Assessment of Heavy Metal Pollution (Cd, Cu, Pb, Hg) in Urban Soils of Roadsides in Brno

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DOI: 10.2478/v10158-010-0021-1

ABSTRACT: This environmental study is focused on the distribution of heavy metals in the soils of selected localities in Brno. The soils samples were collected near roadsides and the concentrations of Cd, Cu, Pb and Hg were determined with using atomic absorption spectrometry. The contamination of soils from selected localities was evaluated on the basis of the pollution index, contamination factor and degree of contamination; and the limit contents of heavy metals in soils which is listed in the Guidance MȚP Czech Republic were also used for assessing the contamination. Mercury and cadmium have been identified as the main polluting metals in selected localities with a high transport load. The obtained results also confirmed that the environment of Brno can be characterized as an area of uncontaminated to a moderate degree contaminated in relation to the contamination factor and contamination degree of the environment in the case of metals (Cd, Cu, Pb, and Hg).

KEY WORDS: Heavy metal, soil, roadsides, pollution index, contamination factor.

1 INTRODUCTION

Environmental pollution due to human activity in cities is still a hot topic, and this problem has been the subject of many studies. Increased levels of hazardous metals not only affect soil quality, water, and the environment, but also human health. The main sources of air pollution in urban and suburban areas are growing industries (chemistry, metallurgy, electronics, and construction, factories), burning fuel, waste management, and transport (EEA, 2007). With regard to increasing transport, the following factors have the major impact on pollution: traffic volume, the quantity and composition of fuel, road type, type and condition of engines, and transport mode. The rapid increase in cars leads to a lot of pressure on the urban environment and transport is becoming the biggest contributor to pollution in the city (Adamec, 2006). Heavy metals in urban soils exist in various forms, in changed or adsorbed form, which affects their behaviour in soil, especially their mobility and bioavailability (Adriano, 2001). The total concentration of heavy metals in the soil is usually regarded as an indicator of urban environmental quality (Oliva et al., 2007; et al., 2006).

Sources of cadmium in the urban environment are few and there are several sources of Cd accumulation in the urban environment. In fact, most of the cadmium extracted worldwide is used in Ni-Cd batteries, while the remainder is used for the coating and plating of plastics and pigments. Cadmium is also used in the manufacture of automotive radiators and in the manufacture of electronics components. It makes up a part of tires, gasoline, diesel and lubricating oils. Copper is widely used for industrial production and electrical and electronic equipment, which are an emerging source of copper. Therefore, copper tends to accumulate in urban areas. In fact, 2 kg of copper waste is produced per capita each year in Europe. In comparison with other elements, the information on soil mercury is limited, particularly for urban areas. The melting of copper and zinc, coal burning, and waste incineration, and industrial processes, such as the production of chlorine and caustic soda are the most important human activities that can release mercury into an urban environment. Mercury is also released into the environment by fluorescent lamps, thermometers, thermostats, electrical switches, pressure sensors, etc. The urban areas together with mining localities belong to major areas for the accumulation of mercury in the soil (Ajmone-Marsan and Biasioli, 2010, Biasioli et al., 2007).

The selected metals (Cd, Cu, Pb and Hg) are characterized by a high toxicity and have a significant impact on environmental components. To assess the level of contamination indexes such as the pollution index (PI), integrated pollution index (IPI), contamination factor (C_f) and the degree of contamination (C_{deg}) can be used (Loska et al., 2004, Wong et al., 2006).

Pollution index (PI) and integrated pollution index (IPI)

The pollution index (PI) is calculated by dividing the measured concentration of the element by the tolerable limit of the metal and the integrated pollution index (IPI) is calculated using the formula 1.

$$IPI = \frac{1}{N}\left(\frac{M_1}{TL_1} + \frac{M_2}{TL_2} + \ldots \frac{M_n}{TL_n}\right) \qquad (1)$$

where M_1, M_2, M_n are the 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 classification of PI values for each metal-contaminated soil was characterized on the basis of criteria such as virtually uncontaminated soils ($PI \leq 1$), moderately contaminated soils ($1 < PI \leq 3$) or highly contaminated soils ($PI > 3$). The integrated pollution index (IPI) of metals characterized the contamination of soils from study area as follows: low contaminated soils ($IPI \leq 1$), moderate contaminated soils ($1<IPI<2$) or high contaminated soils ($IPI > 2$).

Contamination factors and degree of contamination

The contamination factor (C_f) and degree of contamination evaluate soil contamination. The calculation of C_f is made according to equation 2:

$$C_f = \frac{C_M}{C_n} \qquad (2)$$

where C_M is the mean concentration of metals from at least five samples and C_n is the preindustrial concentration of the individual metal. The preindustrial concentration is expressed as the concentration of elements in the Earth's crust. The classification is in relation to the C_f index: $C_f < 1$ low contamination factor indicating low contamination, $1 \leq C_f \leq 3$ moderate contamination factor, $3 \leq C_f \leq 6$ considerable contamination factor and $6 \leq C_f$ very high contamination factor. The sum of contamination factors (C_f) for all metals represents the contamination degree (C_{deg}) of the environment. The classification of the contamination degree: $C_{deg} < 8$ low degree of contamination, $8 \leq C_{deg} < 16$ moderate degree of contamination, $16 \leq C_{deg} < 32$ considerable degree of contamination, and $32 \leq C_{deg}$ very high contamination factor.

2 MATERIALS AND METHODS

2.1 Study area and sampling

Brno (49° 12' N – 16° 34' E) is located in Moravia and it is the second largest city in the Czech Republic, the population this city is 405 337 people and population density is 1 760.65 people per km^2 (2009). The city itself lies in the basin of the Svratka and Svitava rivers. Brno has been an important long-term crossroad not only in the Moravian region, but also for the Czech Republic, due to its specific geographical situation. The high density of roads and the main Czech expressway (D1) results in pollution by heavy metals. The city is situated at the crossing of expressways D1 (Prague, CZ) and D2 (Bratislava, SK), and expressways R52 (Vienna, A) and R43 (Svitavy, CZ). For this study, localities with various incidence of road transport and industry were chosen for the evaluation of soil contamination within Brno. Traffic is characterized as high and the number of vehicles of up to 48,000 / per day. The simplified traffic situation in Brno is shown in Figure 1, where the sampling sites are also marked.

Table 1: The basic characteristics of sampling sites.

Localities	GPS (latitude, longitude)	Basic characteristic	A_h [m]
L1 Cimburkova (Ponava)	49°13'4.392"N, 16°36'19.454"E	Traffic localities Road R43 (to 1.5 km)and R42 (to 0.4 km) and Královopolská a.s.	218
L2 Koliště (centre)	49°11'56.859" N 16°36'41.161" E	Traffic locality with usual traffic jams, city ring road, roadside (20m from road)	215
L3 Botanická (centre)	49°12'16.688"N, 16°36'7.875"E	Traffic locality/park (10m from road)	232
L4 Purkyňova (Medlánky)	49°13'53.514" N 16°34'35.22" E	Peripheral urban locality, 0.5 km to road E461, 640	260
L5 Průmyslová (Slatina)	49°10'16.673" N 16°40'18.861" E	Peripheral urban industrial zone (distribution, trade and storage buildings), 0. 8 km from D1, E462 and E50	340
L6 Jedovnická (Juliánov)	49°11'24.255" N 16°39'52.332" E	Peripheral zone, 2 km from incinerator SAKO Brno a.s ., 50 m from road 373	272
L7 Údolní (centre)	49°11'53.552" N 16°35'53.637" E	Traffic locality, 80 m to crossroads Úvoz - Údolní	231
L8 Opuštěná (Trnitá)	49°11'7.716" N 16°36'46.827" E	Traffic locality, bus terminal (Zvonařka, 0.1 km distance), city circle road, roadside 20 m road	200
L9 Vídeňská (Štýřice)	49°10'24.189" N 16°35'47.548" E	Traffic locality, city ring road, roadside (0.14 km from E461 and 52)	212
L10 Okruṭní (Lesná)	49°14'12.461"N, 16°36'56.873"E	Periphery of city, 2 km to R43, without urban built-up area	259

A_h – Altitude; height above sea level of locality

The selected sites are typical for different levels of traffic and are situated in both the central part of the city, peripheral part of city, and the city ring road of Brno. The aim of this study was (1) to determine the concentrations of Cd, Cu, Pb, and Hg in urban soils near roads, (2) to assess the degree of heavy metal pollution in urban soils using various indices that describe the degree of contamination of the site and the degree of contamination in the localities with regard to long-term pollution stress.

Samples were collected six times from each site from October 2009 to March 2010. A total of 60 samples were collected from 10 localities and sampling was conducted as described in ISO 10381-5:2005. Plastic containers were used to collect and store samples. The climatic conditions of sampling were also recorded (temperature, moisture). Soil samples were obtained that were taken from a depth of 20 cm, sieved through a 2 mm mesh, and dried at 40°C. For each sample (sample number 60) dry weight was determined at 105°C.

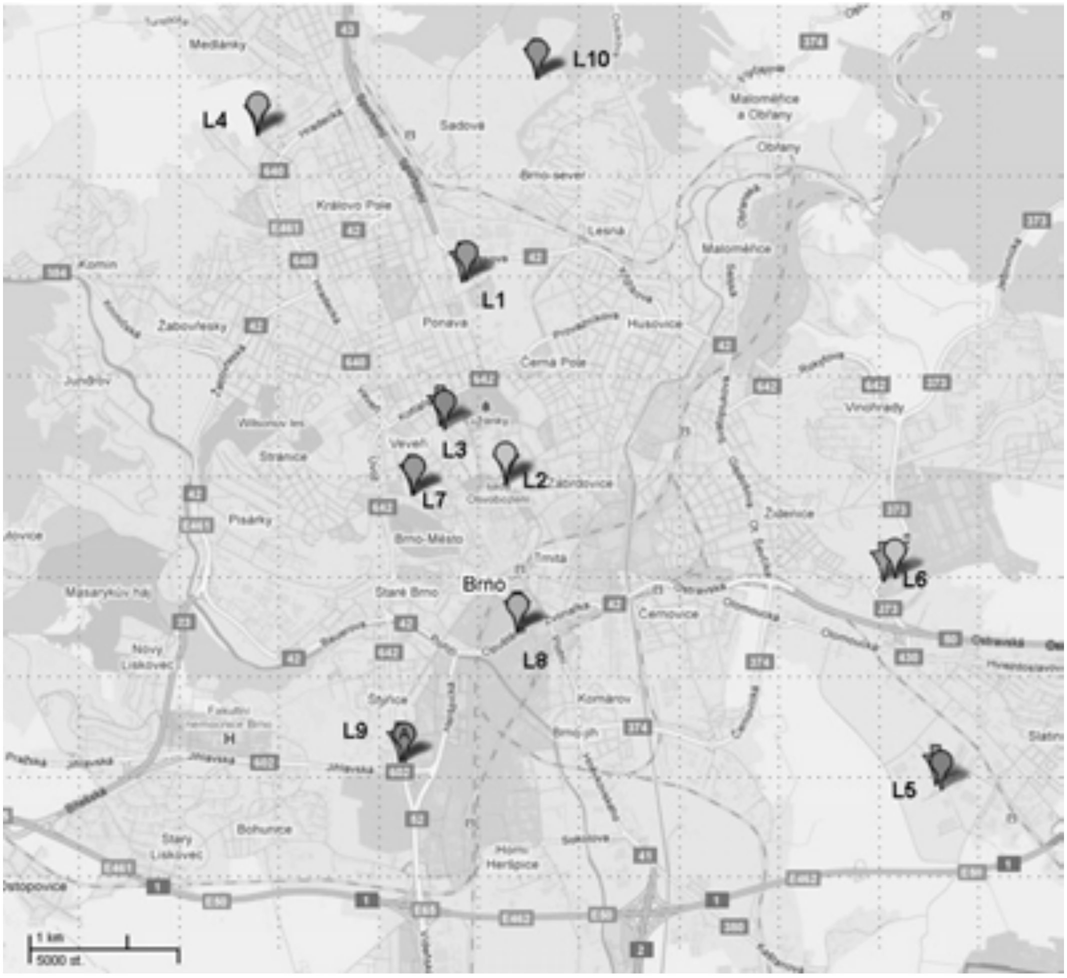

Figure 1: Map of Brno with sampling localities and a simplified scheme of the traffic situation (adapted from Mapy CZ).

2.2 Chemical analysis of soil samples

Extract acidic soils were prepared for analysis from 5 g soil with 50 ml 2M HNO_3 (pa, Lachema). This suspension was shaken continuously for 16 hours at 22 ± 1°C and then filtered through a 0.45 µm membrane filter. Blanks were prepared in the same manner as soil samples. Simple acid extraction represents the ease of mobility of trace metals in the soil.

The concentrations of Pb and Cu were determined by using flame atomic absorption spectrometry (F AAS; SpectrAA 30, Varian). The model AAS ZEEnit 60 (Analytic Jena) atomic absorption spectrometer was equipped with a transversely-heated graphite furnace (GF AAS) and Zeeman background corrector. This spectrometer was used for the determination of Cd. The background and interference of matrix were monitored throughout the analyses.

The atomic vapour generator AMA254 was used for the accurate determination of trace mercury in the solid soil samples. Standards of metals were prepared with HNO_3 from 1 ± 0.002 g/L solution of lead, cadmium and copper (Analytica, s.r.o. Praha). The standard of mercury was prepared using 0.5 ml concentrated HNO_3 (p.a.), 0.5 ml concentrated HCl and 0.5 ml solution $K_2Cr_2O_7$ (1%) and adding 10 μl of calibration standard mercury with a concentration of 1g/L in 50 ml. The soil samples were analyzed three times and the data were considered acceptable when RSD was less than 10%. The analytical procedure of the method used was verified using certificated standard reference materials (CRM CZ 7004 – Loam Soil, Analytika spol. s.r.o.).

3 RESULTS AND DISCUSSION

Results from chemical analysis of heavy metals in soils samples and statistical treatment (means, medians, ranges, standard deviations SD) are given in Table 2. The obtained data shows the wide ranges of the concentration of metals. The concentration of Cd in the urban soils was in the range 0.05 – 0.60 mg/kg with a mean 0.21 mg/kg and median 0.13 mg/kg. The total concentration of Cu was in the range from 5.41 to 25.33 mg/kg with a mean 12.42 mg/kg and median 9.63 mg/kg. The total concentration of Pb in soil samples varied from 10.84 mg/kg to 66.62 mg/kg with a mean 30.75 mg/kg and median 30.14 mg/kg. The concentration of Hg ranged from 0.05 to 0.92 mg/kg with a mean 0.37 mg/kg and median 0.30 mg/kg.

These wide ranges of metals in urban soils are due to the long-term accumulation of metals from polluting sources in the urban environment, such as mobile sources (transport) and stationary sources. The statistical date from the analysis marked in mean, median, SD suggest that the data come from different contaminated localities and also that the distribution is not normal. Results indicated a high potential of anthropogenic influences on the concentration of heavy metals. The highest concentration of Cd and Cu were found in samples from localities L7 (80 m to crossroads Úvoz - Údolní) and L8 (bus terminal Zvonařka, 0.1 km distance from L8), and in comparison L7 > L8. The maximal concentration of Pb and Hg were identified in samples from localities L8 and L7 (L8 > L7) as is shown in Figure 2.

The high levels of metals in study localities arise from high traffic stress at localities. Localities L7 with high transport at the crossroads Úvoz - Údolní and L8 - main bus terminal Zvonařka and its high stress from transport are highly contaminated by heavy metals. Locality L2 is also highly contaminated with lead, mercury, and copper. This locality (L2) Koliště is part of the city circle and typically has high traffic stress. The minimal concentrations of metals were found in the localities L6, L9 and L10; these localities are on the peripheral zone of city and the contents of metals were generally low. The method of assessing the contamination of localities for each contaminant is possible with the use of various indices, such as index pollution and integrated index pollution, that are known in the environmental field. The pollution index PI is defined for each metal as the ratio of heavy metal concentration in the soil to the limit value of the metal.

The index is calculated for each element for all localities together and the values represent the contamination of all areas, which means the total pollution of the city of Brno by metals and this is represented by the integrated pollution index. The calculation of the index for each metal for each sampling locality represents the pollution index and its means the possibility of comparing individual localities and the contribution of metals.

Considering that the limits of concentration of heavy metals in urban soils listed in the Guidance MŢP (1996), the indices of pollution (PI) of metals also integrated pollution index (IPI) for each localities and area Brno also were calculated with using limit contents of metals in soils.

Table 2: Chemical analysis of soil samples from 2009-2010 (statistics – mean, median, range, standard deviation SD for heavy metal concentration mg/kg in urban soils).

Locality	Statistics	Cd	Cu	Pb	Hg
L1	Mean	0.11	18.39	38.45	0.48
	Median	0.14	16.50	43.98	0.35
	Range	0.05-0.15	13.36-25.33	26.25-45.12	0.30-0.81
	SD	0.03	2.25	4.59	0.08
L2	Mean	0.21	19.77	53.06	0.71
	Median	0.26	20.93	51.02	0.73
	Range	0.08-0.28	19.77-21.65	50.63-57.45	0.56-0.84
	SD	0.07	0.36	2.07	0.11
L3	Mean	0.24	10.83	41.35	0.52
	Median	0.21	10.26	41.34	0.52
	Range	0.11-0.41	9.55-12.69	40.85-41.86	0.41-0.64
	SD	0.0.9	0.56	3.28	0.08
L4	Mean	0.13	10.35	19.40	0.13
	Median	0.12	8.37	20.12	0.14
	Range	0.12-0.14	7.84-14.5	17.14-20.95	0.10-0.16
	SD	0.02	0.95	1.01	0.05
L5	Mean	0.09	7.67	15.99	0.10
	Median	0.09	7.39	16.07	0.10
	Range	0.05-0.15	6.97-8.65	12.85-19.07	0.07-0.13
	SD	0.01	0.16	0.41	0.05
L6	Mean	0.07	6.11	15.77	0.08
	Median	0.09	6.05	16.07	0.07
	Range	0.04-0.10	5.41-6.88	13.20-18.6	0.05-0.12
	SD	0.02	0.37	0.98	0.02
L7	Mean	0.41	21.98	40.66	0.47
	Median	0.47	21.33	40.17	0.45
	Range	0.17-0.60	20.61-24.02	31.26-50.55	0.43-0.45
	SD	0.05	1.22	2.24	0.10
L8	Mean	0.31	19.73	54.12	0.83
	Median	0.35	19.81	54.06	0.80
	Range	0.19-0.40	17.51-21.87	41.69-66.62	0.77-0.92
	SD	0.03	1.44	8.28	0.14
L9	Mean	0.11	9.68	13.27	0.11
	Median	0.11	8.99	12.31	0.08
	Range	0.08-0.14	8.80-11.25	10.84-16.66	0.06-0.19
	SD	0.01	0.86	1.55	0.04
L10	Mean	0.10	4.64	13.37	0.14
	Median	0.11	4.61	12.38	0.14
	Range	0.08-0.12	3.66-5.66	12.23-15.50	0.12-0.17
	SD	0.01	0.27	2.22	0.01

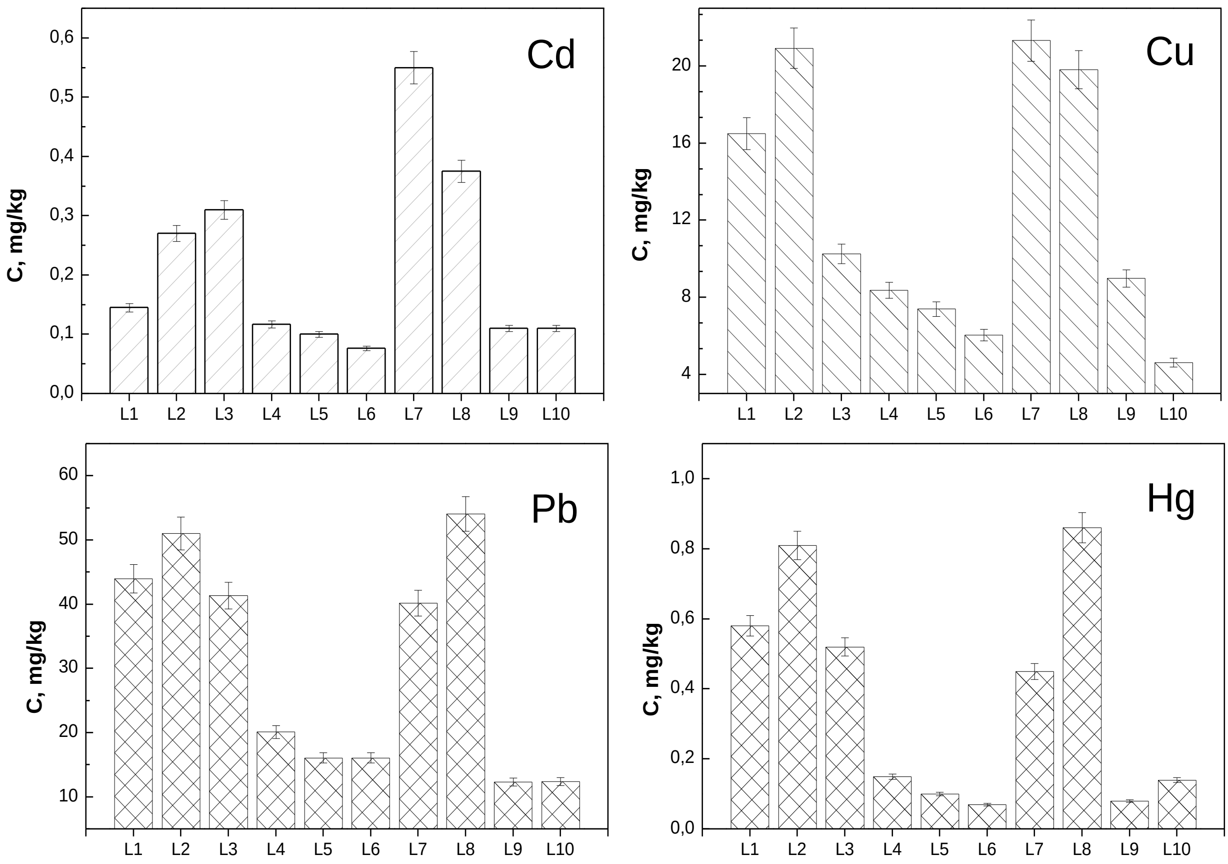

Figure 2: The mean concentration of metals (Cd, Cu, Pb, and Hg) in urban soils samples in localities L1-L10.

The limit concentration of metals listed in Guidance MȚP according to criteria A are as follows : Cd - 0.5 mg/kg, Cu - 70 mg/kg, Pb - 80 mg/kg and Hg – 0.4 mg/kg. Criteria A approximates the natural content of controlled substances in nature. Exceeding the criteria is considered a component of pollution of the environment, except in areas with higher levels of natural substances of concern. Criteria B are designed as a level of metal content, above which it is necessary to further address the pollution. Exceeding the B criteria requires the identified pollution sources and determines its effects and decides on further exploration and the start of monitoring of elements. According to criteria B the content limit of metals in soil are the following : Cd - 10 mg/kg, Cu - 500 mg/kg, Pb - 250 mg/kg and Hg – 2.5 mg/kg. Exceeding criteria C means that pollution has a significant risk to human health and components of the environment, the limited contents of metals in this criteria are : Cd – 20 mg/kg, Cu - 600 mg/kg, Pb - 300 mg/kg and Hg – 10 mg/kg.

The pollution index PI of Cd, Cu, Pb, and Hg varied depending on the type of metal, soil, and locality. The PI value of Hg according to criteria A varied from 0.17 (L6) to 2.15 (L8), criteria B from 0.02 (L6) to 0.34 (L8), and criteria C from 0.007 (L6) to 0.086 (L8). In the case of Pb, using tolerable limit in criteria A the PIs were in the range 0.15 (L10) – 0.67 (L8), in criteria B PIs were from 0.04 (L10) to 0.22 (L8), and using criteria C PIs varied from 0.04 (L10) to 0.18 (L8). The PIs of Cd varied according to criteria A 0.22 (L9, L10), 1.1 (L7); criteria B 0.01 (L9, L10), 0.05 (L7); and criteria C $5.5.10^{-3}$ (L9, L10), $1.8.10^{-2}$ 1.1 (L7). The PI value were exceeded only in the case of mercury for localities L8 (2.15), L2 (2.02), L1 (1.45), L 3 (1.30) and L7 (1.12) when using criteria A. The data obtained show that in the case of mercury when using criteria A the calculated PIs are over 1, which means that localities can be considered to be moderately contaminated by mercury. The pollution indices of other metals in other localities did not exceeded the limit value 1, which means that the localities are unpolluted when using the criteria in Guidance MȚP.

Figure 3 shows the integrated pollution indices (IPI) for each locality and the total IPI of the Brno area; the IPI varied depending on the locality. The highest IPI were found for localities L8 (0.96), L2 (0.87) and L7 (0.76) when using the tolerable limit in criteria A; a typical high transport load characterized these localities. Figure 3 shows that no case exceeded the value of the IPI - 1 when using the limit contents of metals in criteria A, B, or C (MȚP, 1996), which means that the studied localities can be considered unpolluted, and that Brno can also be considered to be an unpolluted city in relation to the pollution index, integrated pollution index when using the limits contents of metals listed in Guidance MȚP.

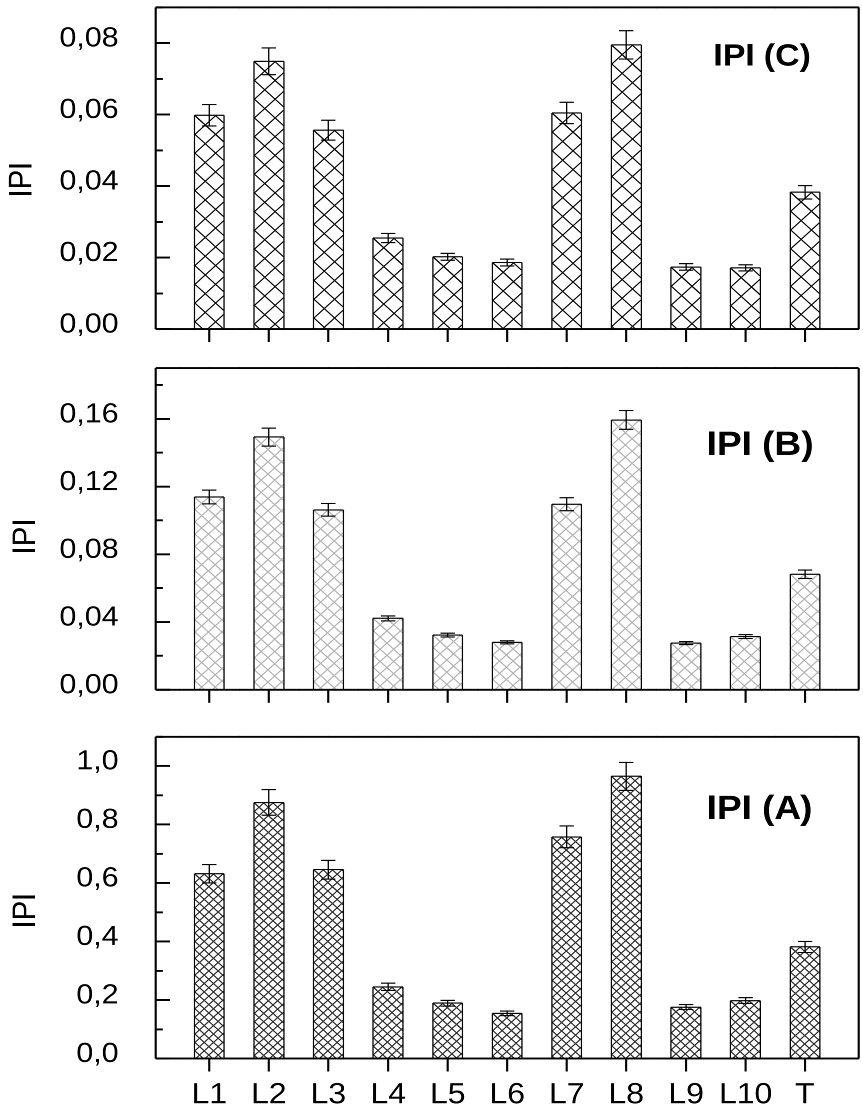

Figure 3: The IPI for localities L1-L8 and T (total IPI for area Brno) in relation to criteria A, B, and C in Guidance MŽP

The contribution of metals to pollution for Brno localities was calculated from the contamination factors C_f of metals that are represented in Figure 3. The preindustrial concentrations of elements (Loska et al., 2004) are used for the calculation of the contamination factor C_f that reflects the long-term effect of pollution to the area. The majority of the contribution to pollution by mercury (C_f – 10.75) and lead (C_f –3.18) was found at locality L8. The main contribution to pollution by cadmium (C_f – 5.5) was confirmed in locality L7.

These contamination factors refer to the pollution of localities L1-L10 and its range from low contamination ($C_f < 1$) to very high contamination $6 \leq C_f$. The value 6 was exceeded in the case of mercury in localities (L1,L2,L3 and L8). The high transport load and frequent traffic jams are typical for these localities. The contamination factors decreased Hg > Cd > Pb > Cu.

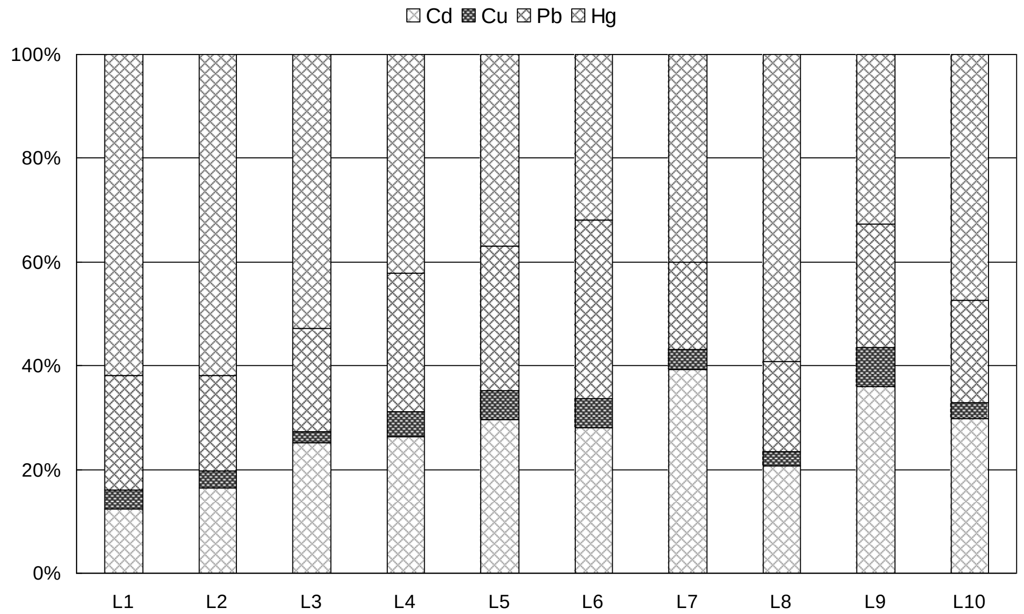

Figure 4: The contribution of Cd, Cu, Pb, and Hg to pollution for the studied localities L1-L10.

The contamination degree (C_{deg}) of the environment when expressed as a sum of the contamination factor (C_f) for all metals confirmed that the total environment in the studied area has been characterized as having a moderate degree of contamination (mean of C_{deg} = 8.99). The maximal contribution of the degree of contamination was found for mercury and lead.

The calculated Pearson's correlation of metals indicates a very strong positive correlation among the Cd, Cu, Pb, and Hg. The values of Pearson's correlation coefficients are over 0.5. A very strong correlation is between Pb and Hg (r^2 = 0.979) and this significant correlation reveals their common sources. A low correlation was found for Cd and Hg (r^2 = 0.642).

4 CONCLUSION

The obtained results show the impact of anthropogenic activities on the environment, mainly the influence of transport on the pollution of soils in the urban area. The data confirmed that the highly toxic metals cadmium and mercury are a major contribution to metal pollution. The localities with typical high transport stress are characterized with high contents of metals and long-term and continuous pollution of the area. These results were confirmed by the contamination factors and also the degree of contamination. The studied localities were selected and characterized according to varying traffic load, population density, or by occurrence of organizations and businesses with a potential impact on the environment. Localities with a greater frequency of automotive transport (Opuštěná L8, Koliště L2, Údolní

L7) were included in selected localities, for which high contents of metals were confirmed and these localities were marked as contaminated localities in Brno. The other localities were Cimburkova (L1) which is adjacent to an establishment producing emissions (Královopolská a.s.) and Jedovnická (L6), which is near the SAKO Brno a.s. (incinerator). The contamination by metals were low in these localities. The content of mercury, lead, copper, and cadmium in soils corresponds mostly to the situation at the site, showing that the majority contribution of contamination is transport.

The concentrations of metals in soils were compared with Guidance MŢP and the result is that the Brno belongs to a practically uncontaminated area. More accurate results confirmed the contamination factor and degree of contamination, and that Brno localities belong to an area with a moderate degree of contamination as concerns cadmium, cooper, lead, and mercury.

5 ACKNOWLEDGEMENTS

This research has been supported by Project FCH-S- 11-2.

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