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Heavy metal Contaminations of Urban soils in Ostrava, Czech Republic: Assessment of Metal Pollution and using Principal Component Analysis

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ABSTRACT: This study investigates the status of heavy metals contaminations in urban soils of Ostrava in the Czech Republic. The main aim of this study was determination of concentration of Cd, Pb, Zn, Cu, Mn, V and Hg, assessment of contamination levels of metals in urban soils and verification of potential source of metals contamination. Soil samples were collected from soil layer of 20 cm and metals were determined by atomic spectroscopy methods (F AAS, GF AAS, AMA 254). It was concluded that metals concentrations in studied soils increased in the following order: Hg < Cd < Cu < Pb < V < Zn < Mn, with mean values of Hg (0.17 mg/kg), Cd (0.20 mg/kg), Pb (66.93 mg/kg), Zn (209.51 mg/kg), Cu (38.49 mg/kg), V (105.18 mg/kg) and Mn (1349.85 mg/kg). The results obtained from assessment of metals pollution by means of index of geoaccumulation (I_{geo}), enrichment factor (EF), contamination factor (CF), pollution load index (PLI), pollution index (PI) and integrated pollution index (IPI) confirmed that urban soils were contaminated in the range from moderately through strongly polluted up to highly contaminated soils. Multivariate statistics approach (Principal Component Analysis) was adopted for the data treatment for identification of contamination sources. This study verified that soil contamination was the result of the industrial processing that occurred in the studied area. All of these data confirmed that Cd, Pb, Zn, Cu, Mn, V and Hg come from anthropogenic activities, especially from industrial processes.

Key words: Contamination, Heavy metals, Urban soils, Industrial city, Correlation, Principal Component Analysis

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INTRODUCTION

Soil pollution by heavy metals is still actual problem in many environmental studies. The urban soil can be considered as a reservoir of pollutants, then also as potential source for subsequent pollutions. The polluting substances can be released from soils under specific conditions back into the environment and soils can be a source of the pollution with the high capacity to transfer pollutants to groundwater, into food chain and into the human body (Lu and Bai, 2010; Wong *et al.*, 2006). Hazardous metals accumulate in soils mainly due to atmospheric deposition from various sources and the most important origin comes form emissions from industry (chemistry, metallurgy, building and electronics industry, etc.), fuel combustion and transport. Therefore, this fact leads to various distributions of metals in the urban environment (Joshi and Balasubramanian, 2010; Maas *et al.*, 2010; Johansson *et al.*, 2009). Increasing the concentration of heavy metals in the soils and sediments takes place by these mechanisms: atmospheric deposition, physico-chemical adsorption, biological uptake and accumulation (Silva *et al.*, 2009). The high ability of persistence and bioaccumulation present a problem with the prevailing heavy metals in environment for a long time (Anu *et al.*, 2009; Oliva and Espinosa, 2007; Imperato *et al.*, 2003).

The content of heavy metals in soils is highly dependent on geochemical behaviour, pedogenic processes and anthropogenic influences. Nevertheless, their accumulation in the soils is considerable because they are persistent, non-biodegradable. The hazardous metals are also toxic to biota if threshold limit is exceeded (Massas *et al.*, 2009, Birke and Rauch, 2000). Metals in soils exist in various forms, such as exchangeable or in the adsorbed forms. The bioavailability of metals and their compounds is influenced by pH value, temperature, redox potential, cation exchange capacity

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of solid phase, competition with other ions, composition and quality of soil solutions (Oliva and Espinosa, 2007; Skordas and Kelepertsis, 2005; Moon *et al.*, 2000). The total concentration of heavy metals in soils is usually regarded as an indicator of urban environmental quality and the severity of pollution depends not only on the total concentration of heavy metals in soils, but also on the their mobile and bioavailable forms (Morton-Bermea *et al.*, 2009; Biasioli *et al.*, 2006, 2007). The concentration of hazardous metals in soils can vary in dependence on locality due to change in the character and intensity of the human activity (Tuccillo, 2006; Manta *et al.*, 2002). Many studies have been focused on the aim to reveal the current state of the urban soils contamination by hazardous metals and metalloids. The environmental studies of soils in many cities around the world confirmed significantly higher concentrations levels of Cd, Cu, Pb, Zn, Hg and other metals (Ajmone-Marsan and Biasoli, 2010; Maas *et al.*, 2010, Jarva *et al.*, 2009; Biasioli *et al.*, 2007; Biasioli *et al.*, 2006; Lee *et al.*, 2006; Wong *et al.*, 2006; Chen *et al.*, 2005; Chirenje *et al.*, 2004; Wong *et al.*, 2002). These studies have provided valuable and precise information about the contamination of metals in urban and suburban soils, in chemistry, or mobility and bioavailability of metals in environment, respectively. The concentrations of hazardous metals in soils, sediments and waters are usually reported as an indicator of environmental quality in regions and the total content of metals in urban topsoil, are also the atmospheric quality characterized (Linde *et al.*, 2001; Ljung *et al.*, 2006; Nicholson *et al.*, 2003). Thus, soils and dust in urban and suburban areas can be successfully used as indicators for the evaluation of the environmental contaminations by hazardous metals due to anthropogenic and industrial activities and related with it atmospheric depositions (Ajmone-Marsan and Biasioli, 2010; Yang *et al.*, 2006).

The enrichment factor (EF), pollution index (PI), integrated pollution index (IPI), contamination index (CF), pollution load index (PLI), contamination degree (C_{deg}) and geoaccumulation index (I_{geo}) were calculated to assess the contamination levels of metals in soils (Serbaji *et al.*, 2012; Kargar *et al.*, 2012; Doležalová Weissmannová and Debnárová, 2011; Ali and Malik, 2011; Lu and Bai, 2010). Another method for the assessment of contaminated soils is the use of multivariate statistical method such as Principal Component Analysis (PCA). This method and derivative method have been used in geochemical application in the identification of pollution sources and the determination of the natural vs. anthropogenic contribution. This method can be used as suitable tool to identify of the source contamination (Li *et al.*, 2013; Lu and Bai, 2010; Jarva *et al.*, 2009; Tariq *et al.*, 2008; Lee *et al.*, 2006; Fachinelli *et al.*, 2001). The objectives of this study in this article were: (1) to determine the concentration of Cd, Pb, Zn, Cu, Mn, V and Hg of urban soils in Ostrava city, (2) to assess the contamination levels of metals in soils, (3) to evaluate the potential source of metals contamination source of contamination of metals using various statistical methods.

MATERIALS & METHODS

Ostrava is highly industrial city with production of bituminous coal and metallurgical industry, with population 305 998 and population density of 1500/ km^2 (2013) and with area about 215 km^2. The city has a history longer than 800 years and coal production began at the late 18th century. In the 20th century, the city was highly focused on the development of mining, steel and other heavy industries (steelworks, metallurgical industry, production of steel alloys, metalworking, etc.). Geographically, the city is located in the northeast of the Czech Republic, near the border with Poland and lies between northern latitudes 49° 482 - 49° 502 N and eastern longitudes 18° 172 - 18° 142 E. The area has a flat topography with average height of 210 m and it is located at the confluence of rivers Lučina, Odra, Opava and Ostravice in Ostrava Basin. Climatically, the city falls into the warm climate and in comparison with other regions also differ by certain peculiarities caused by the high concentration of industry, dense settlement and specific conditions in the Ostrava basin. Therefore, the climate belongs to a slightly warm area MT 10, which are characterized by relatively high average annual temperatures; are higher than 8 °C, annual rainfall is approximately 600 mm. Soils are typically alluvial and predominant soil types are fluvial greying soils on noncarbonated sediments. Various sites in this region are strongly anthropogenically by presence of tailings from mining influenced. Anthropogenic soils formed on the reclaimed dumpsites after opencast brown coal mining cover an important part of this region.

The sampling points were systematically distributed in locations of Ostrava (Fig. 1) and these sampling points were selected in order to cover the main locations of various land use and suitable geographical distribution. An intensive investigation for soils was accomplished during 2010 - 2011 from 51 locations and samples were collected in accordance with ISO 10381-5:2005. A total of 153 soils samples were collected. Each sample of soil were taken from 1 x 1 m areas, collected from a depth of 20 cm, approximate mass of primary samples of soils was 500 g. Soil samples were placed in hermetically sealed

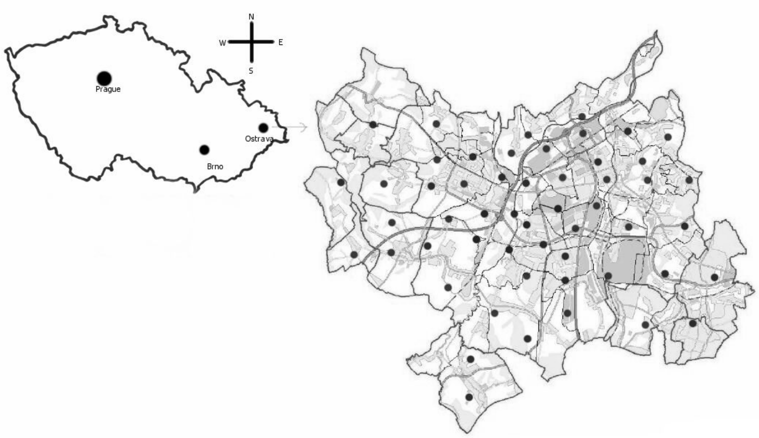

Fig. 1. locations of Ostrava and sampling points

Table 1. Detection (LOD) and quantification (LOQ) limits of Cd, Pb, Zn, Cu, Mn and V in mg/L

Elements	Cd	Pb	Zn	Cu	Mn	V
LOD	4.09×10^{-4}	0.95	0.26	0.25	0.20	9.15×10^{-3}
LOQ	1.37×10^{-3}	3.17	0.87	0.95	0.67	3.05×10^{-2}

polyethylene bags to prevent sample oxidation and transferred to laboratory for chemical analysis. Geographical coordinates were recorded by GPS system (TOMTOM). Numerous studies have shown that surface layer can be used as the main and representative indicator for metal pollutants (Dao *et al.*, 2010; Pagotto *et al.*, 2001). Thus, the depth of 0-10 cm soils surface is the most obvious as fingerprint environmental pollution metals, especially. Before the chemical analysis, the samples were spread out on polyethylene foil and disposed of pieces of roots and other rough undesirable materials. The samples were air-dried at laboratory temperature (22±2 °C) to constant weight. Samples were sieved through 2 mm sieve to remove extraneous materials and all the samples were again sieved through a 150 mm nylon sieve. The dry matter of each sample from weight 1 g of soils was determined at temperature 105±2 °C to constant weight by gravimetric method (ISO 11465:1993). For preparation of samples, standards, and blank solutions, high purity Milli-Q water (Millipore purification system) with resistivity higher than 18 MW/cm was used. Measurements of pH values were in accordance of method ISO 10390:2005. The mixture of soils and 0.01 mol/L $CaCl_2$ (p.a. purity) with ratio 1:5 was shaken for 60 minutes three times at temperature 22±1 °C and the pH values were determined electrochemically using a glass electrode (WTW pH 320 system). The dry samples with adding HNO_3 (2 mol/L, p.a. purity) solution were continuously shaken for 16 hours at temperature of 22±1 °C and then filtered through 0.45 mm membrane filter. Afterwards, samples were analyzed for Cd, Pb, Zn, Cu, Mn, V, and Hg and reported data in this study as dry weight were calculated. The contents of Pb, Zn, Cu, and Mn by flame atomic absorption spectrometry (SpectrAA 30, Varian) were determined. The ZEEnit model AAS 60 (Analytical Jena) atomic absorption spectrometer was equipped by transversely heated graphite furnace (GF AAS) and Zeeman background corrector was used for the determination of Cd and V elements. The atomic vapour generator AMA 254 (Advanced Mercury Analyzer) was used for the precise determination of residual mercury content in the solid soil samples. The standard of mercury solution (check standard) was prepared using 0.5 mL concentrated HNO_3 solution and 0.5 mL concentrated HCl and 0.5 mL $K_2Cr_2O_7$ (1%) solutions and adding 10 mL calibrating standard of mercury solution with the concentration of 1 g/L in 50 mL. Analytical quality control was carried out with certified reference materials CRM CZ 7004 – loam soil with higher contents of analysts, company Analytika) using certified contents of metals (Pb 71.7 ± 2.5 mg/g, Cd 1.36 ± 0.01 mg/g, Cu 137 ± 4 mg/g, Zn 119 ± 5 mg/g, Mn 527 ± 24 mg/g, V 29.9 ± 2.3 mg/g and Hg 0.094 ± 0.014 mg/g). The accuracy and precision of the analytical method were calculated according to Maas *et al.*, 2010. The accuracy of the metal concentrations in soils samples determined by F AAS, GF AAS were ensured through 10 repeated analyses of metal standards and the results in the range ± 5 % of certified values were found. Detections (LOD) and quantifications (LOQ) limits were also calculated (Table 1). Moreover, metal concentrations were determined on three different replicate soils samples in order to assess the homogeneity of sample and the repeatability of the analysis and data were considered acceptable if standard deviation was lower than 10 %. The reported data in this study were calculated on the dry weight. The range, mean, and other descriptive statistical analyses were performed using Excel program and XLSTAT 2013 for Windows statistics software. Different ranges have been proposed in various studies to convert the calculated numerical results into broad descriptive bands of pollution with low to high intensity (Abrahim and Parker, 2008). In this study, several methods have been discussed as follows:

The geoaccumulation index (I_{geo}) was originally used for the evaluation of sediment contamination, but it was successfully used to assess of soil contamination (Müller, 1969). This index I_{geo} is defined as the ratio of the concentrations of heavy metals in soils to background of metal levels in soils or in corresponding soils. The concentration of metal in background is multiplied by constant 1.5. This constant allows use to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences (Lu and Bai, 2010; Ji *et al.*, 2008, Loska *et al.*, 2003). The calculation of geoaccumulation index is described by the following equation;

$$I_{geo} = \log_2 \left(\frac{c_n}{1.5\, B_n} \right) \qquad (1)$$

c_n is the measured concentration of the element in soil; B_n is the value of geochemical background. The index of geoaccumulation consists of seven grades, whereby the highest grade (6) reflects 100-fold enrichment above background values. The I_{geo} was classified into six categories: $I_{geo} < 0$ (practically unpolluted, $I_{geo} = 0$), $0 \leq I_{geo} < 1$ (unpolluted to moderately polluted, $I_{geo} = 1$), $1 \leq I_{geo} < 2$ (moderately polluted, $I_{geo} = 2$), $2 \leq I_{geo} < 3$ (moderately to strongly polluted, $I_{geo} = 3$), $3 \leq I_{geo} < 4$ (strongly polluted, $I_{geo} = 4$), $4 \leq I_{geo} < 5$ (strongly to extremely polluted, $I_{geo} = 5$) and $I_{geo} > 5$ (extremely polluted, $I_{geo} = 6$).

The enrichment factor (EF) value was calculated using formula given by based on equation suggested by Buat-Menard and Chesselet (1979). The enrichment factor (EF) is based on the standardization of a tested element against a reference one. A reference element is the one characterized by low occurrence variability (Loska *et al.*, 2004).

$$EF = \frac{\dfrac{c_{n\,(sample)}}{c_{Ref\,(sample)}}}{\dfrac{B_{n\,(background)}}{B_{Ref\,(background)}}} \qquad (2)$$

c_n *(sample)* is the content of the examined element in the examined environment, c_{Ref} *(sample)* is the content of the reference element in the examined environment, B_n *(background)* is the content of the examined element in the reference environment and B_{Ref} *(background)* is the content of the reference element in the reference environment. Five contamination categories are recognized on the basis of the enrichment factor (Sutherland, 2000). The EF values were classified into five categories of designation of quality: EF < 2 (deficiency to mineral, deficiency to minimal enrichment), EF = 2 - 5 (moderate enrichment), EF = 5 - 20 (significant enrichment), EF = 20 - 40 (very high enrichment) and EF > 40 (extremely high enrichment). The most referenced elements are Sc, Mn, Ti, Al, Fe and Ca (Reimann and de Caritat, 2000). Due to the considerable influence of anthropogenic transformation, soils contamination was also evaluated using the percentage enrichment factor, defined by Zonta *et al.*, 1994 and Loska and Weichu³a 2003, using

$$\%\,EF = \left(\frac{c - c_{min}}{c_{max} - c_{min}} \right).100 \qquad (3)$$

where c is the mean total concentration in the soil, c_{min} is the minimum concentration determined during the study period, c_{max} is the maximum concentration determined during the study period.

The contamination factor (CF) evaluates the soil contamination. Hakanson (1980) suggested this factor and Loska *et al.* (2004) modified this factor, they enable an assessment of soil contamination through reference of the concentrations in the surface layer of bottom sediments to preindustrial concentration using Earth's crust levels of metals as references value. The calculation of *CF* is according to equation:

$$CF = \frac{c_M}{c_n} \qquad (4)$$

where c_M is the mean concentration of metals from at least five samples and c_n is the preindustrial concentration of individual metal. The concentration of elements in the Earth's crust as a reference value is used as the preindustrial concentration. This factor assesses the degree of pollution and take value: CF < 1 low contamination factor, $1 \leq CF \leq 3$ moderate contamination factor, $3 \leq CF$ 6 considerable contamination factor and 6 d $\leq$ very high contamination factor.

The pollution level was computed by following procedure of Pollution Load Index (PLI) of Tomlinson *et al.* (1980):

$$PLI = \sqrt[n]{CF_1 \,.\, CF_2 \,.\, CF_3 . \ldots . \, CF_n} \qquad (5)$$

In this formula, CF_1 to CF_n indicate the contamination factors calculated for the first soils sample to the n^{th} one. PLI value close to one indicates heavy metal loads near the background level, while values above one indicate soil pollution (Liu *et al.*, 2005).

Pollution index (PI) is determined according to the method of Lee *et al.*, (1998). The *PI* is obtained by calculating the average ratios of metal concentration (c_M) to the tolerance levels (c_{TL}) given national guidance and exceeding this concentration are considered hazardous for human health. It was computed using the formula as stated below:

$$PI = \frac{c_M}{c_{TL}} \qquad (6)$$

Classification of PI values for each metal contaminated soil was characterized on the basis of criteria such as practically uncontaminated soils (PI ≤ 1), moderate contaminated soil (1 < PI ≤ 3) or high contaminated soil (PI > 3).

Integrated pollution index (IPI) assesses pollution level by considering the joint effect of all polluting metals in soil and IPI is calculated using the formula

$$IPI = \frac{1}{n}\left(\frac{c_1}{TL_1} + \frac{c_2}{TL_2} + \ldots + \frac{c_n}{TL_n}\right) \qquad (7)$$

where c_1, c_2, c_n are average concentration of the polluting metals and TL_1, TL_2, TL_n are the tolerable levels for each metals, n is the number of polluting metal considered. Tolerable levels of pollutants (limits) are given in each state legislative document or criteria for soil pollution. The integrated pollution index (IPI) of metals characterized contamination of soils from study area as follows low contaminated soils (IPI ≤ 1), moderate contaminated soils (1 < IPI < 2) or high contaminated soils (IPI > 2).

RESULTS & DISCUSSION

Basic statistical parameters (arithmetic mean, median, range, quartiles and other relevant statistical parameters) for presented row data of mercury, cadmium, lead, zinc, copper, vanadium, manganese concentrations and pH values are summarized in Table 2 in which the values of metals concentrations in the Earth crust (Yaroshevsky, 2006) are also reported. The data of metal concentrations show wide ranges. This range probably related to differences in various pollution degrees of sampling places. The Fig. 2 presents the box-plot graphs for individual metal elements with means and maximum/minimum values of concentrations. Determined pH values of urban soils varied from 6.93 to 7.86 and it means that the soils were nearly neutral to slightly alkaline. The differences of pH values can be attributed to presence of carbonates, ash, or cinders from anthropogenic activity in region, which can increase the pH value of the urban soils. The calculated arithmetic mean values of metals were as follows: Hg (0.17 mg/kg), Cd (0.20 mg/kg), Pb (66.93 mg/kg), Zn (209.51 mg/kg), Cu (38.49

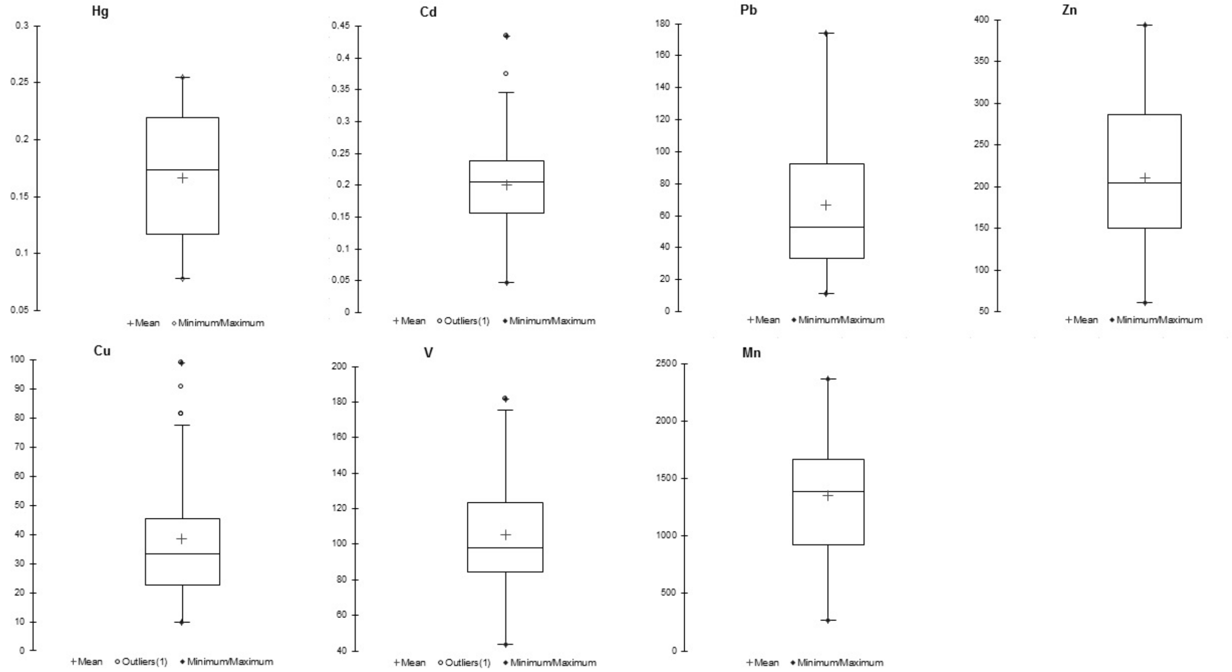

Fig.2. the box-plot graphs for individual metal elements with means and maximum/minimum values of concentrations

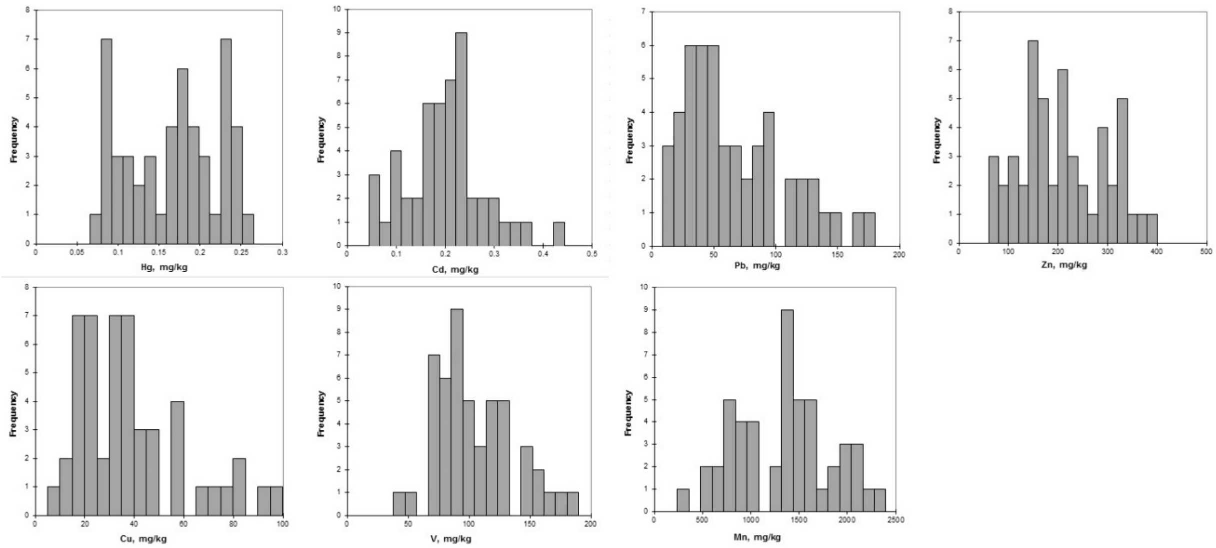

Fig. 3. histograms for individual metal elements

Table 2. Descriptive statistical parameters of Hg, Cd, Pb, Zn, Cu, Mn and V in soils samples of Ostrava (n = 153, unit in mg/kg)

Statistical parameters	Hg	Cd	Pb	Zn	Cu	V	Mn	pH
Minimum	0.08	0.05	11.09	60.91	9.76	43.46	263.72	6.93
Maximum	0.25	0.43	174.03	393.08	98.83	181.80	2368.31	7.86
Range	0.18	0.39	162.94	332.17	89.07	138.34	2104.59	0.93
1st Quartile	0.12	0.16	33.59	150.40	22.68	84.41	925.49	7.25
Median	0.17	0.20	53.12	204.60	33.20	97.89	1389.08	7.41
3rd Quartile	0.22	0.24	92.13	285.85	45.48	123.29	1665.77	7.59
Arithmetic mean	0.17	0.20	66.93	209.51	38.49	105.18	1349.85	7.40
Standard deviation (S.D.)	0.06	0.08	41.57	85.82	21.39	30.37	492.54	0.93
Lower bound on mean (95%)	0.15	0.18	54.99	184.88	32.34	96.46	1208.45	0.26
Upper bound on mean (95%)	0.18	0.22	78.86	234.15	44.63	113.89	1491.25	7.33
Percentile 95%	0.24	0.33	143.90	341.83	81.27	159.06	1964.58	7.80
Percentile 90%	0.23	0.30	126.93	326.58	72.14	146.57	1838.92	7.78
Percentile 10%	0.08	0.09	21.28	85.26	15.66	73.17	263.72	6.97
Percentile 5%	0.08	0.05	16.94	70.99	13.50	62.72	263.72	6.95
Geometric mean	0.16	0.18	54.49	190.35	33.20	100.88	1244.25	7.48
Geometric standard deviation	1.45	1.62	1.96	1.59	1.74	1.34	1.55	7.40
Harmonic mean	0.15	0.16	43.45	169.75	28.63	96.61	1113.56	1.03
Skewness (Pearson)	-0.11	0.36	0.81	0.25	1.05	0.57	0.01	-0.16
Kurtosis (Pearson)	-1.32	0.49	-0.27	-0.88	0.43	-0.14	-0.71	-0.86
Earth crust*	0.08	0.13	16.00	83.00	47.00	90.00	1000.00	-

* Yaroshevsky, 2006

mg/kg), V (105.18 mg/kg) and Mn (1349.85 mg/kg). The concentration of Hg in urban soil was in the range from 0.08 mg/kg to 0.25 mg/kg and with median at 0.17 mg/kg. The total concentration of Cd was in the range from 0.05 mg/kg to 0.43 mg/kg with median at 0.20 mg/kg, being four-fold higher than the background concentration of studied locality. The total concentration of Pb varied from 11.09 mg/kg to 174.03

mg/kg with median at 53.12 mg/kg. This value exceeded the background value eighteen-fold. The concentration of Zn was in the range from 60.91 to 393.08 mg/kg with median at 204.60 mg/kg, while minimum of concentration was almost equal to the background concentration of Zn. The total content of Cu varied from 9.76 mg/kg to 98.83 mg/kg with median at 33.20 mg/kg and the minimal concentration was equal to the value of the background. The concentration of V ranged from 43.46 mg/kg to 181.80 mg/kg with median at 97.89 mg/kg and the median exceeded two-fold the background content of vanadium. The concentration of Mn varied from 263.72 mg/kg to 2368.31 mg/kg with median at 1389.08 mg/kg and median was exceeded five-fold than background value.

According the Table 2 the arithmetic mean and median values of metals have increasing character in the order Hg < Cd < Cu < Pb < V < Zn < Mn. The content of metals in the Earth crust was exceeded in all cases of determined concentrations (arithmetic mean and median). The typical averages content of metals in soils are follows: Hg (0.05 – 0.5 mg/kg), Cd (0.50 – 1.00 mg/kg), Pb (10 – 30 mg/kg), Zn (20 – 200 mg/kg), Cu (10 – 40 mg/kg), V (30 – 150 mg/kg) and Mn (300 – 1000 mg/kg) (Adriano, 2001, Kabata-Pendias, 2000). Contents (arithmetic mean and median) of mercury, copper and vanadium are in range of metals in soils, but the concentrations of lead, zinc and manganese are higher and the cadmium contents are lower in comparison with the reported data of typical averages contents metals in soils. However, the range average metals contents in soils was exceeded for 78 % of lead, 51 % of zinc, 33 % of copper, 10 % of vanadium and 68 % of manganese. All of these samples were taken in the industrial area of the metallurgical company and from the centre of Ostrava with the high traffic density. The observed differences between arithmetic means and medium and large values of standard deviation (S.D.) in the case of lead, zinc, copper, manganese and vanadium are assumed that the data comes from the non-normal distribution. The positive skewness value also indicates the anthropogenic influence on metal pollution of soils in Ostrava with the exception of mercury skewness value. Thus, high concentration levels of these elements also indicate that anthropogenic and industrial emissions are source of metals pollution in study area, because the metallurgical industry and urban dense traffic are typical for this locality. In Ostrava city metals contents can enter in the soil from various sources such as traffic, emissions from industrial establishment, combustion of fossil fuels and municipal wastes. In particular, Pb and Cu seem to be mainly associated with traffic, combustion, Cu resulting from brake pads wear (Van Bohemen and Janssen Van de Laak, 2003). Other sources of these elements in urban environments can be waste incinerators, pipes, cables, paints, and colors (Biasioli *et al.*, 2006). The soils also receive Cu, Pb, Cd, and Hg mainly from atmospheric deposition, irrigation water, applications of fertilizers, pesticides, manures, sewage sludge which can applied in parks, grass, gardens and other scattered diffuse pollution sources such as incinerators, traffic, industries, etc., respectively (Nicholson *et al.*, 2003; Wong *et al.*, 2002, 2006). Other sources of these elements could be from local heating units using low quality fuel, metallurgical industries, car factories, and traffic.

In the Fig. 3, histograms for individual metal elements are shown. The histogram can be used as a useful diagnostic tool. Majority of statistical tests are based on the same population samples and come from the same distribution. The factors affecting the geochemistry of soils, such as geology, climate,

Table 3. Average heavy metal concentrations in urban soils of European cities (mg/kg)

Metal	Hg	Cd	Pb	Zn	Cu	V	Mn	References
Torino, Italy	–	–	277	235	107	–	–	Biasioli *et al.*, 2006
Warsaw, Poland	0.13	0.30	20	–	10	–	–	Birke and Rauch, 2000
Berlin, Germany	0.42	0.90	119	–	79	–	–	Birke and Rauch, 2000
Uppsala, Sweden	0.13	0.21	25	98	26	–	573	Ljung *et al.*, 2006
Stockholm, Sweden	0.41	0.40	79	–	55	–	–	Linde *et al.*, 2001
Ljubljana, Slovenia	–	–	102	–	48	177	–	Ajmone-Marsan *et al.*, 2008
Athens, Greece	–	–	577	449	233	–	–	Riga-Karandinos *et al.*, 2006
Aveiro, Portugal	–	–	72	86	46	–	–	Ajmone-Marsan *et al.*, 2008
Murella, Spain	–	0,23	68	22	12	–	149	Acosta *et al.*, 2009
Ostrava, CZ	0.17	0.20	66.93	209	38	105	1349	this study

Table 4. The correlation coefficient matrix between metals in samples; (significance level $\alpha = 0.05$, $p < 0.001$)

	Hg	Cd	Pb	Zn	Cu	V	Mn
Hg	1.000						
Cd	0.172	1.000					
Pb	0.417	0.430	1.000				
Zn	0.261	0.430	0.637	1.000			
Cu	0.478	0.544	0.682	0.534	1.000		
V	0.252	0.328	0.657	0.646	0.398	1.000	
Mn	0.290	-0.059	0.341	0.630	0.223	0.482	1.000

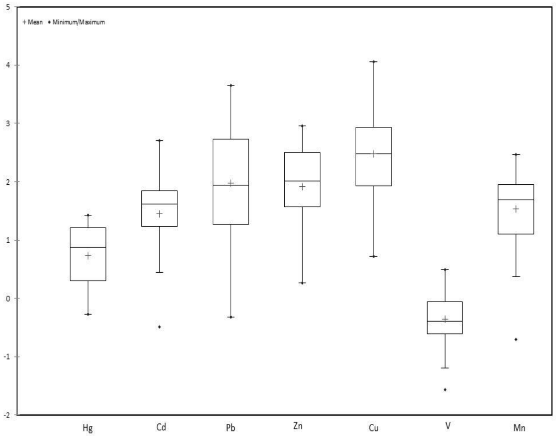

Fig. 4. values of geoaccumulation index were much

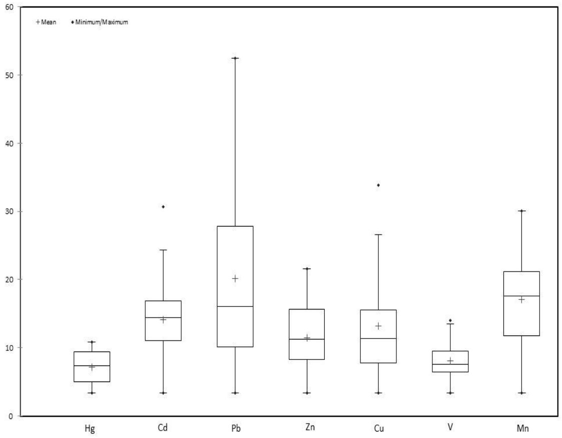

Fig. 5. The EF values for elements

vegetation, elevation of natural mineralization and mainly human activities in urban area, respectively, suppose that the samples come from mixed populations, such as urban land (Jordan *et al.*, 2007). The histograms in Fig. 3 indicate that monitored elements, which are characterized by a non-normal distribution. The histograms also confirm that the samples came from mixed populations from different contaminated sites, causing a multi-function character on the histogram. This means that the problem of mixed populations must be taken into consideration as it relates to the distribution of metals in urban soils in which is significantly different metal concentrations. The comparison of frequency histograms shows the characteristic positively skewed distribution of metals in contaminated localities. The values of skewness in histograms were determined for Hg (0.5), Cd (0.72), Pb (0.68), Zn (0.79), Cu (0.84), V (1.11) and Mn (0.95), these values confirmed non normal distribution. As it seen in the Table 3., where average total heavy metal concentration (mg.kg-1) from various European cities and urban areas are listed, the mean of total concentration of Hg in Ostrava soils is generally among lower values (Warsaw, Uppsala), the level of Cd also belongs among lower value as Uppsala, the concentration of Pb is near as level of Pb observed in Murrela, but the level of Zn is high as identified in Torino, identified concentration of Cu is typical for most of the listed cities, but the high level of Mn was found only in Ostrava. The reason of high level of Mn may be in geological bedrock of Ostrava basin. This comparison should be considered only approximately because the levels of metals depend on many factors: sizes of the city, density of population, number of green spaces, parking places, volume and intensity of traffic, sampling area, depth of sampling of soils, pH factor of soils, type of soils, and mainly type of manufacturing and industry activities. Ostrava soils are not considerably different from those reported in the literature for urban top soils (Table 3.) although Ostrava is considered the most polluted area in Czech republic due mining activity and heavy industries that directly affects amount of emitted pollutants. The relationships among metals concentrations can provide important information on hazardous metal resources and their pathways in the environment (Manta *et al.*, 2002; Johanson *et al.*, 2009). The correlations between the elements in soils are generated using Pearson's correlation matrix. The details of the correlations matrix are presented in Table 4. The correlation matrix of metals data indicate positive correlation with correlation coefficient $r^2 > 0.5$ among Cd – Cu and Pb – Zn – Cu – V in region of Ostrava. Excellent positive correlations between these metals indicated their common sources of the pollution; these metals had similar pollution levels and similar pollution sources (Lu and Bai, 2010). Therefore, the close relationships among Cd – Cu and Pb – Zn – Cu – V in soils indicate on the combined soils pollution by heavy metals because of long-term industrial and human activities in the environment. The highest positive correlation ($r^2 = 0.637 - 0.682$) was found for Pb – Zn – Cu – V and this fact reflects the similar behaviour of metals in soil, mainly adsorption characteristics, accumulation, similar metals deposits and anthropogenic sources. The weak positive correlation with correlation coefficient $r^2 < 0.5$ reflected the various source of metals. This section is focused on data analysis and evaluation of contamination using of several factors and indexes, which were derived for assessment contamination of soils and reflect actual metal concentrations and specific limits in relation of their concentrations in soils. Different factors and indexes have been proposed in various studies and their calculated numerical levels allow converting the calculated numerical results into numerous class of pollution with low to high intensity. The results metals contaminations of Ostrava city were verified and exactly evaluated on the based Geoaccumulation index (I_{geo}), Enrichment factor (EF), Contamination factor (CF), Pollution Load Index (PLI), Pollution Index (PI) and Integrated Pollution Index (IPI).

Geoaccumulation index (I_{geo}) ranged from unpolluted to strongly polluted soil quality. Mean I_{geo} for Hg (0.87) and V (-0.35) indicated unpolluted to moderately polluted surface soils. Soils were moderately polluted by Cd (1.44), Pb (1.93), Mn (1.53) based on geoaccumulation index. In the case of Zn (1.91) and Cu (2.48), the geoaccumulation index indicated moderate to strongly polluted soils. Nevertheless maximum values of geoaccumulation index were much higher; the maximum of I_{geo} value is increased in the following order 0.49 (V), 1.43 (Hg), 2.46 (Mn), 2.70 (Cd), 2.71 (Zn), 3.65 (Pb) and 4.06 (Cu), see Fig. 4. Just as regards geoaccumulation index I_{geo} for copper, it is value about eight times higher than for I_{geo} of vanadium and about three times higher than that for I_{geo} of mercury. These maximum values were obtained in some sampling localities and soil from these localities indicate high pollution, by classification soils were from moderately polluted for V, to moderately polluted for Hg, to moderate to strongly polluted for Cd, Zn, Mn, to strongly polluted for Pb and to very strongly polluted soil for Cu.

This clearly reveals that high levels of Cd, Zn, Pb, Mn and Cu were due anthropogenic activities, especially soils with high maximum levels of geoaccumulation indexes were situated near of industrial effluents and vehicular emissions. As a reference element for calculating of enrichment factor (EF) for Hg, Cd, Pb, Zn, Cu, V and Mn, the value of Fe were used at crustal abundance 35000 mg/kg (Taylor and McLennan, 1995). The EF values for all elements show extremely high enrichment. The mean of EF for Hg was 7.13 and others EF are in the following order V (8.09), Zn (11.05), Cu (13.19), Cd (14.12), Mn (17.12) and Pb (20.18), see Fig. 5. The high enrichment factor values indicate a significant contribution of anthropogenic activity in region as regards of lead, manganese, cadmium and zinc (for lead is the value of EF three times higher than in the

Table 5. Total variance of explained and component matrices (two components are extracted)

n	Initial eigenvalues			Extraction sum of squared loadings			Rotation sum of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	3.610	51.573	51.573	3.610	51.573	51.573	2.448	34.181	34.181
2	1.207	17.238	68.811	1.207	17.238	68.811	1.430	27.959	62.140
3	0.891	12.723	81.534						
4	0.492	7.023	88.558						
5	0.398	5.690	94.247						
6	0.224	3.199	97.447						
7	0.179	2.553	100.000						

case EF of mercury). Due to the considerable influence of anthropogenic transformation, soils contamination was also evaluated using the *percentage enrichment factor*, with using mean of total concentration, minimum and maximum concentration of metals in the soils, the obtained values were growing in the following order 31.98 % (Cu), 33.79 % (Pb), 39.09 % (Cd), 44.08 % (V), 44.51 % (Zn), 49.32 % (Hg) and 50.71 % (Mn). The contamination factor (CF) evaluated the soil contamination. The range of CF for Hg was from 0.98 to 3.19, for Cd from 0.36 to 3.34, for Pb from 0.69 to 10.88, for Zn from 0.73 to 4.73, for Cu from 0.21 to 2.10, for V from 0.48 to 2.02 and for Mn from 0.26 to 2.37. The median and mean of this factor were for Hg (2.17, 2.087), Cd (1.58, 1.54), Pb (3.32, 4.18), Zn (2.47, 2.52), Cu (0.71, 0.82), V (1.09, 1.16) and Mn (1.39, 1.35). This value in the case CF of Pb is considerable, in the case CF of Hg, Cd, Zn, V and Mn moderate and in the case of Cu is CF low. The median and mean are in the case CF of lead two times higher than for CF of mercury. The results of CF (box plot graph) are shown in Fig. 6. The pollution level was computed by the procedure of Pollution Load Index (PLI) with using contamination factors (CF). No only values PLI were near the background levels (close to one) but all calculated PLI values came over one that indicated soils pollution. The PLI increased from 1.01 (Cu) to 2.32 (Zn), other

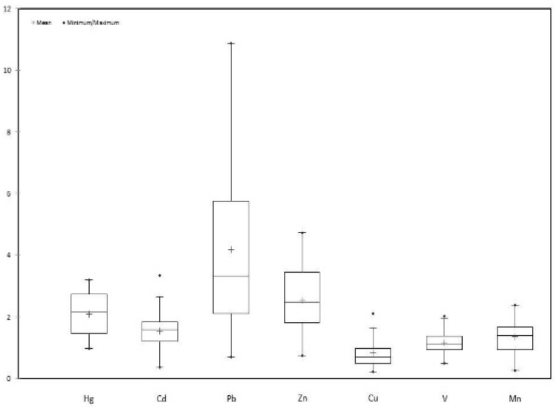

Fig.6. The results of CF

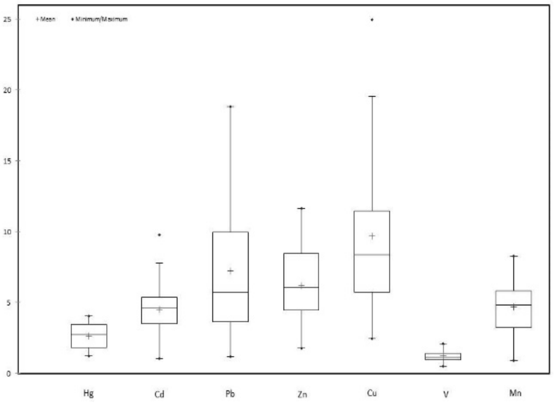

Fig. 7. Mean of PI

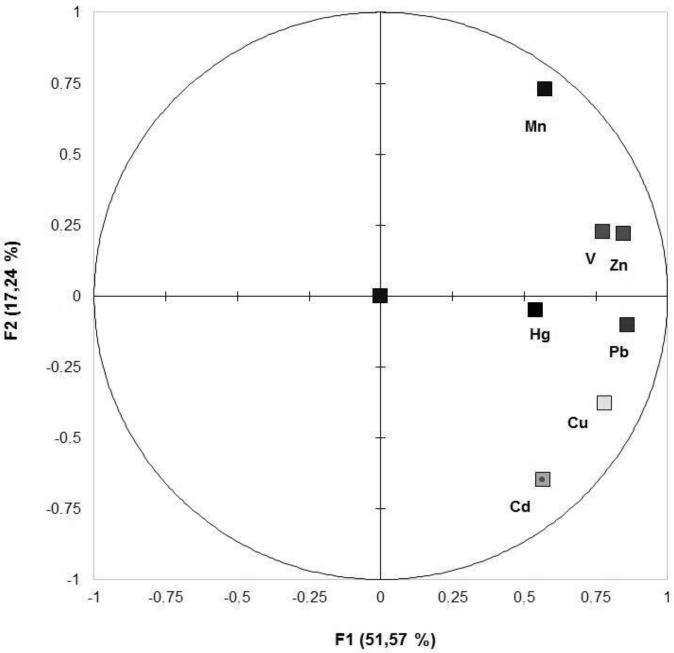

Fig.8.The principal component analysis

values were 1.39 (Cd), 1.04 (Pb), 1.11 (V) and 1.22 (Mn). Mean of PI increases in the following order 1.22 (V), 2.64 (Hg), 4.51 (Cd), 4.72 (Mn), 6.21 (Zn), 7.23 (Pb) and 9.71 (Cu), see Fig. 7. These values clearly indicate highly contaminated soils by Cd, Mn, Zn, Pb and Cu. In the case of V and Hg the soils can be characterized as moderate contaminated soils. Very strong pollution calculated by PI is mainly observed for copper and lead. The reason of this contamination is fact that steelworks emissions and traffic emission are the highest in Moravia region and also in the Czech Republic. Integrated pollution index (IPI = 5.14), which use national tolerance and maximum allowable limits (Regulation 13/1994 Coll.) indicated that soils from Ostrava are highly contaminated and content of metals can be considered hazardous for human health. In this region the atmospheric emission limits are very often exceeded, mainly limit of PM particles and oxides (CZSO, 2013).

In multivariate statistical analysis, principal component analysis (PCA) can be used to identify the sources of contamination (Fachinelli *et al.*, 2001). The principal component analysis loading plots of the metal content of the soils from Ostrava is presented in Fig. 8 and the results of the PCA for metal concentrations in urban soils are summarized in Table 5. According to the results of the initial eigenvalues, two principal components were considered and grouped metals into two-component model accounting for 68.81 % of the total variance. All of the elements are consequently well represented by these two principal components. The initial component matrix (Table 5) indicated that Hg, Cd, Pb, Zn, Cu and V are tightly associated with the first principal component (PC1), which explained 34.18 % of the total variance, while manganese is distributed with the second component (PC2) with 27.96 % of the total variance. However, not all heavy metals could be distributed on one component; for example, Zn and V were mainly associated with PC1, and partially with PC2. This suggested that all of the metals might be controlled by more factors. The metals in the PC1 mainly come from anthropogenic sources, such as industrial production and traffic activities. Manganese is (PC2) strongly correlated and separate from the other heavy metals regarding their correlation coefficient analysis and PCA. This separation between them and other heavy metals may suggest Mn originated from local natural sources.

CONCLUSIONS

The present study contributed to the understanding the content of Hg, Cd, Pb, Zn, Cu, V and Mn in urban soils of Ostrava, factors for risk assessment of metals in soils and potential sources of metals in urban soils in Ostrava in Czech Republic. This study investigated heavy metal soils concentrations of the industrial city - Ostrava. Results showed that high values of Hg, Cd, Pb, Zn, Cu, V and Mn were present as major pollutants in the urban soils and values of individual metals had an increasing character in the order Hg < Cd < Cu < Pb < V < Zn < Mn. Strong positive linear correlation were found between Cd – Cu and Pb – Zn – Cu – V and this correlations between these metals indicate their anthropogenic common sources, mainly industrial emissions. Thus, high concentration levels of these elements also indicate that, main source of contamination are the metallurgical and historical mining industry and urban dense traffic (Pb and Cu are connected with traffic, combustion, mainly Cu from the wear of brake pads). The assessment of metal pollution by means of specific indexes confirmed that urban soils of Ostrava are predominantly moderate to high contaminated by Hg, Cd, Pb, Zn, Cu, V and Mn. Principal Component Analysis had verified the anthropogenic sources of metals except manganese, which can originated also from natural sources as contribution of high level. This study clearly highlights the urgent need to make a concerted effort to control industrial emissions and to remediate heavily polluted urban soils, and also the other monitoring of metals concentrations in urban soils.

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