In Figure 16 there are values of portion available for plants in percentage related to pH values of the soil. The correlation coefficient
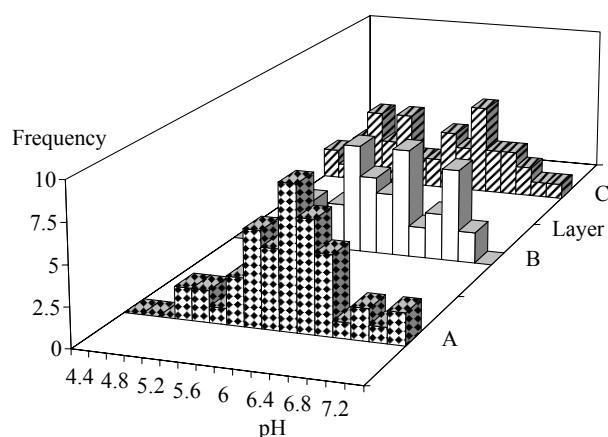
Figure 15. pH data set histogram (A-, B-, C-layers)

of exponential regression for Cd $r = -0.799$, which means close dependence especially at pH level below 6. It is explained by a strong binding of Cd above pH 6 (Blume 1994). Most of Cd which is strongly pH dependent, is bound mainly on sesquioxides in soil (Száková et al. 2001).

The following graph (Figure 17) shows the dependence for Pb. Correlation coefficient $r = -0.787$. Pb is tightly bound in soil organic matter and sesquioxides above pH value of 4 (Blume 1994, Száková et al. 2003).

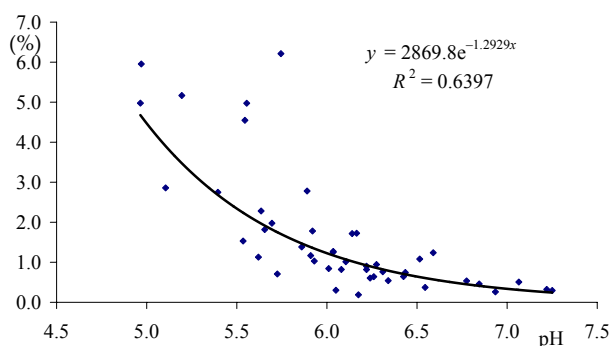For soil sampling, used for the description and determination of main areas corresponding to



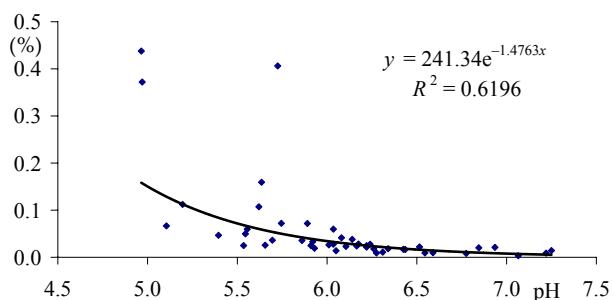Figure 16. The influence of soil pH on plant-available contents of Cd in soil (A-layer)



Figure 17. The influence of soil pH on plant-available contents of Pb in soil (A-layer)

different levels of a studied factor, the density of samplings is an important parameter. With higher density the variability between nearby samples decreases (Brodský 2003). Romic and Romic (2003) studied trace elements distribution at the area of 860 km² in the Zagreb vicinity. They carried out analyses of 331 soil samples from a regular 1 × 1 km square grid. The results were maps of concentrations in the surface horizon. One sampling point represented an area of 2.6 km². Our region of contamination is not so extensive and we used a higher density of soil samples. We made 46 samplings on an area of 4 km², i.e. area of 0.09 km² to one sampling point.

Rieuwerts et al. (1999) made samplings at 61 locations in Příbram region and processed data to graphical maps depicting the contamination of the region. They found out Pb concentrations up to 58 500 mg/kg. But it was forestland, which due to higher organic matter content usually reaches about one order higher values than that of arable land, which is affected by agricultural activities, mainly by soil tillage (Dumat et al. 2001).

The maximum allowable values of aqua regia extractable content of trace elements in soil are determined by Act 334/1992 Coll. and Act 13/1994 Coll. According to these regulations, the maximum acceptable values for given soil types are 140 mg Pb/kg and 1 mg Cd/kg of soil. Newly proposed regulations define 3 levels of contamination (Bulletin of Ministry of Environment of the Czech Republic 1996). Our analyses of soil samples from this region determined the contents in ranges from 0.9 to 13.1 mg/kg for Cd and from 116 to 2500 mg/kg for Pb. Most of the contents for Cd exceeded the first limit, which characterizes a level of trace element, when further monitoring of contamination is not necessary. In most locations the Pb concentration exceeds 300 mg/kg. There were exceeded limits here, which presents a danger of adverse effects on plants, animals and humans. Therefore, it is necessary to study this locality and to determine the exact boundaries of contamination for this locality, especially for areas where remediation measure will be necessary.

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## ABSTRAKT

**Horizontální a vertikální variabilita těžkých kovů v půdách znečištěné oblasti**

Oblast Příbrami patří k nejvíce poškozeným v ČR. Ke kontaminaci oblasti došlo především atmosférickou depozicí rizikových prvků při zpracování olověných rud a při výrobě olova. Zaměřili jsme se na imisemi nejvíce zatíženou část území, která se nachází severovýchodně od zdroje kontaminace (komín Kovohutě). Z míst přesně lokalizova-

ných GPS byly odebrány půdní vzorky, které byly analyzovány na celkové obsahy Pb a Cd a na jejich pro rostliny přijatelné podíly, a byla u nich stanovena hodnota pH. Celkové obsahy prvků dosahují ve sledované lokalitě ve svrchní vrstvě půdy až 13 mg Cd/kg a více než 2500 mg Pb/kg. Koncentrace obou prvků klesá s hloubkou půdního profilu a ve vrstvě 40–60 cm byly nalezeny maximální koncentrace 6 mg Cd/kg a 400 mg Pb/kg. Rostlinám přístupný podíl Cd a Pb souvisí s hodnotou pH půdy. Korelační koeficient této exponenciální závislosti je pro Cd –0,799 a pro Pb –0,787. Na základě těchto výsledků byly v programu Surfer 7 vytvořeny digitální mapy vypovídající o horizontální a vertikální kontaminaci této lokality. Byl potvrzen převážně imisní původ kontaminace, který se projevil poklesem obsahů těchto prvků s hloubkou půdního profilu, zároveň však byla zmapována místa se silnou lokální geogenní kontaminací, jejíž rozsah je nutné dále zpřesnit.

**Klíčová slova:** toxické prvky; kadmium; olovo; plošná variabilita; půda; kontaminovaná oblast Příbram

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