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The Content of Heavy Metals (Cu, Zn, Cr, Ni, Pb) in The Soil Near The Arterial Roads in Wroclaw (Poland)

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Abstract. The concentrations of heavy metals in soils along the motorway bypass of Wroclaw (AOW) and the Eastern Ring Road of Wroclaw (WOW), Poland, have been determined. The soil samples were collected from the levels of 0-25 cm within 2 m from the edge of the road. The mineralizates were prepared in HNO_3, 60%, using the Microwave Digestion System. The content of Cu, Zn, Cr, Ni and Pb in soils were determined using FAAS method. The physicochemical parameters, the conductivity and pH of the soil solutions were measured to evaluate the salinity of the soils and their active and exchangeable acidity. The pollution indexes (W_N) showing the enrichment of soils in metals have been determined. Excess of metal concentrations in soils compared to the geochemical background in uncontaminated soils of Poland has been observed. Permissible concentrations of heavy metals relative to the standard for soils, according to the Polish Ministry of Environment Regulation from September 1st, 2016, have not been exceeded.

1 Introduction

The number of cars on Polish roads, both private and from the transport sector (mainly transit), has been steadily increasing. The large majority of vehicles is powered by petrol (approx. 54%) and diesel fuel (approx. 41%). Pollution of the atmosphere and the soil is often caused by the exploitation of vehicles constructed with out-of-date production technologies. Anthropogenic sources of heavy metals in soils along the roads most commonly include: liquid spills of transported cargo, leakages of fluid operating systems of the car (Pb: liquid in the battery, formerly a component of gasoline), exploitation of wear parts of vehicles (Pb – in the bearing and solder alloys, covers of the electric cables, Pb and Ni in anti-corrosion agents, Cu in the brake system and radiator), abrasion of car tires (Zn), accidents and collisions (Cr in paints and varnishes) and dusts appearing as a result of incomplete combustion of diesel fuels and abrasion of brake pads and the clutch [1–4]. The concentrations of heavy metals in soils of Poland were shown in Table 1.

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Table 1. The content of heavy metals in soils along the Polish roads.

Location	Zn [mg/kg]	Pb [mg/kg]	Cu [mg/kg]	Ni [mg/kg]	Cr [mg/kg]
Soils along the Warsaw roads [5]	329.0 – 352.0	186.0 – 246.0	37.4 – 70.3	-	-
Soil along the arteries of Olsztyn [6]	19.6 – 112.4	19.7 – 196.0	7.2 – 26.9	7.3 – 23.6	5.4 – 21.6
Soils along the road no. 7 Olsztynek – Płońsk [7]	19.7 – 75.6	6.8 – 17.4	3.3 – 11.3	-	-
Dust road in Lublin [8]	202.0	23.0	65.0	27.0	53.0
Drainage ditches along the roads of Roztocze National Park and Przemysl Foothills Landscape Park [9]	40.0 – 256.0	10.2 – 29.0	4.0 – 23.0	4.0 – 37.3	-

Heavy metals accumulate in soils and then in the living organisms. In the organism, there are not decomposed, only deposited in tissues and organs. As a rule, they are toxic, especially if present in excess. They may interfere with biochemical and biological processes, endangering health. Over time, the concentration of heavy metals increases and they begin to react with the enzymes, causing the disease. The activation mechanism of metals is also based on the impact of the stress factor on the organism [10].

2 Materials and methods

The soil samples have been collected in June 2016 from the surface layer of the soil profile (up to 25 cm of depth), approx. 2 m from the edge of the motorway bypass of Wroclaw (AOW, no. 1-5) and the Eastern Ring Road of Wroclaw (WOW, no. 6-10) – map.1.

No.	Location
1	AOW Długołęka (intersection of road no. 98 and Widawska Street)
2	AOW Node of North Wroclaw (exit from the roundabout into road no. 5)
3	AOW Node of Stadium Wroclaw (Kosmonautów Street)
4	AOW Node of Airport Wroclaw (exit from the roundabout into Graniczna Street)
5	AOW Node of South Wroclaw (exit from road no. E40 into road no. A8)
6	WOW Jagodno (exit from the roundabout into road no. 395)
7	WOW Siechnice (exit from the roundabout into Opolska Street)
8	WOW Blizanowice (exit direction Blizanowice)
9	WOW Kamieniec Wrocławski (exit from the roundabout into Wrocławska Street)
10	WOW Dobrzykowice (exit from the roundabout into Strachocińska Street)

Map 1. Descriptions of test stands.

In a given location, the soil samples were collected from three points located within the distance of about 50-100 cm from each other. Three soil samples from a given location were screened and averaged after drying. The measurements of pH in water and 1M KCl and the electrical conductivity EC were made according to PN-ISO 10390:1997. The soil solutions were made in a stoichiometric ratio of soil to a solution 1:2.5 (m:v). Soils used for the mineralization process were prepared in accordance to PN-ISO 11465:1999. The soil

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sample weighing about 0.2 grams of dry matter digested in 8 ml of 60%-nitric acid. The microwave mineralization process was conducted with the use of Start D device (Milestone). The concentrations of zinc, copper, nickel, chromium and lead have been determined through the Flame Atomic Absorption Spectroscopy (FAAS) method. In the spectroscopy analysis the iCE 3500 Solaar Thermo device (Thermo Scientific) [PN-ISO 11047:2001] was used. The arithmetic mean and the standard deviation were calculated with the three replicates of the sample.

Chemical analyses have been carried out in the certified Laboratory of Toxycology and Environmental Research in the Faculty of Environmental Engineering at the Wroclaw Uniwersity of Science and Technology.

3 Results and discussion

Measurements of pH indicated active acidity (pH in H_2O) and exchangeable acidity (pH in 1 M KCl solution) in the soil solutions. The pH parameter allows to evaluate the risk of migration of heavy metals deep into the soil profile. The measurement of proper conductivity indicated the content of ions in the soil. The EC parameter allowed to evaluate the salinity of soils. The result below 25 mS/m indicated low salinity and above 75 mS/m showed high levels of salinity [11]. Spectroscopic analysis informs about the content of Cu, Zn, Pb, Cr and Ni in soils. On that basis the indexes of the enrichment of soils in heavy metals compared to the uncontaminated geochemical background in Poland can be calculated [12].

3.1 pH and EC measurements in soil solutions

The most alkaline character of the soil (pH of 8.08 in H_2O and pH of 7.66 in 1 M KCl) was identified in sample no. 7 WOW Siechnice (Fig. 1). It may be due to the ongoing work at the metallurgical waste landfill in Siechnice, located approx. 200 m from the road. Transportation of waste contributes to the pollination of the road and surrounding area. pH in the waste solution is 8.92 in H_2O and 8.52 in 1 M KCl. In a slightly alkaline environment most of the heavy metals are immobilized (hydroxide forms), which causes the low ability of metals to migrate deep into the soil. Soil sample no. 10 (WOW Dobrzykowice) demonstrated acidic character (pH 6.67 in H_2O and pH 5.71 in 1 M KCl). In the medium with pH below 6.5 metals have mostly cation forms. The ability of metals to migrate is much higher, which may pose a threat to the environment.

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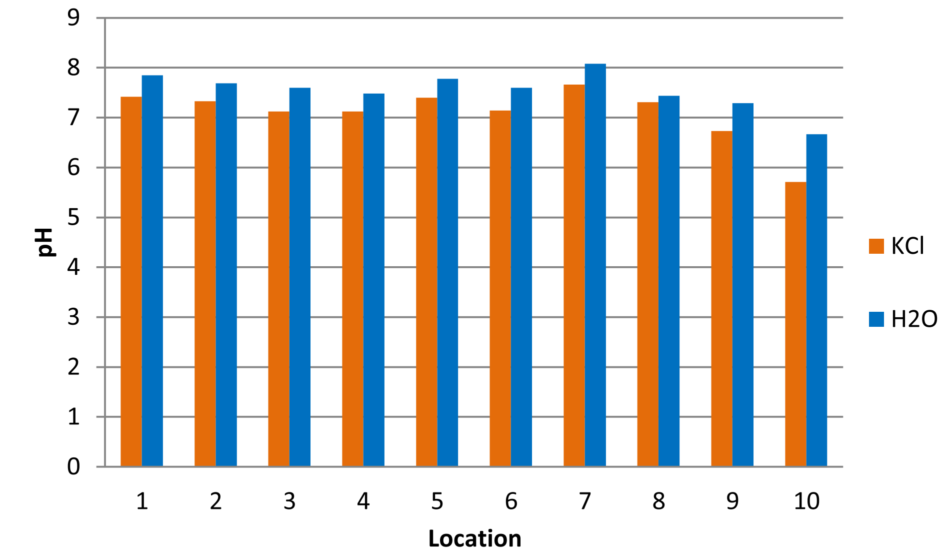

Fig. 1. pH measurement in soil solutions.

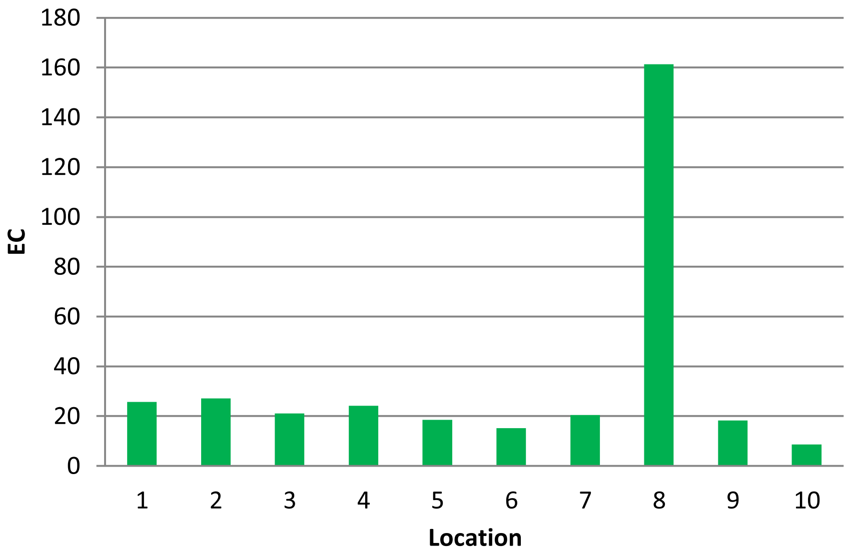

Fig. 2. EC measurement in soil solutions.

The results of the measurement of proper conductivity show that essentially the soils are slightly salted, the EC values are below 25 mS/m (Fig. 2). In sample no. 2 (AOW Node of North Wroclaw) exceeds the EC limit by about 2.16 mS/m, therefore the soil is of medium salinity. The highest conductivity of 161.35 mS/m is in sample no. 8 (WOW Blizanowice). The high salinity of the soil is probably the effect of the accumulation of the road salt during winter. Anions have lesser sorption ability than cations, therefore only irrational human activities can result in such a high soil salinity.

3.2 The content of Cu, Zn, Pb, Ni and Cr in soils

None of soil samples exceeds the permissible concentrations of heavy metals, relative to standard for soils, in accordance with the Polish Ministry of Environment Regulation from September 1st, 2016 (Table 2, Fig. 3) [13].

Table 2. The content of heavy metals in soils.

No.	Cu [mg/kg]		Zn [mg/kg]		Pb [mg/kg]		Ni [mg/kg]		Cr [mg/kg]	
	x	s	x	s	x	s	x	s	x*	s
1	27.79	0.93	72.75	0.17	17.18	1.80	34.08	0.88	13.54	1.29
2	41.21	0.20	298.27	1.12	30.17	0.11	18.53	0.28	28.60	1.18
3	29.71	1.13	116.71	0.67	23.01	0.64	6.86	0.46	11.54	1.38
4	17.70	0.46	83.57	1.19	13.79	1.60	9.41	0.53	3.58	0.78
5	11.52	0.88	48.97	1.11	6.50	0.93	7.38	0.43	12.43	0.36
6	14.76	0.16	68.04	1.25	10.91	1.54	5.74	0.99	15.14	1.33
7	8.73	0.22	52.53	1.10	3.59	0.50	17.46	0.53	79.99	0.70
8	21.32	1.00	93.43	0.48	11.57	0.81	12.02	0.99	114.54	2.44
9	10.45	0.67	71.23	1.08	5.93	0.51	24.26	0.65	12.54	0.81
10	6.84	0.30	29.96	0.97	no	no	4.39	0.94	6.13	0.29

x - arithmetic mean; s – standard deviation for 3 measurements, no - below the limit of Pb quantification by FAAS method.

The highest concentrations of copper, zinc and lead were recorded in sample no. 2 (AOW Node of North Wroclaw). The content of heavy metals is respectively 41.21 mg Cu/kg of dry matter, 298.27 mg Zn/kg of dry matter and 30.17 mg Ni/kg of dry matter. In general, the lowest concentration of metals are observed in soil sample no. 10 (WOW Dobrzykowice): 6.84 mg Cu/kg of dry matter, 29.96 mg Zn/kg of dry matter. The concentration of lead is below the limit of quantification of Pb by Flame AAS method.

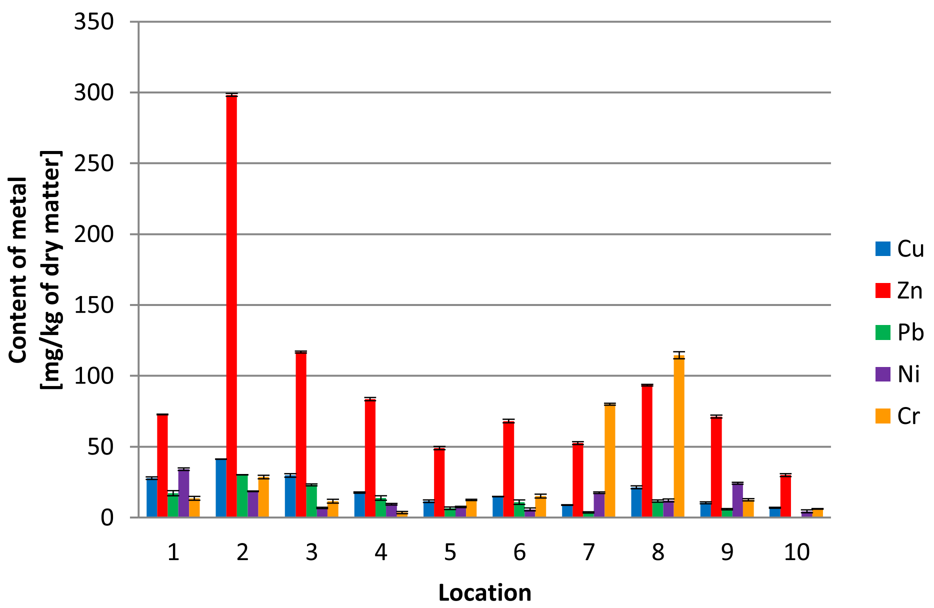

Fig. 3. The content of trace elements in soils.

The highest concentration of nickel was 34.08 mg/kg of dry matter and it was observed in sample no. 1 (AOW Długołęka). Again, the lowest concentration of heavy metal (4.39 mg Ni/kg of dry matter) was recorded in soil sample no.10 (WOW Dobrzykowice). Very high content of chromium (114.54 mg/kg of dry matter) was observed in sample no. 8 (WOW Blizanowice). The contamination of soil with chromium may be connected with the transport of metallurgical waste (compounds of iron and chromates) from the heap in Siechnice. The lowest content of chromium is 3.58 mg/kg of dry matter in soil sample no. 4 (AOW Node of Airport Wroclaw).

3.3 The pollution index

The pollution index (W_N) determines the enrichment of soils with heavy metals in relation to the geochemical background in the soil surface levels for the entire surface of Poland. The geochemical background in Poland is as follows: 6.5 mg Cu/kg; 33 mg Zn/kg; 18 mg Pb/kg; 11 mg Ni/kg; 40 mg Cr/kg [12].

Table 3. The pollution indexes of heavy metals in soils compared to the geochemical background.

Pollution indexes (W_N)					
No.	**Cu**	**Zn**	**Pb**	**Ni**	**Cr**
1	4.28±0.14	2.20±0.01	0.95±0.10	3.10±0.08	0.34±0.03
2	6.34±0.03	9.04±0.03	1.68±0.01	1.68±0.03	0.72±0.03
3	4.57±0.17	3.54±0.02	1.28±0.04	0.62±0.04	0.29±0.03
4	2.72±0.07	2.53±0.04	0.77±0.09	0.86±0.05	0.09±0.02
5	1.77±0.13	1.48±0.03	0.36±0.05	0.67±0.04	0.31±0.01
6	2.27±0.02	2.06±0.04	0.61±0.09	0.52±0.09	0.38±0.03
7	1.34±0.03	1.59±0.03	0.20±0.03	1.59±0.05	2.00±0.02
8	3.28±0.15	2.83±0.01	0.64±0.05	1.09±0.09	2.86±0.06
9	1.61±0.10	2.16±0.03	0.33±0.03	2.21±0.06	0.31±0.02
10	1.05±0.05	0.91±0.03	no	0.40±0.09	0.15±0.01

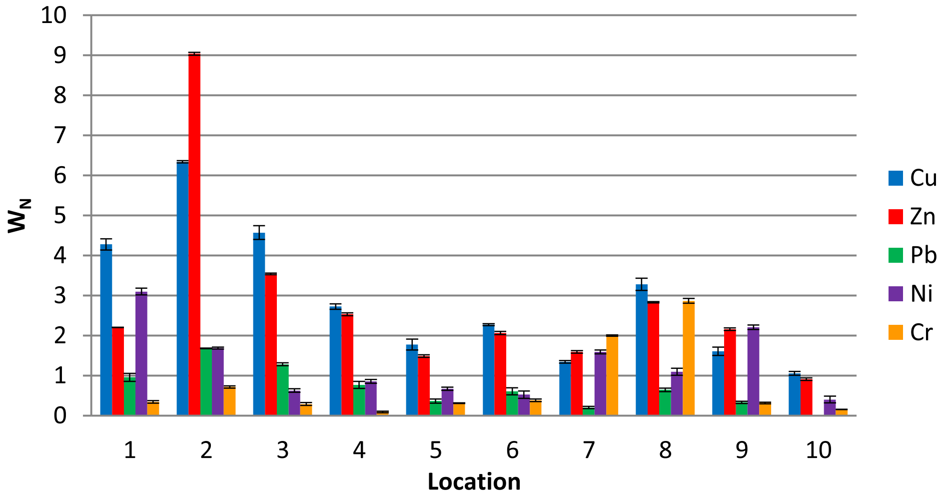

Fig. 4. The pollution indexes (W_N) of trace elements in soils.

The test soils are enriched with copper and zinc (table 3, fig. 4), except for sample no. 10 (WOW Dobrzykowice), in which there is no excess of zinc (W_N 0.91). The highest values of pollution index (W_N) of copper and zinc are in sample no. 2 (AOW Node of North

Wroclaw), 6.34 and 9.04 respectively. The W_N indexes in the remaining soils are in the range of 1.05-4.57 for Cu and 2.06 - 3.54 for Zn. Exceeding of lead content in soil is observed again in the sample no. 2 (W_N 1.68, AOW Node of North Wroclaw) and also in the sample no. 3 (W_N 1.28, AOW Node of Stadium Wroclaw). Two soil samples: no. 7 (WOW Siechnice) and no. 8 (WOW Blizanowice) are enriched with chromium. The values of W_N are respectively 2.00 and 2.86. Five locations demonstrate excess of nickel concentration in compared to the geochemical background of Poland. The W_N indexes range from 1.09 to 3.10.

4. Conclusions

- Soil sample no. 7 (WOW Siechnice) is of alkaline character (pH 8.08 in H_2O and pH 7.66 in 1M KCl). The reason may be the current ongoing work on the metallurgical waste landfill in Siechnice commune. pH of the waste sample from the heap is of 8.92 in H_2O and 8.52 in 1 M KCl. In this environmental conditions, the ability of heavy metals to migrate into the soil is inhibited.
- Soil sample no. 10 (WOW Dobrzykowice) is of faintly acidic character (pH in H_2O – 6.67, pH in 1M KCl – 5.71). In soil environments, at pH below 6.5, most elements appear in the cation forms and can migrate into the soil profile depth, causing the environmental hazard.
- Soil samples are generally faintly salified, with EC below 25 mS/m. Only sample no. 8 (WOW Blizanowice) has a very high EC value of 161.35 mS/m. High salinity of the soil may be caused by a large accumulation of salts after winter thaw in the hollow area.
- None of the soil samples exceeds the permissible concentrations of heavy metals, in accordance with the Polish Ministry of Environment Regulation from September 1^{st}, 2016, regarding the manner of conducting the assessment of the contamination of ground.
- All soil samples are enriched with copper with reference to the geochemical background. The content of zinc is not exceeded only in soil sample no. 10. The enrichment of the soils with copper and zinc is on average three-fold. Sample no. 2 (AOW Node of North Wroclaw) has the highest Wn indexes of copper, zinc and lead, 6.34, 9.04 and 1.68 respectively.The accumulation of lead was observed in two soil samples. The enrichment of soil with nickel was observed in five samples.
- Average values of the pollution indexes (W_N) are combined into the following order: Cu > Zn > Ni > Pb > Cr.

References

1. K. J. Aslam, S.A. Khan, S.H. Khan, J. Saudi Chem. Soc., 17 (2013)
2. R. Czubaszek, K. Bartoszuk, CEE, **2** (2011)
3. A. Chrzan, G. Formicki, PECO, **6**, 2 (2012)
4. A. Hołtra, D. Zamorska-Wojdyła, EPE **42**, 3 (2016)
5. K. Czarnowska, T. Kozanecka, Soil Sci. Ann., **54**, 4 (2001)
6. A. Bieniek, B. Bieniek, Soil Sci. Ann., **59**, 3 (2008)
7. Z. Ciećko, A. Żołnowski, M. Wyszkowski, *Integrated monitoring of the natural environment* (Turpress, Toruń, 2004)
8. A. Kiebała, M. Kozieł, W. Zgłobicki, Eng. and Protection of Environ. **18**, 3 (2015)

 DOI: 10.1051/e3sconf/20171700083

9. J. Szyszlak-Bargłowicz, T. Słowik, G. Zając., W. Piekarski, Annual Set The Environment Protection, **15** (2013)
10. A. Kabata-Pendias, H. Pendias, *Trace elements in soil and plants* (CRC Press, Inc., USA, 2011)
11. J. Minczewski, Z. Marczenko, *Analytical chemistry* (PWN, Warsaw, 2011)
12. A. Kabata-Pendias, H. Pendias, *Biogeochemistry of trace elements* (PWN, Warsaw, 1999)
13. The Polish Ministry of Environment Regulation from September 1st, 2016, regarding the manner of conducting the assessment of the contamination of ground, Journal of Laws 2016 pos. 1395