SOIL SCIENCE ANNUAL
2020, 71(2), 118–124

https://doi.org/10.37501/soilsa/122402

The accumulation of selected heavy metals in soils in the vicinity of a busy road

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Received: November 19, 2019
Accepted: April 16, 2020
Associated editor: B. Rutkowska

Keywords

Heavy metals
Urban soils
Road transport

Abstract

The paper presents the results of research on the accumulation of selected heavy metals (Zn, Cu, Pb, Ni and Cr) in soils in the vicinity of a busy road in Bydgoszcz, which is the eighth-largest city in Poland. Soil samples were taken at three depths, at sample points 25, 50, 150 and 175 m at the side of Jagiellońska Street on the premises of the PKS bus station. The amounts of soil zinc, copper, lead, nickel and chromium were determined by atomic absorption spectrometry after mineralisation in a solution of HF and $HClO_4$ acids. The total metal contents were ordered as follows: Zn > Pb > Cu > Cr > Ni. The study confirmed the impact of the traffic-heavy Jagiellońska Street on their concentrations, which decreased with distance from the road. Principal component analysis (PCA) and Pearson linear correlations analysis showed statistically significant positive relationships between the heavy metals and organic carbon. The enrichment factor (EF) confirmed that the surface horizons were significantly enriched in the tested heavy metals.

1. Introduction

Densely built-up urban agglomerations with a dense street network, dense industry and a diversity of human activities affect the natural environment, which includes the soil. In addition to hydrocarbon compounds, pesticide residues and sulphur, another main factor that threatens soil cleanliness is heavy metals (Niedbała et al., 2010; Czubaszek and Bartoszczuk, 2011; Dzierżanowski and Gawroński, 2011; Athanasopoulou and Kollaros, 2016; Kowalczyk and Szulc, 2017; Kajka and Rutkowska, 2018). One source of toxic gases, dusts and aerosols that contain heavy metals is traffic-heavy roads. The problem of automotive heavy-metal pollution of soils in the vicinity of major thoroughfares is most intense in city districts with high population density and a dense communication network. Here, very large numbers of vehicles move in a relatively small area, and traffic congestion contributes to high emissions (Binggan and Yang, 2010). City soils, which are usually a mosaic of various types and classes, usually present with increased heavy-metal contents. This is the result of long-term accumulation in the soil caused by the continuous emission of pollutants, including from traffic (Ptak et al., 2010). A significant proportion of the emitted pollution is deposited on the surface of the ground close to the emission source (Klimowicz and Melke, 2000). Automotive pollution is more dangerous than industrial pollution because it spreads in high concentrations at low altitudes in the immediate vicinity of people (Właśniewski, 2007).

To assess the state of the soil environment, it is enough to know the total forms of heavy metal total content, which determine the potential for each component to enter into circulation in the natural environment (Kabata-Pendias and Pendias, 2001). The total content of heavy metals in soil includes their various forms, which have various mobilities and abilities to transition from solid to soil solution, as well as those that are permanently bound in soil minerals and practically unavailable to plants.

The aim of the study was to assess the contamination of soils in the immediate vicinity of the Bydgoszcz bus station and one of the city's most important streets (Jagiellońska Street) in terms of the following selected heavy metals: zinc (Zn), copper (Cu), lead (Pb), nickel (Ni) and chromium (Cr).

2. Material and methods

2.1. Location of soil sampling

Bydgoszcz is one of the largest cities in Poland. It is eighth in terms of population, which the latest data estimates at over 350,000. The city covers just under 176 km^2. It is located on the Bydgoszcz Canal, the Brda River and the Vistula River. Bydgoszcz is a major centre of industry, trade and logistics, as well as being a road, rail and inland waterways junction. The city is a major communication hub.

The research area is located in the PKS bus station and depot in Bydgoszcz, between the Brda River and one of the city's most important thoroughfares – Jagiellońska Street. The choice of sampling site is no accident; at rush hour in particular, Jagiellońska Street is one of the city's most traffic-heavy roads.

Soil samples were taken from four points located on lawns. A total of 12 representative soil samples were taken. The first two sampling points, named "DW I" and "DW II" (from the abbreviation of the Polish for "station" – *dworzec*) were located between Jagiellońska Street and the station building. The first was about 25 metres from the street, while the second was about 50 metres away. The two other points ("DW III" and "DW IV") were located between the building of the PKS station and the banks of the Brda River, which flows through Bydgoszcz close to the bus depot. The "DW III" point was located about 150 metres from the street (just behind the bus parking lot), while "DW IV" was near the river bank, about 175 metres from Jagiellońska Street (Fig. 1). In order to determine the relationship between the content of analysed metals and the depth of soil samples taken from each of the sites taken soil samples from different depths at 0–20 cm, 40–60 cm and 90–120 cm.

2.2. Soil analysis

In the air-dried soil samples with disturbed structure sieved through a ø 2-mm mesh, the selected physiochemical properties pH in H_2O and pH in 1M KCl were measured potentiometrically (PN-ISO 10390: 1997), as was organic carbon (C_{org}) with the Tiurin method (PN-ISO14235 2003) and granulometric composition by laser diffraction using a Mastersizer MS 2000 analyser. In the samples analysed, the total content of zinc, copper, lead, nickel and chromium was measured after mineralisation in a mixture of HF+ $HClO_4$ acids by the Crock and Severson method (1980). The total contents of forms were determined by atomic absorption spectroscopy using a PU 9100X spectrometer (Philips). The

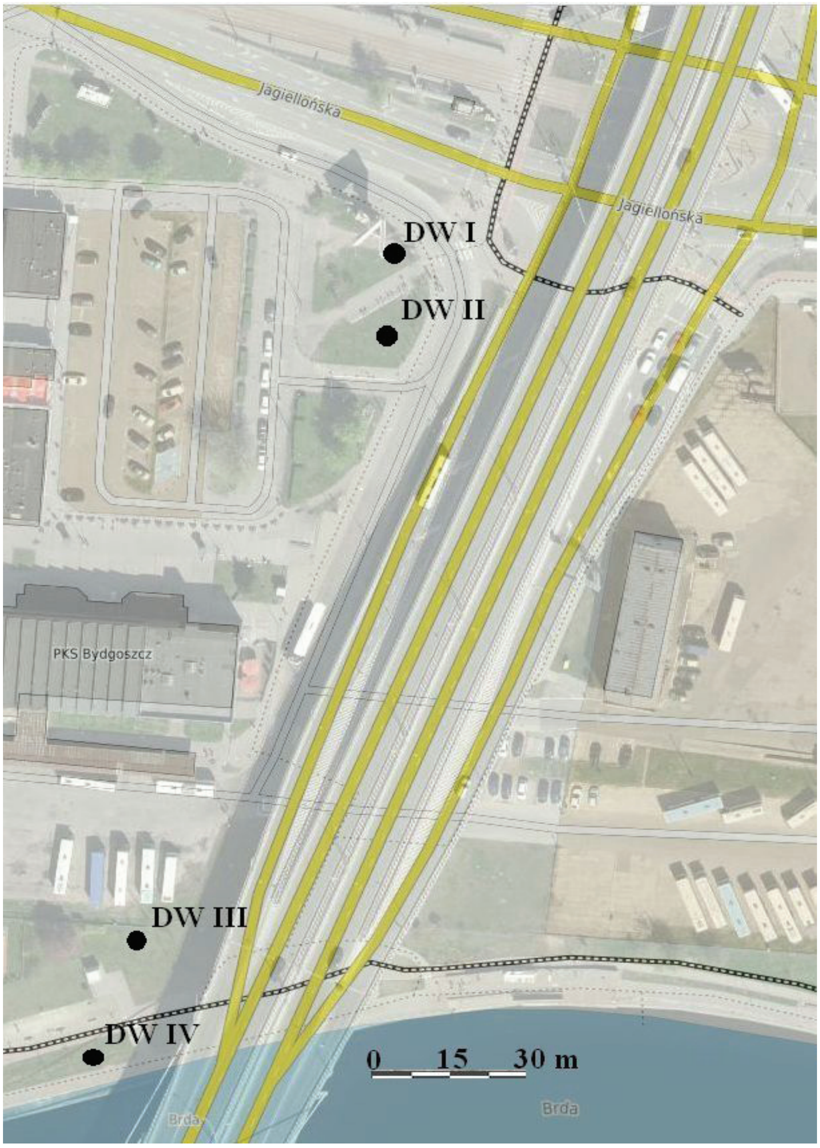

Fig. 1. Localization of study area

limit of determination for all analysed metals were 0,2 mg·kg^{-1}. To verify the accuracy of the results, the analysis of the certified material Loam Soil No. ERM – CC141 as well as the so-called zero tests were conducted, which were exposed to the identical analytic procedure as the soil samples. Good compatibility between the certified and determined values was obtained. All the determinations were made in triplicates. The results are presented as arithmetic means.

2.3. Statistical analysis

Due to the considerable influence of anthropogenic transformations in surface horizons, the soil was also evaluated using the percentage enrichment factor (EF) defined by Zonta et al., (1994) and Loska and Weichula (2003), using

$$\% \text{ EF} = C - C_{min} / (C_{max} - C_{min}) \times 100$$

where: C – mean total concentration in the soil, C_{min} – minimum concentration and C_{max} – maximum concentration.

Enrichment factor can help in differentiating an anthropogenic source from a natural origin. Five contamination categories are recognised on the basis of the enrichment factor, where EF<2 is deficiency to minimal enrichment, EF 2–5 is moderate enrichment, EF 5–20 is significant enrichment, EF 20–40 is very high enrichment and EF>40 is extremely high enrichment (Sutherland 2000).

Principal component analysis (PCA) was performed using a correlation matrix for heavy metals and physicochemical properties. The first two principal components (*PC1* and *PC2*) were selected for further interpretation of the results. In addition, Pearson linear correlation coefficients were determined between all analysed variables using the Statistica 13.0 computer program.

3. Results and discussion

According to the Polish Soil Classification (2019), the studied soils are Anthropogenic soils, mechanically transformed with artefacts, building debris and technical materials in profiles, with increased content of heavy metals and modified pH (Urbisoils). Table 1 presents selected physical and chemical properties of the analysed soil samples. In most of the tested samples, the clay fraction content ranged from 2.95 to 4.67%, allowing the analysed soils to be classified as sandy loams (PTG 2009). Only the samples from the depths of 40–60 cm and 90–120 cm at DW I deviated, with 8% and 14.59% of clay fraction respectively.

Regardless of location, the tested soils were neutral and slightly alkaline (pH in 1 mol dm^{-3} KCl 7.1–7.62). Hydrolytic acidity was low, ranging from 0.23 to 1.65 cmol·kg^{1}. Similar results for Bydgoszcz soils were obtained by Malczyk et al., (1996) and Różański and Dąbkowska-Naskręt (2011). This is a typical reaction for anthropogenic soils. Soil alkalisation may be the result of changes taking place in this area. There is rubble in the soils, which can increase pH. Additionally, the soil samples were taken from lawns that may have been limed on multiple occasions. The use of NaCl to remove snow from streets and pavements also contributes to increasing pH.

The organic carbon in the soils varied, ranging from 6.90 to 40.50 g·kg^{1}. The values of this parameter were highest in the surface-most horizons. The varied organic carbon contents in the soils of lawns, green areas, squares and parks are the result of these soils having been enriched with organic matter by fertilisation with peat, compost and such. This is a characteristic feature of urbanised areas.

Among the analysed heavy metals, the highest values were found for zinc (from 37.21 to 500.88 mg·kg^{1}) and the lowest for nickel (from 6.01 to 31.28 mg·kg^{1}). The content of other elements was lead from 14.63 to 179.00 mg·kg^{1}, copper from 6.73 to 149.5 mg·kg^{1} and chromium from 16.54 to 44.60 mg·kg^{1}. The

Table 1
Selected physicochemical properties of soil

Objects	Depth	pH		Hh	Corg	Fraction%		
	cm	H_2O	KCl	cmol·kg^{-1}	g·kg^{-1}	Sand	Silt	Clay
DW I	0–20	7.41	7.14	0.38	19.50	62.11	34.00	3.89
	40–60	7.84	7.37	0.23	11.55	53.91	38.09	8.00
	90–120	7.75	7.32	0.30	11.75	34.89	50.52	14.59
DW II	0–20	7.70	7.54	1.65	12.65	62.72	32.68	4.67
	40–60	7.53	7.37	0.38	11.95	62.55	33.88	3.57
	90–120	7.54	7.45	0.45	8.05	62.41	33.25	4.34
DW III	0–20	7.37	7.20	0.45	28.50	61.82	33.98	4.20
	40–60	8.16	7.62	0.30	8.50	67.27	28.85	3.88
	90–120	7.73	7.62	0.53	6.90	72.46	24.49	3.05
DW IV	0–20	7.24	7.10	0.45	40.50	58.14	38.92	2.95
	40–60	7.30	7.17	0.38	35.85	63.21	33.57	3.22
	90–120	7.79	7.35	0.38	14.30	58.01	38.38	3.61

metal content in the soil was, in decreasing order of concentration, Zn > Pb > Cu > Cr > Ni. The highest concentrations of heavy metals were determined in the soil in the point DW IV and the lowest in the point DW III (Table 2). Kajka and Rutkowska (2018) as well as Kowalczyk and Szulc (2017) were obtained, examining the impact on streets and traffic intensity on metal content in Warsaw soils, they found that the concentrations of the studied metals in soils were the highest directly on the edge of the road and significantly decreased with distance from the edge. Similar relationships were noted in own research, but no correlations was found between the depth of sampling and the soil metal content. The content of all analysed metals varied depending on the depth at which soil samples were taken. According to the literature, excessive accumulation of trace elements is limited to about 150 m either side of the roadway, while beyond this distance values are those of unpolluted areas (Nabuloa et al., 2006; Zehetner et al., 2009; Czubaszek and Bartoszuk, 2011; Dzierżanowski and Gawroński, 2011). In the analysed area, the exception was point DW IV, closest to the river, where the concentrations of the indicated metals were found to be highest. This sample point was located on a newly created square. It is probable that the fertilisers and peat (perhaps of unknown origin) used to fertilise the area introduced unfavourable quantities of heavy metals into this soil environment.

The enrichment factor is used to differentiate trace metals originating from human activities from those of natural sources. The enrichment factors (EF) calculated for the study area's surface soil horizons indicated very high enrichment in zinc (27%), nickel (36%) and chromium (40%), and extreme contamination in lead (59%) and copper (43%) (Fig. 2). The literature states that elevated EF coefficients in urban soils are mainly the result of industrial and automotive emissions (Ali and Malik, 2011; Atiemo et al., 2011; Loska and Wierchuła 2003).

The heavy metals accumulated in the surface soil horizons show high chemical affinity for this horizon's amount of organic matter, consequently slowing its degradation and decreasingbioavailability (Hernandez et al., 2003). Correlation analysis showed statistically significant positive relationships

Table 2
Total content of heavy metals in the soil samples

Objects	Depth	Zn	Cu	Pb	Ni	Cr
	cm	$mg \cdot kg^{-1}$				
DW I	0–20	105.86	31.50	102.25	16.13	25.75
	40–60	99.84	47.10	51.20	26.80	40.58
	90–120	116.34	45.10	48.66	27.78	30.78
DW II	0–20	108.76	21.26	51.86	12.30	21.59
	40–60	85.975	14.33	32.92	10.83	18.46
	90–120	86.21	18.26	38.75	12.30	19.33
DW III	0–20	87.95	9.24	14.30	9.63	17.03
	40–60	86.05	13.53	27.20	9.81	18.61
	90–120	37.21	6.73	14.63	6.01	16.54
DW IV	0–20	500.88	56.93	105.50	29.28	38.05
	40–60	416.04	149.5	93.75	31.28	44.60
	90–120	127.75	48.68	179.00	22.23	26.10

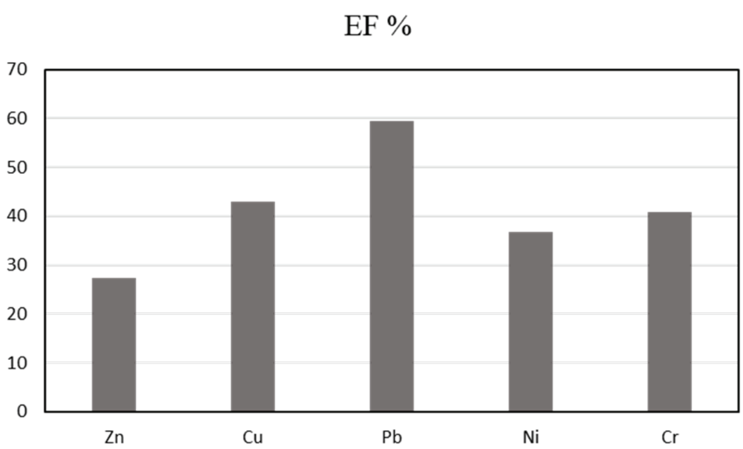

Fig. 2. Enrichment factor

between the amount of organic carbon and total zinc content (r=0.871) and copper (r=0.613) (Table 3). A similar relationship was noted by Gondek and Filipek-Mazur (2003) in studying the binding of heavy metals by humus in soils exposed to traffic pollution. According to the scientific literature, the binding strength of individual heavy metals to organic matter varies. However, humic compounds are important in shaping the binding, activation and migration processes of heavy metals, and this can fundamentally change these elements' mobility in soil. Organic matter is therefore a factor that can both release and immobilise metals in soil. The solubility of heavy metals, and their uptake by plants, are particularly high under acidic soil conditions. Correlation analysis found a statistically significant positive relationship between the concentration of H^{+} cations and zinc content (0.747). The high Pearson coefficients found between the tested heavy metals (Table 3) indicate a common source of soil contamination. These heavy metals are considered typical of brake-pad wear, and are present in tyre rubber (Lin et al., 2005).

The principal component analysis (PCA) identified two main components (*PC1* and *PC2*) that explained 72.23% of the total change in variance (Table 4). Component 1 (*PC1*) was responsible for 47.55% of all variable component elements and correlated strongly with active acidity (0.834), organic carbon (0.774), total zinc (0.821), copper (0.813), nickel (0.933) and chromium (0.880). Component 2 (*PC2*), which explained 24.68% of the total variance, was associated with the fractions of sand (0.833), silt (0.715) and clay (0.940). The graph (Fig. 3) shows that the vectors of factors representing the total content of zinc, copper, nickel, chromium and organic carbon show the largest negative linear relationships, meaning they can be grouped into part of the first principal component. The longer the vector inside the circle, the greater the correlation with the component. The second component was most heavily influenced by the contents of the sand, silt and clay fractions. On analysis of the distribution of the soil's basic properties and the quantity of metals extracted from it in the coordinate factor graph, it can be concluded that the total contents of zinc and copper correlated most strongly with organic carbon content. The principal component analysis also confirmed the correlations between the metals tested. The figure shows that the zinc, copper and lead contents correlate negatively with the soil reaction expressed as pH (Fig. 3).

Table 3
Pearson's correlation coefficients ($p<0.05$) between soil properties and content of heavy metals in soil

Variable		r
Independent	Dependent	
pH KCl	Zn	0.747
Corg	Zn	0.871
Corg	Cu	0.613
Zn	Cu	0.741
Zn	Ni	0.708
Zn	Cr	0.729
Cu	Ni	0.800
Cu	Cr	0.845
Ni	Cr	0.946

Table 4
Values of the two extracted factor loadings for 12 elements

Elements	Component matrix	
	PC1	PC2
Sand	0.500	**–0.833**
Silt	–0.623	**0.715**
Clay	–0.194	**0.940**
pH H_2O	**0.834**	0.186
pH HCl	0.570	0.523
Hh	0.283	–0.197
Corg	**–0.774**	–0.506
Zn	**–0.821**	–0.403
Cu	**–0.813**	–0.169
Pb	–0.590	–0.116
Ni	**–0.933**	0.240
Cr	**–0.880**	0.067
Variation (%)	47.54	24.68
Eigenvalue	5.705	2.961

Bold value are statisticaly signification

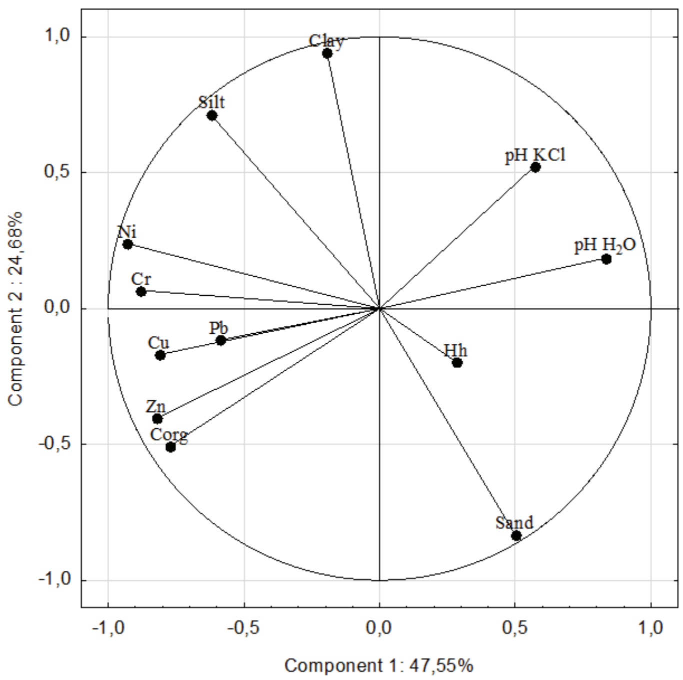

Fig. 3. Configuration of variables in the system of the first two axes PC1 and PC2 of principal components

4. Conclusions

1. The contents of the analysed heavy metals were in the order: Zn > Pb > Cu >Cr>Ni.
2. The enrichment factor (EF) for the surface horizons of the analysed soils indicates "very high" and "extremely high" enrichment with the metals tested.
3. Statistically significant positive correlations between the examined metals indicated a common source of soil contamination.
4. Principal component analysis (PCA) and Pearson linear correlations analysis showed statistically significant positive relationships between the heavy metals and organic carbon content in soil.
5. The research confirmed the impact of traffic-heavy roads on the total content of zinc, lead, copper, nickel and chromium in soils in the road's immediate vicinity.

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Akumulacja wybranych metali ciężkich w glebach w sąsiedztwie ulicy o dużym natężeniu ruchu

Słowa kluczowe

Metale ciężkie
Gleby miejskie
Transport uliczny

Streszczenie

W pracy przedstawiono wyniki badań dotyczące akumulacji całkowitych zawartości wybranych metali ciężkich (Zn, Cu, Pb, Ni i Cr) w glebach w sąsiedztwie ulicy o dużym natężeniu ruchu w ósmym co do wielkości mieście Polski – Bydgoszczy. Próbki glebowe pobrano z trzech głębokości, z punktów badawczych oddalonych o 25, 50, 150 i 175 m od krawędzi ulicy Jagiellońskiej na terenie dworca PKS. Ilości cynku, miedzi, ołowiu, niklu i chromu w glebach oznaczono metodą absorpcyjnej spektrometrii atomowej po mineralizacji w mieszaninie kwasów HF i $HClO_4$.
Zawartość całkowita metali kształtowała się w następujący sposób Zn > Pb > Cu > Cr > Ni. Badania potwierdziły wpływ obciążonej ruchem ulicy Jagiellońskiej na ich zwartość, która malała wraz z odległością od drogi. Przeprowadzone analizy głównych składowych (*PCA*) oraz korelacji liniowych Pearsona wykazały istotne statystyczne dodatnie zależności pomiędzy metalami ciężkimi a węglem organicznym. Wskaźnik wzbogacenia (EF) potwierdził znaczne wzbogacenie poziomów powierzchniowych w badane metale ciężkie.