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ORIGINAL PAPER

ASSESSMENT OF THE CONTENT OF TRACE ELEMENTS IN SOILS AND ROADSIDE VEGETATION IN THE VICINITY OF SOME GASOLINE STATIONS IN OLSZTYN (POLAND)*

Elżbieta Rolka, Andrzej Cezary Żołnowski, Karolina Anna Kozłowska

Department of Environmental Chemistry
University of Warmia and Mazury in Olsztyn, Poland

Abstract

The purpose of this study has been to determine the impact of selected gasoline stations on the content of trace elements in soil and roadside vegetation in areas adjacent to these facilities. Four gasoline stations chosen for analysis were located in Olsztyn, along streets exposed to urban and transportation pressure. The material for analyses was collected from a strip of lawn between each station and the street, and from a land parcel behind the station. Soil and plant samples (roadside common grasses) were submitted to the determination of the content of trace elements, and some soil properties. The research material varied in the content of determined trace elements. Significant differences were detected in soil between the analysed sites, regarding the content of Ni, Zn, Pb and Fe, namely a much higher concentration of Fe was detected at station I, while Zn and Pb were much more abundant at station II, and the highest content of Ni was at station IV. In plants, significant differences occurred with regard to their content of Co, Cr, Cu, Zn, Pb and Fe, such as the significantly highest Cr content at station I, Zn, Pb and Fe at station II, Cu at I, II and III, while Co reached the highest content in plants at stations III and IV. The research results did not demonstrate any cases of concentrations of trace elements in soils exceeding the threshold levels binding in the Polish law, although the EF value achieved indicated considerable anthropogenic enrichment of these soils in Pb and moderate enrichment in Cd, Cu and Zn.

Keywords: pollution, xenobiotics, trace elements, gasoline station, road traffic, enrichment factor (EF).

Andrzej Cezary Żołnowski, PhD, DSc, Department of Environmental Chemistry, University of Warmia and Mazury, Plac Łódzki 4, 10-721 Olsztyn, Poland, e-mail: andrzej.zolnowski@uwm.edu.pl,

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INTRODUCTION

In urbanised areas, road transportation, beside industries and combustion of fossil fuels for heating, contributes considerably to the pollution of the natural environment with trace elements (Czarnowska, Milewska 2000, Onder et al. 2007, Brown, Jasra 2016, Hołtra, Zamorska-Wojdyła 2016, Radziemska 2018). Trace elements such as Pb, Cd, Zn, Cu, Mn and Fe, when emitted by road traffic are mostly contained in suspended solids, and originate from the wearing of tyres, brakes and road surfaces, from corroded car bodies, from oil leaks and from exhaust pipes (Budai, Clement 2011, Jain et al. 2014, Jankowski et al. 2014, Adamiec et al. 2016, Hołtra, Zamorska-Wojdyła 2016, Nwankwoala, Ememu 2018). The literature indicates the wear of brakes as the main source of Cu and Pb, while the wear of tyres is the main contributor of Zn and Cd. Emission of these metals from both sources depends on the type of vehicles and intensity of traffic. Higher emission of the above elements is determined due to the traffic in urban areas than on motorways (Budai, Clement 2011). In urban areas, street dust is found to be substantially polluted with trace elements, including Cu, Cr, Ni, Zn, Fe and Pb (Adamiec et al. 2016). This can be an indirect cause of soil and plant pollution with these elements in areas exposed to more intensive traffic, for example close to gasoline stations. Gasoline stations are particularly exposed to a risk of being contaminated with trace elements (Demkowá et al. 2017). The main sources of trace elements implicated at gasoline stations, beside tank filling and combustion of fuels, are the wear of bearings and brakes, use of greases, wear of tyres and wear of car bodies due to mechanical damage or corrosion (Demková et al. 2007, Emmanuel et al. 2014). Some metals emitted to air by moving cars deposit on the surface of roads and vehicle manoeuvre areas, and some are carried away over large distances (Hołtra, Zamorska-Wojdyła 2016). In urbanised areas, pollutants from such sources are the main threat to plants, soils and to human health and life (Radziemska 2018). Agricultural soils may be contaminated with trace elements through atmospheric deposition or sewage sludge, too (Vollmann et al., 2015).

The purpose of this study has been to determine the content of selected trace elements (Cd, Pb, Cr, Co, Ni, Cu, Zn and Fe) in samples of soil and plants collected from the premises of four gasoline stations situated in Olsztyn.

MATERIAL AND METHODS

Description of study area

Four gasoline stations in Olsztyn, Poland (a town with 173 thousand inhabitants), were selected for the study (Figure 1). The stations are situated in different parts of the city (Figure 2, Table 1). They also differ with respect

Fig. 1. Location of test site on a map of Poland

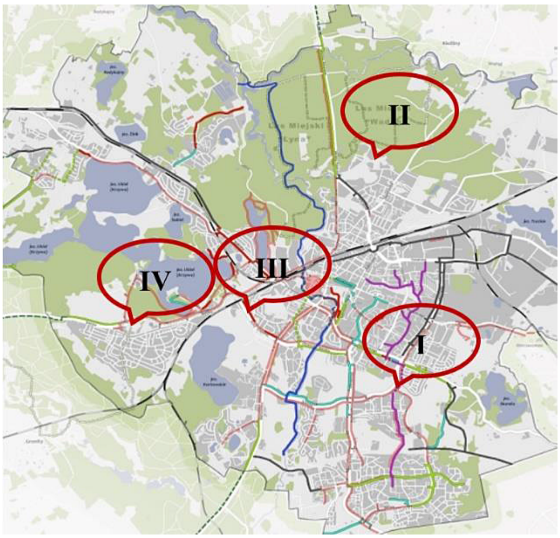

Fig. 2. Location of gasoline stations in Olsztyn (details – see Table 1)

to the transportation pressure. Station I stands at Sikorskiego Street (the city centre), which is part of Provincial Road no 598, on the route from Olsztyn to Zgniłocha (Table 1). Sikorskiego Street is one of the main thoroughfares in Olsztyn, as it connects large housing estates with the city centre, and provides access to several supermarkets and shopping centres. This location translates into intensive traffic of vehicles, which according to the General Director for National Roads and Motorways, GDDKiA (2015*a*) reaches 1,665 vehicles $\cdot 24h^{-1}$. To the east, the station neighbours with a com-

Table 1

Description and location of objects

Number of gasoline station	Company	Geographical coordinates	Sample collection sites
I	Orlen	53°45′31″N, 20°29′14″E	Sikorski Str. 21
II	Orlen	53°47′50″N, 20°28′58″E	Wojska Polskiego Ave. 33A
III	Lotos	53°46′17″N, 20°26′44″E	Sielska Str. 5
IV	Shell	53°46′10″N, 20°24′34″E	Sielska Str. 45A

plex of garden allotments, while to the north and south it is adjacent to areas occupied by commercial and service buildings. The station has 8 fuel pumps. Station II is situated at Wojska Polskiego Avenue, which is part of State Road no 51, on the route from Olsztyn to Dobre Miasto. According to GDDKiA (2015*b*), the average daily traffic along this road section is 9,148 vehicles 24 h^{-1}. The station's premises lie among blocks of flats and warehouses. The station has 7 fuel pumps. Stations III and IV are located at Sielska Street, in the neighbourhood of a residential estate of detached houses, called Dajtki. Sielska Street is part of State Road no 16, on the route from Olsztyn to Ostróda, with the average traffic intensity of 12,215 vehicles 24 h^{-1} (GDDKiA 2015*b*). Station III is near railway tracks, in the close proximity of green areas as well as some shops and workshops. It has 6 pumps. Station IV is on the outskirts of the city (the exit towards Ostróda), and it is directly adjacent to an area occupied by detached residential houses. The station's premises include quite a large car park for passenger cars and lorries. The station has 8 fuel pumps. All the stations sell the same types of fuels, i.e. unleaded gasoline, diesel oil (DO) and liquified petroleum gas (LPG). The pumps at all the stations are protected by roofs.

Soil and roadside vegetation sampling and sample preparation

Soil and roadside common grass samples were collected from the strips of lawn between the stations and the streets, and from the land behind the stations (Table 1). Original soil samples were taken from the soil horizon of 0-0.2 m, using an Egner's sampler (10 samples), along a line at a distance of 10 m (stations I and II) or 20 m from the pumps (stations III and IV), and from 5 to 60 m off the street. In the same places, aerial parts of various grass species were also taken. Soil samples were air-dried and passed through a sieve with the mesh size of Ø = 1 mm. The plant material was dried at a temp. of 60°C and ground in a laboratory mill.

Sample analyses

In line with the procedure US-EPA 3051 (US-EPA 1994), the soil and plant samples were placed in Teflon® vessels HP500 (CEM Corporation, USA) and mineralised in a MARS 5 oven (microwave accelerated reaction system), in a 65% solution of HNO_3 (POCH S.A.). Trace elements (near total content): Cd, Co, Cr, Ni, Cu, Zn, Pb and Fe determined using AAS – SpectrAA-240FS (Varian, Australia), with standard solutions containing 1000 mg of trace metal $\cdot$dm^{-3} (MERCK) according to US-EPA3051 (US-EPA Method 3051. 1994). In addition, the soil samples underwent the following determinations: soil reaction (pH) with the potentiometric method, in neutral salt solution (1M KCl), using a laboratory pH-meter 538 and a WTW electrode; base exchange cations (BEC) and hydrolytic acidity (HAC) with the Kappen's method (Ostrowska et al. 1991). Based on the BEC and HAC determination results, the soil's cation exchange capacity (CEC) and soil base saturation (BS) were calculated.

The results underwent statistical processing according to a one-way analysis of variance at the level of significance $P \leq 0.05$, using statistical calculation software Statistica v. 10.0. (StatSoft) Homogenous groups were determined with the Duncan's test. Additionally, the results served to calculate: standard deviation (SD), variance coefficient (V), and – to illustrate dependences between the analysed characteristics – the Pearson's simple correlation coefficient (*r*), the significance of which was determined on the basis of a table of threshold values at *n*-2 degrees of freedom.

Assessment of soil pollution

In order to assess the degree of soil contamination with trace elements (Cd, Pb, Cr, Co, Ni, Cu and Zn), their soil content was referred to the threshold values for areas serving transportation purposes given in the Regulation of the Minister for the Environment, September 1st, 2016 (*Ordinance*... 2016). And to identify the source of the analysed elements (Cd, Cr, Cu, Co, Ni, Zn and Pb) found in soil, the enrichment factor (EF) was derived from the formula:

$$EF = \frac{(C_x / C_{Fe})_{analysed\ sample}}{(C_x / C_{Fe})_{bedrock}},$$

where: C_x denotes the total content of the analysed metal, and C_{Fe} stands for the total content of Fe, respectively, in the analysed sample and in the bedrock (Salah et al. 2013, Khalilova, Mammadov 2016, Charzyński et al. 2017). The geochemical background values for the determined elements were adopted according to Charzyński et al. (1996), with the following average bedrock content for Poland: Cd 0.18 mg kg^{-1}, Cr 27.0 mg kg^{-1}, Cu 7.1 mg kg^{-1}, Co 4.0 mg kg^{-1}, Ni 10.2 mg kg^{-1}, Zn 30.0 mg kg^{-1}, Pb 9.8 mg kg^{-1} and Fe 12,900 mg kg^{-1} of soil. A value of EF>1.5 indicates an anthropogenic source of trace elements in soil (Zhang, Liu 2002). Five categories of EF are distinguished: minimum enrichment (EF<2), moderate enrichment (2≤EF<5), considerable enrichment (5≤EF<20), very high enrichment (20≤EF<40) and extremely high enrichment (EF≥40) – Charzyński et al. (2017).

RESULTS AND DISCUSSION

The average content of trace elements in the soil collected from the premises of 4 gasoline stations was, in decreasing order, as follows: 7 418 mg Fe>67.52 mg Pb>38.80 mg Zn>15.79 mg Cu>7.939 mg Ni>1.880 mg Cr>0.756 mg Co>0.330 mg Cd kg^{-1} (Table 2). The soils from the analysed gasoline stations were significantly different with respect to the content of Ni, Zn, Pb and Fe, but no significant differences were revealed

Table 2

Content of trace elements in analysed soil (mg kg^{-1})

Element		Gasoline stations				Mean for stations I-IV
		I	II	III	IV	
Cd	mean±SD V(%)	0.425^{a}±0.030 7	0.300^{a}±0.105 35	0.315^{a}±0.237 75	0.280^{a}±0.128 46	0.330±0.142 43
Co	mean±SD V(%)	0.880^{a}±0.347 39	0.690^{a}±0.324 47	0.575^{a}±0.216 38	0.880^{a}±0.118 13	0.756±0.275 36
Cr	mean±SD V(%)	1.940^{a}±0.203 10	1.700^{a}±0.589 35	1.680^{a}±0.107 6	2.200^{a}±0.365 17	1.880±0.393 21
Ni	mean±SD V(%)	6.140^{a}±0.757 12	7.748^{b}±0.734 9	7.310^{ab}±1.215 17	10.56^{c}±0.803 8	7.939±1.858 23
Cu	mean±SD V(%)	14.50^{a}±1.45 10	18.55^{a}±1.25 7	16.75^{a}±10.22 61	13.35^{a}±0.53 4	15.79±5.10 32
Zn	mean±SD V(%)	24.90^{a}±8.62 35	57.30^{b}±19.99 35	37.75^{ab}±27.71 73	35.25^{ab}±5.94 17	38.80±20.05 52
Pb	mean±SD V(%)	66.06^{ab}±58.11 88	102.0^{b}±14.66 14	52.38^{ab}±18.74 36	49.66^{a}±4.51 9	67.52±35.44 52
Fe	mean±SD V(%)	9411^{b}±441.5 5	7557^{ab}±1637 22	5676^{a}±967.0 17	7030^{a}±148 21	7419±1766 24

Means followed by the same letter do not differ at p=0.05 by the LSD – test, n=16

regarding the content of Cd, Co, Cr and Cu. The highest Ni content was determined in soils near station IV, where on average it equalled 10.56 mg Ni kg^{-1}. At station IV, the content Ni in the soil was in 27-42% higher than at the other stations. Ni did not show any significant correlations with the other analysed metals, either in the soil or in the plant samples, and the only factor that had a significant negative impact on the Ni content was soil reaction (r=-0.693**) – Table 3. This correlation is confirmed by the data

Table 3

Coefficient of correlation between analysed trace elements

Correlation between analysed trace elements in soils								
Trace elements	Cd	Pb	Cr	Co	Ni	Cu	Zn	Fe
Pb	0.136							
Cr	-0.469	-0.254						
Co	0.427	0.354	-0.208					
Ni	-0.142	-0.036	0.222	0.404				
Cu	0.602*	0.313	-0.215	0.026	0.030			
Zn	0.206	0.347	0.037	-0.315	0.111	0.818**		
Fe	0.140	0.178	0.545*	0.154	-0.238	0.189	0.138	
Correlation between analysed trace elements in plants								
Trace elements	Cd	Pb	Cr	Co	Ni	Cu	Zn	Fe
Pb	0.353							
Cr	0.312	0.232						
Co	-0.326	-0.685**	-0.585*					
Ni	-0.371	0.354	0.043	-0.421				
Cu	-0.029	0.752**	-0.027	-0.506	0.278			
Zn	0.635*	0.640*	-0.088	-0.236	0.213	0.309		
Fe	0.752**	0.619*	0.090	-0.358	-0.042	0.486	0.841**	
Correlation between analysed trace elements in plants and soils								
	Soils							
Plants – Trace elements	Cd	Pb	Cr	Co	Ni	Cu	Zn	Fe
Cd	-0.014	0.821**	0.227	0.339	-0.371	0.313	0.453	0.395
Pb	-0.151	0.623*	-0.272	-0.137	-0.526	0.123	0.174	0.266
Cr	0.283	0.378	0.060	0.578*	-0.203	-0.186	-0.295	0.614*
Co	-0.007	-0.459	0.087	-0.404	0.283	-0.053	0.117	-0.569*
Ni	-0.219	-0.301	0.064	-0.411	-0.395	0.005	0.075	0.290
Cu	0.179	0.339	-0.447	-0.170	-0.714**	0.366	0.133	0.134
Zn	-0.200	0.608*	0.078	-0.373	-0.105	0.451	0.764**	0.233
Fe	0.184	0.769**	-0.012	-0.037	-0.137	0.695**	0.758**	0.417
Correlation between analysed trace elements in soil and some properties of soils								
Properties of soils	trace elements in soils							
	Cd	Pb	Cr	Co	Ni	Cu	Zn	Fe
pH	0.320	0.248	0.172	-0.219	-0.693**	0.390	0.303	0.743**
HAC	-0.323	0.028	-0.499	0.155	0.329	-0.419	-0.325	-0.750**
BEC	0.720**	0.426	-0.294	0.192	-0.519	0.638*	0.351	0.576*
CEC	0.720**	0.428	-0.299	0.194	-0.519	0.638*	0.350	0.573*
BS	0.747**	0.440	-0.146	0.249	-0.283	0.723**	0.507	0.626*
Correlation between analysed trace elements in plants and some properties of soils								
Properties of soils	trace elements in plants							
	Cd	Pb	Cr	Co	Ni	Cu	Zn	Fe
pH	0.202	0.486	0.352	-0.357	0.241	0.582*	0.375	0.589*
HAC	-0.173	0.025	-0.199	0.034	-0.037	-0.182	-0.142	-0.398
BEC	0.236	0.469	0.455	-0.493	0.173	0.610*	0.286	0613*
CEC	0.236	0.471	0.455	-0.495	0.174	0.611*	0.286	0.613*
BS	0.386	0.298	0.469	-0.381	-0.283	0.359	0.349	0.657*

HAC– hydrolytic acidity, BEC – base exchange cations, CEC – cation exchange capacity, BS – base saturation, * coefficient of correlation *r* significant for p=0.05, ** highly significant for p=0.01

Table 4

Some physicochemical properties of analysed soils

Parameter			Gasoline stations				Mean for stations I-IV
			I	II	III	IV	
HAC		mean±SD V(%)	1.01^{a}±0.14 14	1.35^{a}±0.35 26	1.28^{a}±0.26 20	1.31^{a}±0.07 6	1.24±0.25 20
BEC	(cmol(+) kg^{-1} soil)	mean±SD V(%)	102.0^{c}±0.00 0	84.4^{bc}±1.82 2	58.7^{ab}±41.9 71	34.6^{a}±6.73 19	69.9±32.5 47
CEC		mean±SD V(%)	103.0^{c}±0.14 0	85.75^{bc}±1.52 2	59.98^{ab}±41.7 69	35.91^{a}±6.78 19	71.16±32.4 46
BS	(%)	mean±SD V(%)	99^{b}±0.14 0	98^{ab}±0.43 0	96^{a}±3.00 3	96^{a}±0.59 1	97±2 2
Reaction (pH)	1 M KCl dm^{-3}	mean±SD V(%)	7.36^{c}±0.04 1	7.22^{bc}±0.18 2	7.17^{ab}±0.09 1	7.03^{a}±0.02 1	7.20±0.15 2

HAC – hydrolytic acidity, BEC – base exchange cations, CEC – cation exchange capacity, BS – base saturation; means followed by the same letter do not differ at p=0.05 by the LSD – test, n=16.

presented in Table 4, where the soil from station I – with the highest reaction equal pH_{KCl}=7.36 – was distinguished by the lowest Ni content equal 6.14 mg kg^{-1} (Table 2). Alkaline soil reaction (pH) can immobilise trace elements in soil (Losak et al., 2012). A high content of Zn (57.30 mg kg^{-1}) and simultaneously a high Pb content (102.0 mg kg^{-1}) were noted in soils collected in the vicinity of station II. These levels were higher by 34-57% and 35-51%, respectively, than in soil near the other stations. The Zn content was significantly correlated with the soil content of Cu (r=0.818**) – Table 3. A highly significant correlation between Cu and Zn in soil was also reported by Salah et al. (2013), Emmanuel et al. (2014), and Hołtra and Zamorska-Wojdyła (2016). Modrzewska and Wyszkowski (2014) showed that Cu also correlated positively with Cd. The content of Pb determined in soil did not correlate significantly with the content of the other metals, although it was demonstrated that the soil Pb correlated significantly positively with the plant content of Cd, Zn and Fe. In this study, the content of Pb in soil and plants was not evidenced to be significantly correlated with the soil properties (Table 3). The highest Fe content (9.411 mg kg^{-1} of soil) was characteristic for the soils around station I. In this case, the determined value was by 20-40% higher than the levels noted in the soils sampled at the other stations. The Fe determined in soil statistically significantly correlated with the soil content of Cr, which confirms data of Salah et al. (2013). Meanwhile, it was demonstrated in the current study that plants growing on soils with a lower content of Fe were also characterised by a higher content of Cr (r=0.614*) and a lower content of Co (r=-0.569*) – Table 3. Compared with the average concentrations of Ni, Zn and Pb determined in unpolluted soils in Poland, the content detected in the soils around the analysed gasoline stations was higher by 3.16 mg kg^{-1} with respect to Ni, and by 11.4 mg and 83.7 mg kg^{-1} in the case of Zn and Pb (Dudka 1993, Kabata-Pendias et al. 1989, Kabata-Pendias, Dudka 1991). An analysis of the coefficients of variance (V) for the above metals manifested diverse variation both within and between the gasoline stations (Table 2). The lowest variation between the determined values was observed for station IV, which is the newest among the four facilities. The variation values recorded there were 8, 17 and 9% for Ni, Zn and Pb, respectively. The trace elements which demonstrated much higher fluctuations were Pb (9%≤V≤88%) and Zn (17%≤V≤73%). Despite the determined variation, the highest noted content of trace elements in the soils from the analysed gasoline stations in Olsztyn did not exceed the threshold values for areas connected with transportation as specified in the *Ordinance of the Minister for the Environment* (2016). While analysing the soil properties, it was observed that the concentrations of Cd and Cu were strongly influenced by such parameters as BEC, CEC and BS (Table 4), a finding verified by the high positive correlation coefficients (Table 3). The content of Fe was positively correlated with all soil parameters except HAC, for which the correlation was negative.

The levels of trace elements detected in soils in the vicinity of Olsztyn-based gasoline stations were often much lower than reported by other authors. For instance, relatively high concentrations of Zn and Cu were determined in soil near gasoline stations in Wrocław (Hołtra, Zamorska-Wojdyła 2016). Research conducted in different parts of the world suggests that elevated concentrations concern more often such metals as Cd (Dauda, Odoh 2012, Emmanuel et al. 2014, Brown, Jasra 2016), Cr (Emmanuel et al. 2014, Brown, Jasra 2016), Ni (Dauda, Odoh 2012, Emmanuel et al. 2014) or sum of Co, Zn, Cu and Pb (Dauda, Odoh 2012). In turn, lower concentrations of Cu, Zn, Fe and Pb in comparison with current study were demonstrated by Emmanuel et al. (2014), less Ni, Zn, Pb and Fe was reported by Nwankwoala and Ememu (2018), and less Cu and Pb was detected by Brown and Jasra (2016). Such differences may be caused by different intensity of the traffic serviced by given gasoline stations, or by the natural content of trace elements in the analysed soils; other factors could include the technical condition of vehicles and the length of time during which particular stations have produced pollution over the analysed area. Antonkiewicz and Macuda (2005), who analysed soils from the premises of seven gasoline stations in Kraków, demonstrated large discrepancies in the concentrations of Cr (3.0-202.0 mg kg^{-1} of soil), Cu (5.4-57.0 mg), Zn (18.0-323.0 mg) and Pb (10.0-400.0 mg kg^{-1} of soil). Varied and often elevated content of trace elements in soils near gasoline stations and on areas exposed to transportation depends on the intensity of traffic and distance from the road (Onder et al. 2007, Elbagermi et al. 2013, Modrzewska, Wyszkowski 2014, Khalilova, Mammadov 2016), as well as the factors which have direct influence on the accumulation of metals in soils, including such manoeuvers as pulling down, pulling out and accelerating a car (Elbagermi et al. 2013).

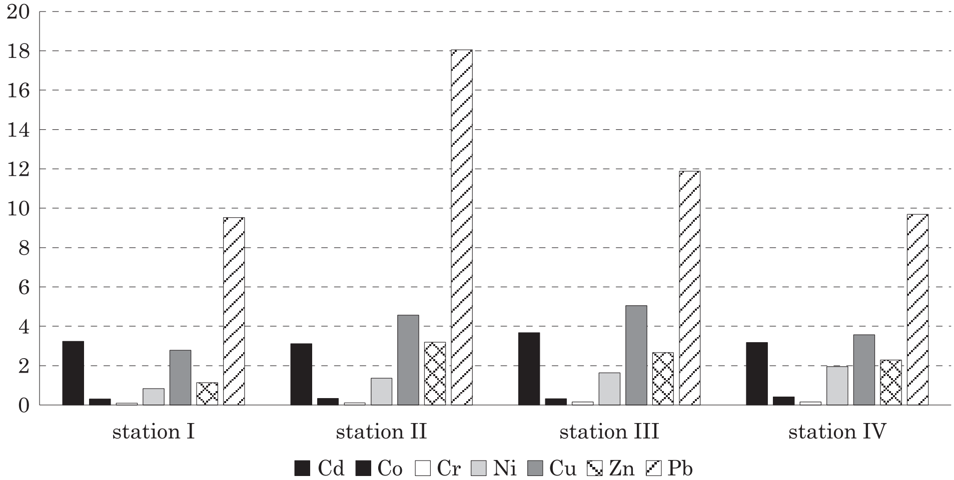

Fig. 3. Mean values of enrichment factors (EF) of trace elements in analysed soils

Although the soil samples obtained in the vicinity of the gasoline stations in Olsztyn did not exceed the threshold values, the enrichment factor (EF) in many cases reached the values indicating the anthropogenic origin of metals in soil (Figure 3). The mean EF values for soils around the analysed stations was within the following ranges: Cd=3.11-3.68, Co=0.31-0.41, Cr=0.10-0.15, Ni=0.83-1.95, Cu=2.79-5.05, Zn=1.13-3.19 and Pb=9.53-18.05. Values of EF>1.5 confirming the anthropogenic accumulation of an element (Zhang, Liu 2002) were calculated for Cd, Cu and Pb in soil samples from all the stations, and for Zn in soil from stations II, III and IV, as well as for Ni in soil from stations III and IV. According to the categories established by Charzyński et al. (2017), values of the EF achieved in our study implicated minimal enrichment of soils with Co, Cr and Ni, moderate enrichment with Cd, Cu and Zn, but considerable enrichment with Pb. A particularly high enrichment factor value for Pb was obtained at station II. This might have resulted from the past, when gasoline was enriched with $Pb(C_2H_5)_4$ (Adamiec et al. 2017), but another contributing factor might be the relatively low mobility of Pb in the soil environment.

The EF accounts for the natural content of trace elements in soil according to a relatively stable bedrock content of Fe, which is only minimally affected by anthropogenic pressure. Hence, the EF is a tool that can provide precise information about the man-made influence on the chemical composition of soil. Numerous authors have verified experimentally that an elevated EF detected in soils lying in the proximity of gasoline stations most often applies to Pb (Khalilova, Mammadov 2016), Cd, Zn and Cu (Nwankwoala, Ememu 2018). The comparison of the EF values obtained in the current study, which were 0-6 (with the exception of Pb=9.5-18.0), with the ones reported by Dauda and Odoh (2012) and Emmanuel et al. (2014), which equalled Pb=73.34, Cd=138 or Cr=18.2, shows that the analysed soils lying proximally to gasoline stations in Olsztyn are characterised by a relatively low level of the anthropogenic impact. Higher EFs than obtained in our study were also reported by Hołtra and Zamorska-Wojdyła (2016) for Zn (9.86) and Cu (12.50). In the case of soils sampled from the urbanised area of Toruń (Charzyński et al. 2017), the EFs for Cd, Cr, Cu, Ni, Zn and Pb were within similar ranges as in the current research.

The average content of trace elements in plants collected from the areas near the analysed gasoline stations (Table 5) was as follows (in decreasing order): 264.4 mg Fe, 44.96 mg Pb, 32.61 mg Cu, 31.28 mg Zn, 13.26 mg Ni, 1.212 mg Cd, 0.696 mg Cr and 0.504 mg Co kg^{-1} d.m. The variance coefficients (V) for the tested plants material showed very high variation in the content of Co and Zn (61%≤V≤76%) as well as moderate variation in the content of Cd, Cr, Cu, Pb and Fe (23%≤V≤34%). The most convergent results, regardless of which gasoline station was considered, were obtained for the plants' content of Ni (V=1%). In turn, the value of the variance coefficient for most of the metals in plants from particular stations did not exceed 40%. Co was an exception, as it demonstrated very high variation at stations I, II, and IV (64%≤V≤81%). The analysis of variance proved significant diffe-

Table 5

Content of trace elements in roadside vegetation (mg kg^{-1} d.m.)

Element		Gasoline stations				Means for stations I-IV
		I	II	III	IV	
Cd	mean±SD V(%)	1.158^{a}±0.442 38	1.448^{a} ±0.315 22	0.970^{a} ±0.231 24	1.273^{a} ±0.115 9	1.212±0.323 27
Co	mean±SD V(%)	0.224^{a}±0.181 81	0.227^{a}±0.179 79	0.769^{b}±0.017 2	0.794^{b}±0.505 64	0.503±0.383 76
Cr	mean±SD V(%)	0.980^{c}±0.167 17	0.720^{b}±0.103 14	0.405^{a} ±0.036 9	0.679^{b}±0.087 13	0.696±0.232 33
Ni	mean±SD V(%)	13.27^{a} ±0.121 1	13.31^{a} ±0.022 0	13.23^{a} ±0.041 0	13.21^{a} ±0.052 0	13.25±0.074 1
Cu	mean±SD V(%)	36.28^{b}±2.130 6	36.82^{b}±0.773 2	38.87^{b}±2.108 5	18.49^{a}±3.985 22	32.62±8.778 27
Zn	mean±SD V(%)	21.10^{a}±2.575 12	57.79^{b}±23.19 40	25.40^{a}±5.362 21	21.12^{a}±1.893 9	31.35±19.16 61
Pb	mean±SD V(%)	48.92^{b}±9.211 19	62.31^{c}±5.802 9	43.12^{b}±7.111 16	25.50^{a}±6.886 27	44.96±15.15 34
Fe	mean±SD V(%)	259.2^{ab}±38.15 15	325.3^{b}±66.70 21	251.9^{ab}±67.35 27	221.1^{a}±12.78 6	264.4±60.48 23

Means followed by the same letter, do not differ at p=0.05 by the LSD-test, n=16.

rences between the compared objects in the plants' content of Co, Cr, Cu, Zn, Pb and Fe. Demonstrably the highest content of Zn (57.79 mg), Pb (62.31 mg) and Fe (325.3 mg) was determined in plants sampled at station II, Cr (0.980 mg) at station I, Co at stations III and IV (0.769 and 0.794 mg), and Cu at stations I, II and III (36.28, 36.82 and 38.87 mg kg^{-1}). With respect to the plant content of Cd and Ni, no significant differences were determined between the analysed objects. The content of Cd in plants ranged between 0.970-1.448 mg kg^{-1}, and that of Ni was within 13.21-13.31 mg kg^{-1} d.m. Our comparison of the chemical composition of plants collected from the areas around the analysed stations in Olsztyn justified the claim that these plants had nearly 3-fold less Zn and 2-fold less Cu than plants growing near roads in Wrocław (Hołtra, Zamorska-Wojdyła 2016). Moreover, plants from green areas in Warsaw contained more Zn and Fe, but less Cu, Pb, Ni and Cd (Czarnowska, Milewska 2000, Czarnowska, Nowakowski 2006). Less Pb and Cd than in our study was determined by Jankowski et al. (2014) in plants collected from the roadside along Expressway S2 (the ringroad of Siedlce). Finally, Onder et al. (2007), who analysed grass from an urban area, determined a much higher content of Zn and Cr, but a lower content of Pb, Cu, Cd, Ni and Co than detected in our research.

Changes in the chemical characteristic of soils adjacent to gasoline stations due to anthropogenic pressure influenced the relationships between trace elements contained in plants. Among the analysed trace elements, the Pb and Zn content found in the soil was significantly positively correlated with the content of these metals in plants (Table 3). Regarding the other metals, such relationships were not found. However, it was detected that a higher concentration of Pb in plants caused a parallel increase in Cu (r=0.752**), Zn (r=0.640*) and Fe (r=0.619*) as well as a decrease in the content of Co (r=-0.685**). A higher concentration of Cr was correlated with a lower content of Co (r=-0585*), while a higher content of Zn contributed to an increase in the content of Fe (r=0.841**). Moreover, a higher content of Cd was positively correlated with the concentration of Zn (r=0.635*) and Fe (r=0.752**). Vollmann and Losak (2016) found out that Zn was positively correlated with the Cd content in soybean seeds. Among the analysed trace elements, only content of Cu and Fe positively correlated with such soil parameters as pH, BEC, CEC, and additionally with BS in the case of Fe (Table 3). The positive correlations demonstrated in our experiment with respect to the relationships Cd:Zn and Pb:Zn in plants were supported by findings reported from the surroundings of a gasoline station in Prešov, Slovakia (Demková et al. 2017) and in Warsaw in areas adjacent to streets (Czarnowska, Milewska 2000), where positive correlations were demonstrated for the following pairs of metals: Fe:Zn, Fe:Pb, and Fe:Cd. Numerous and significant correlations between trace elements are generally seen as an argument pointing to the same source of origin (Salah et al. 2013).

CONCLUSIONS

The average content of trace elements in soils in the vicinity of gasoline station showed the following decreasing order: Fe>Pb>Zn>Cu>Ni>Cr>Co>Cd. The content of Cd, Zn and Pb was characterised by high variation (43%≤V≤52%), and that of Co, Cr, Ni, Cu and Fe was moderately varied (21%≤V≤36%). The highest Fe content was determined at station I, Zn and Pb determined in soil reached the highest levels at station II, while Ni was most abundant in soil at station IV. The content of the remaining metals (Cd, Co, Cr and Cu) was similar in soil samples from all stations. The content of trace elements in plants growing in the vicinity of gasoline stations showed a slightly different decreasing order: Fe>Pb>Cu>Zn>Ni>Cd>Cr>Co. The content of Co and Zn was highly varied (61%≤V≤76%) while that of Cd, Cr, Cu, Pb and Fe showed moderate variation (23%≤V≤34%). The highest content of Zn, Pb and Fe was recorded in plants collected at gasoline station II. The highest Cr content was found in plants from station I, while the highest content of Co was found in plants from stations III and IV. Plants from stations I, II and III were characterized by the highest Cu content. The content of Cd and Ni in the roadside plants did not vary significantly between the stations. The content of trace elements in soil and plant samples from the vicinity of gasoline stations generally demonstrated positive correlations between particular trace elements, which may indicate their similar source of origin. Moreover, a significantly positive dependence was found between the sorption properties of soil and the soil content of Cd, Cu and Fe as well as the plant content of Cu and Fe. Furthermore, the soil reaction significantly and positively correlated with the plant content of Cu and the soil and plant content of Fe. Despite the considerable variation in the content of trace elements in soil samples from the gasoline stations researched in the current study, the Polish threshold levels were not exceeded. The value of the enrichment factor EF, however, indicates considerable anthropogenic enrichment of soils with Pb, and moderate enrichment with Cd, Cu and Zn. On the other hand, high soil reaction was demonstrated (7.03-7.36), and quite high sorption complex saturation with cation ions (96%≤BS≤99%) identified in the study may constitute a barrier to migration of the trace elements accumulated in the soil.

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