GEOCHEMICAL CHARACTERIZATION OF SOILS FROM EXPECTED CONTAMINATED SITES IN THE ODRA HILLS AND DRAHANY UPLAND

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Abstract: The aim of the study paper was to evaluate a rate of soil contamination by heavy metals from the expected contaminated site 1 (Odra Hills) and expected contaminated site 2 (Drahany Upland) using Coefficient of Industrial Pollution (CIP). In the total, 37 topsoil samples were collected. The pH and ORP parameters were used to evaluate changes in environment. Among the study elements are arsenic, copper, zinc and lead and to evaluate them the X-ray spectroscopy was used. The Coefficient of Industrial Pollution (CIP) reported medium soil contamination at the Shooting Range areas from ECS1 as well as from ECS2. The main source of copper and lead probably come locally from the munitions. The heavy metal content in the other anthropogenic-changed landscapes was compared to the natural background.

Key Words: heavy metals, soil contamination, pH, redox potential, X-ray spectroscopy

INTRODUCTION

The Drahany Upland and Odra Hills are chosen to evaluate heavy metal contamination in their topsoils. Human activity (practice shooting, traffic) may contribute to enhance heavy metal levels in the soil environment (Alloway 2015, Ash 2013). The Drahany Upland considers being a geomorphologic unit, falling down into the Brno Highlands. The area is 1 178.68 km² and it extends among the cities Brno, Vyskov, Prostejov, Boskovice and Konice. The second site is receded from the first site approximately 60 km towards to south-east, falling down into a geomorphologic unit the Odra Hill and a geomorphologic complex the Nizky Jesenik. The area of Odra Hills is 580 km^2 and it extends among the cities Olomouc, Lipnik nad Becvou, Hranice, Potstat and Sternberk (Demek et al. 2006). Shale, greywacke and siltstone are the dominant rock types in both areas. These rocks were deposited during Flysch Culm Sedimentation in Carboniferous. The Moravice and Hradec-Kyjovice Formation represents the Nizky Jesenik area while the Drahany Upland by Protivanov, Myslejovice and Rozstani Formation (Kalvoda and Melichar 1999). Galenites with silver content and shales have been mining for centuries in the Odra Hills thus we expect higher natural lead content (Gottvald 1980). This anthropogenic activity had been performed at the Willibald mine and the Franz and Moritz mine in the Barnov Town (Losert 1957). This paper gives an idea about heavy metal contamination in soils from potential contaminated sites.

MATERIAL AND METHODS

The soils from the expected contaminated site 1 (Odra Hills) and the expected contaminated site 2 (Drahany Upland) were investigated. The totals of 37 soil samples were collected in both potentially-contaminated sites. Solid matrices were homogenized and sieved less than 0.063 mm. The X-ray fluorescence was used to accurate analyse of elements in the samples. The tool Innov-X Systems, Inc., Delta was used with following settings. The power of first X-ray was 1–40 kV with exposure time 40

seconds. The power of second X-ray was 2–10 kV with exposure time 40 seconds. The device was calibrated using metal standards supplied by the manufacturer and the mode Geochem-Vanad was used. Each measurement was carried out twice and average of the measurments is presented in results. Total measure time took 260 seconds. The Limits of Detection (LODs) in ppm for appropriate elements are following (As: 1–3; Pb: 2–4; Zn: 3–5; Cu: 5–7). The reproducibility, measurement error and applitcation of this spectroscopic method is reviewed in (Geršl ad Knésl 2009).

The chemical parameters, such as soil active reaction (pH/H_2O) and redox potential (ORP by another name Eh) were measured as well. The pH/H_2O was measured by the all samples according to well-known method ISO 10390 (UNMZ 2011). Solid matrices were undergone to an infusion by the distilled water and resulting suspension were shaken and prepared to measuring by the tool WTW InoLab Multi 720 with SenTix 81 electrod. Soil contamination by heavy metals has been demonstrated using Coefficient of Industrial Pollution (CIP).

RESULTS AND DISCUSSION

Heavy metal content

Soil contents of arsenic, lead, zinc and copper were evaluated. The results show the highest lead (214 ± 2.61 mg/kg and 409 ± 2.32 mg/kg), zinc (431 ± 3.77 mg/kg and 380 ± 2.69 mg/kg), copper (1768 ± 9.08 mg/kg and 578 ± 4.17 mg/kg) and arsenic (33 ± 1.76 mg/kg) levels at the Shooting range area Daskabaty from ECS1 (Table 1).

Table 1 Overview of heavy metals content in soils of various human areas

Territory	Locality	ECS	Sample	Element (mg/kg)			
				As	Pb	Zn	Cu
Shooting range area for fighting vehicles	Praslavice	1	Bar11	16 ± 0.69	34 ± 0.90	93 ± 1.46	150 ± 2.53
	Praslavice	1	Bar16	17 ± 0.71	32 ± 0.92	97 ± 1.52	153 ± 2.61
	Smilov	1	Bar15	21 ± 0.93	68 ± 1.22	125 ± 1.81	186 ± 2.99
	Smilov	1	Bar09	22 ± 0.81	51 ± 1.03	152 ± 1.81	171 ± 2.69
Shooting range area	Daskabaty	1	Bar18	25 ± 0.89	55 ± 1.16	137 ± 1.86	278 ± 3.36
	Daskabaty	1	Bar19	33 ± 1.76	214 ± 2.61	431 ± 3.77	1768 ± 9.08
	Daskabaty	1	Bar20	18 ± 1.66	409 ± 2.32	380 ± 2.69	578 ± 4.17
	Daskabaty	1	Bar21	17 ± 0.86	71 ± 1.13	109 ± 1.59	230 ± 2.95
	Daskabaty	1	Bar22	19 ± 0.77	48 ± 0.99	106 ± 1.56	166 ± 2.65
	Smilov	1	Bar14	22 ± 0.76	32 ± 0.96	112 ± 1.65	167 ± 2.76
	Smilov	1	Bar17	25 ± 0.82	36 ± 1.04	130 ± 1.82	185 ± 2.96
	Smilov	1	Bar10	23 ± 0.81	48 ± 1.03	124 ± 1.69	165 ± 2.70
	Smilov	1	Bar07	22 ± 0.76	35 ± 0.97	118 ± 1.69	192 ± 2.88
	Smilov	1	Bar08	19 ± 0.80	52 ± 1.03	113 ± 1.61	169 ± 2.69
	Ferdinandsko	2	DV35	14 ± 1.20	184 ±1.66	106 ± 1.55	74 ± 2.22
	Ferdinandsko	2	DV36	17 ± 1.51	344 ± 2.11	99 ± 1.46	52 ± 2.00
	Brezina	2	DV37	11 ± 0.62	28 ± 0.82	60 ± 1.19	24 ± 1.78
	Brezina	2	DV38	17 ± 0.71	44 ± 0.92	120 ± 1.53	34 ± 1.83
Water training ground	Barnov	1	Bar04	24 ± 1.02	97 ± 1.34	150 ± 1.88	195 ± 2.92
	Barnov	1	Bar05	10 ± 0.55	25 ± 0.71	106 ± 1.36	123 ± 2.12
Hand-Thrown area	Brezina	2	DV33	4 ± 1.27	234 ± 1.77	121 ± 1.58	39 ± 1.94
	Brezina	2	DV34	6 ± 1.21	206 ± 1.69	174 ± 1.86	62 ± 2.10
Blasting pit	Hanacka louka	2	DV39	18 ± 0.77	50 ± 1.00	126 ± 1.61	43 ± 1.96
	Hanacká louka	2	DV40	21 ± 0.73	33 ± 0.94	124 ± 1.64	51 ± 2.07
	ZMC sv. Anna	2	DV42	21 ± 0.70	33 ± 0.88	75 ± 1.30	23 ± 1.80

Compared to results from ECS1, the highest lead (184 ± 1.66 mg/kg and 344 ± 2.11 mg/kg) concentrations were also reported at Shooting range area as well as at Hand-Thrown area (234 ± 1.77 mg/kg and 206 ± 1.69 mg/kg) from ECS2. Moreover, copper contents are more than three times higher in all anthropogenic-changed areas from ECS1.

Territories, such as the Olovensky Hill, a woodland and a meadow represent natural background in both sites. In the Barnov I the highest lead (143 ± 1.48), zinc (217 ± 2.11 mg/kg) and arsenic (33 ± 1.14 mg/kg) contents were observed while reporting the highest copper concentrations (186 mg/kg) in the woodland at Barnov Town (Table 2). We became conscious of being not significant difference in content of studied elements between natural background and anthropogenic-changed landscape unless it expects elevated lead and copper contents at the Shooting Ranges and Hand-Thrown. Eventually, there are evident higher copper contents in the Odra Hills while naturally lowering in the soils from south-eastern part of the Drahany Upland.

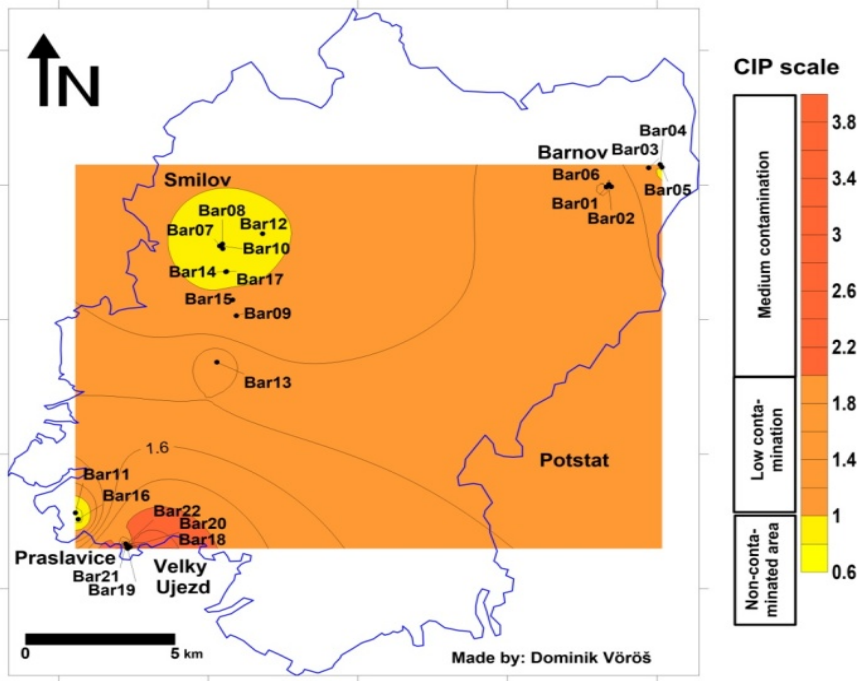
Table 2 Territories related to natural background and heavy metal content in soils

Territory	Locality	ECS	Sample	Element (mg/kg)			
				As	Pb	Zn	Cu
Olovensky Hill	Barnov	1	Bar01	33 ± 1.14	143 ± 1.48	217 ± 2.11	183 ± 2.74
	Barnov	1	Bar02	25 ± 0.79	43 ± 0.98	139 ± 1.76	176 ± 2.73
	Barnov	1	Bar06	26 ± 0.88	66 ± 1.12	181 ± 1.94	176 ± 2.71
Woodland	Barnov	1	Bar03	22 ± 0.90	73 ± 1.17	153 ± 1.85	186 ± 2.81
	Bores castle	1	Bar13	44 ± 1.10	135 ± 1.36	99 ± 1.45	127 ± 2.31
	Brezina	2	DV32	23 ± 0.82	71 ± 1,05	95 ± 1,38	21 ± 1.72
Meadow	Brezina	2	DV30	16 ± 0,72	46 ± 0,93	79 ± 1.31	21 ± 1.75
	Brezina	2	DV31	24 ± 0,75	42 ± 0,93	116 ± 1.54	29 ± 1.85
	Brezina	2	DV41	12 ± 0.63	30 ± 0,83	67 ± 1.23	21 ± 1.76
	Smilov	1	Bar12	24 ± 0.78	44 ± 0.98	145 ± 1.76	153 ± 2.58

Heavy metal contamination

Using the CIP, the soils at the Shooting range area from ECS1 (Figure 1) as well as from ECS2 (Figure 2) are medium contaminated by studied elements. Especially elevated lead and copper content from ECS1 were investigated.

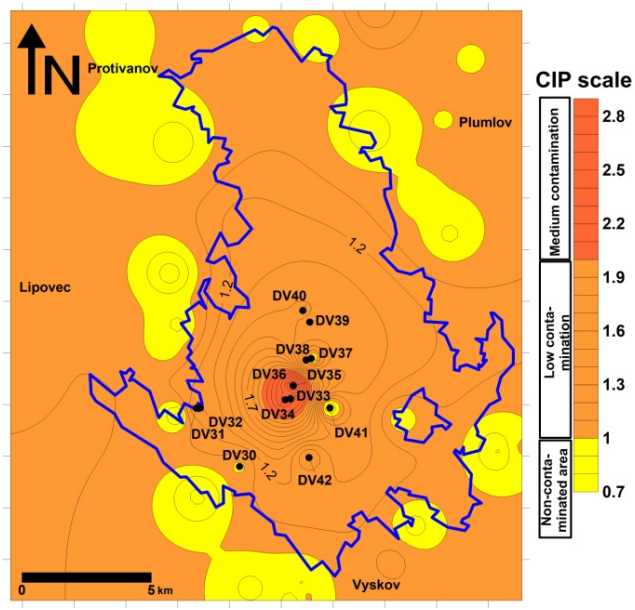
Figure 1 Rate of soil contamination by As, Pb, Zn and Cu from ECS1



According to heavy metal contents (especially copper and lead), human activity locally influences even more to metal composition in the ECS1 soils unlike those from ECS2. These contents might come from ammunition because copper is used to the munitions production. It was investigated in some study pits that bullet core is mostly composed of lead 94.5%, while bulk mantle of copper 83.2% (Ash et al. 2013). Also, a cartridge casing production supports to have enhanced zinc and copper in the environment (Plíhal 2010).

On the contrary, non-contaminated soils were evaluated at the Praslavice village on the south-west as well as at the Smilov ex-village on the north-west where the Shooting range area and the Shooting range areas for fighting vehicles are placed. Adjacent to the Barnov Town there are soils which are non-contaminated by studied elements. As we mentioned above the copper content is significantly distributed in soils from the Odra Hills. It might have caused the last ore mining in the Barnov Town (Losert 1957) thus nowadays copper content is much higher unlike the soils from ECS2 where none ore was mined although the cerusite and galena veins are found (Posmourny 2000).

Figure 2 Rate of soil contamination by As, Pb, Zn and Cu from ECS2



Environmental characterization of soil environment

The pH values in majority of soil samples from ECS1 ranging mostly between 5 and 6 while the soils from ECS2 tend to being a little bit more acidic (4.5–5.0). Moreover, the alkaline pH was observed at soils in the Hand -Thrown area (Figure 3A).

There is a variability in redox potential (ORP) of soils from ECS1 and ECS2 (Figure 3B). Basically, we observed decreasing in Eh values from 275 mV to 100 mV at the soils from ECS1 while achieving the soils from ECS2 higher values (225–375 mV). Two samples DV39 (−41.11 mV) and DV36 (−450.51 mV) are not included in the table, because extremely reduction conditions were observed.

The soil process, denitrification (1) where nitrates are reduced using bacteria to elemental state of nitrogen which is going on especially in the poor-drained and low aerated soils at ORP around 200 to 400 mV (Brady 1984). According to Alloway (2013), this process typically occurs when the Eh achieves values between 200–400 mV. Although, at lower Eh values around 100–200 mV, a Mn^{IV} oxide reduction and dissolution (2) are thought to be the common process in the soil environment (Alloway 2013). Also, Alloway (2013) reported that at pH 6 some cationic and anionic forms are probably bound onto Fe and Mn oxides and metals and metalloids are firstly released unless they are bound onto Fe and Mn oxides.

$$C_3H_6O_3 + 2NO_3^- \rightarrow 3CO_2 + 3H_2O + N_2 \quad (1)$$

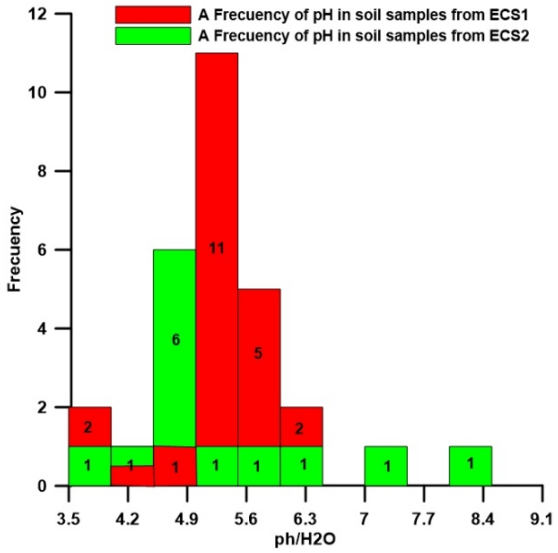
$$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad (2)$$

In principle, we expect to occur soil process denitrification especially in the Odra Hill's soils where natural conditions are probably different unlike the Drahany Upland where is expected to be going

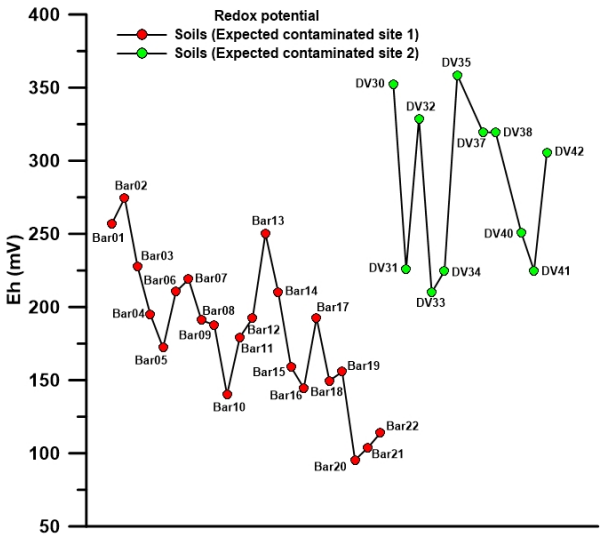
on the Mn^{IV} oxide reduction and dissolution. These interpretations are requiring a caution because soils are generally porous media and biological activity and decay of organic matter highly influence on the ORP (Sposito 2008, Kabata-Pendias 2001).

Figure 3 Changes in the soil environment from ECS1 and ECS2

A) Soil active reaction



B) Redox potential



Heavy metal mobility is patterned on definite environmental conditions (pH and ORP). When pH is more acidic and ORP more oxidative, we could expect increasing in zinc, lead and copper mobilization (Siegel 2002) even though copper is accumulated mostly in the top soil horizons and is also rather immobile (Kabata-Pendias 2009). There is a need to pay attention to heavy metals bounding because, for example copper tends to accumulate itself onto suspended organic matter (SOM), clay minerals and Mn-Fe oxohydroxides.

According to results we could expect moderate zinc and lead mobilization in soils from the Odra Hills. Previous study showed quite good zinc and lead mobility in soils from the Drahany Upland. We became conscious of lead and zinc bounding onto Fe and Mn oxo-hydroxides, representing reducible fraction. An experiment showed also significant arsenic and copper immobility (Voros et al. 2015).

According to pH/H_2O and ORP we can claim the zinc, copper and lead would appear to be more mobile in soils from the Drahany Upland while the arsenic would seem to be more mobile in soils from the Odra Hills because arsenic mobility increases when ORP becomes more reducing and pH more alkaline (Hooda 2010). Arsenic content was higher in soils from the Odra Hills and it might also be considered as an anthropological source.

CONCLUSION

Rate of soil contamination has been evaluated. We conclude that soils from the Shooting range areas in ECS1 and ECS2 and Hand-Thrown area are medium contaminated by arsenic, lead, zinc and copper. The probably source of copper and lead in the anthropogenic-changed landscapes come from ammunition. Except of the Shooting range areas and the Hand-Thrown areas, human activity like a shooting does not significantly distribute studied elements into soils from the others anthropogenic territories which are low contaminated or non-contaminated and their contents is rather comparable with natural background in the Drahany Upland.

Expect high lead content in the Odra Hills has not been proved but higher copper content is related to the natural background because these elevated contents are distributed through the whole area. We suppose to not being mobilized copper in the soil environment from both sites although the arsenic could under specific conditions (low pH and low ORP) happen to mobilize. In the soil media is difficult to understand all processes which are going on however we supposed to have an effect of denitrification

process on soils from the Odra Hills while manganese oxides are reducing in soils from the Drahany Upland. A periodic monitoring in these areas can more reveal geochemical processes in soils.

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