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Heavy metals release from eroded loess soils

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Abstract. The laboratory experiment determined the heavy metals (Cd, Ni, Pb) ions concentration in soil solutions with incubation occurring at 5 and 20°C during 0 to 60 days. The maximum concentration of metals were registered after 10 days for Cd, 60 days for Ni and 10-60 days for Pb. Diversification at metals release between analyzed depth were not found. Increase of temperature from 5 till to 20°C caused release of higher content of heavy metals.

Keywords: heavy metals, loess soil, soil contamination, temperature

INTRODUCTION

Heavy metals are present in most parts of the hydrocycle (Foster and Charlesworth, 1996; Lindstrom, 2001). Rain, surface and ground water transport metals, and in lakes metals originate from many different sources, natural and anthropogenic. Anthropogenic sources could be characterized as point sources *eg* industrial and municipal waste water discharges or diffuse sources *eg* emissions due to corrosion or wear, and also put on a spatial scale *eg* local, regional or global (Hayian and Stuanes, 2003, Lindstrom, 2001). Metals are widely used in the technosphere and the pool of metals in urban areas can be large. This influences lake water and sediments through an increased load, and leads to an increased metal transport to the biosphere (Lindstrom, 2001). Soils represent a major sink for heavy metals in the terrestrial environment (Wong and Li, 2004).

Cadmium is a highly toxic metal that may become incorporated into plants and animals as a result of use of fertilizers (Kabata-Pendias, 1999). Accumulation of Cd in soils due to application of phosphate fertilizers is quite variable (Mann *et al*., 2002). Its concentration, which is present at different kinds of fertilizers may reach the level of 170 mg kg^{-1} (Kabata-Pendias, 1999). The Cd absorption by plants depends not only on its concentration in the soil, but most of all on pH (Adriano, 1992). Cadmium is very mobile at acidic pH, however neutral of alkalic pH caused its inability in the soil environment. The average natural abundance of cadmium in the Earth crust has most often been reported from 0.1 to 0.5 mg kg^{-1} (Cook and Morrow, 1995).

Lead is the most common contaminant of soils, even though it is a biologically non-essential heavy metal. It is teratogenic, carcinogenic, toxic at low concentrations and bioacumulative in organisms (Adriano, 1992). Organic matter, especially, will bind and hold lead and other metals very effectively. Lead is naturally present in all soils, generally in the range of 15 to 40 mg kg^{-1} (Terelak *et al*., 1997). Pollution, however, can increase soil lead levels to several thousand mg kg^{-1}. With a heavily contaminated soil (greater than 300 to 500 parts per million total lead content) the only effective way to eliminate the contamination is to cover it with fresh soil or remove it completely. The study of Wong and Li (2004), provided strong evidence of the anthropogenic sources of Pb contamination of urban soils in Hong Kong. The Pb isotope composition showed that Pb contamination of urban soils could be partially attributed to the use of leaded gasoline in the past. Pb from the past emissions still remained a major contaminant of soils in the urban terrestrial environment of Hong Kong.

Nickel is a silvery-white metal found as well naturally in the Earth's crust as everywhere in the environment but usually only in trace amounts. The metal is also ubiquitous in soil and can be found at higher concentrations in a number of mineral ores including nickel sulfides, oxides and silicates. Most of the nickel in soil is so tightly bound to other minerals that it resists direct uptake by plants and animals and cannot easily affect human health or ecosystems (Gorlach and Mazur, 2001).

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It is well known, that most of soil physico-chemical characteristics, such as: moisture, oxygen diffusion rate, pH or temperature effect on redox potential value. However there is lack of studies concentrated on the relationships between temperature, redox potential and their impact on heavy metals release in the soil environment. Gliński and Stępniewska (2005), who also examined the Ciemięga valley region observed, that indicators of soil redox conditions appeared to be sensitive enough to show their differentiation in such homogenous soils like those formed from loess deposits. The knowledge about the impact of temperature and redox potential state, especially at the areas of small catchments, still agriculturally used, might be very helpful in the prediction of release heavy metals phenomenon, as results of climate change (rain or temperature hesistancy).

This paper is a trial of evaluating which is combined effect of redox potential, temperature and incubation time on release of heavy metal ions (Cd, Ni and Pb), from the loess-eroded soils, constantly managed.

MATERIALS AND METHODS

Area under investigation, where heavy metals (Cd, Ni, Pb) content were determined is situated in the Ciemięga River valley nearby Lublin (SE part of Poland). The river basin is covered mainly by soils derived from loess (90% – Haplic Luvisol). The catchment is located 200-230 m a.s.l. and covers an area of 157 km^2 of a length 41 km.

Undisturbed soil samples (0-20 and 20-60 cm depth) were taken from four resorts: Pliszczyn, Baszki, Snopków and Motycz during spring 2003. Pliszczyn and Baszki characterize the lower part of the catchment, featuring a strongly undulating relief whereas Snopków and Motycz (the upper part of the valley) can be described as a gentle relief. Soils samples after taking them to the laboratory were placed in glass vessels, flooded with distilled water at the ratio of 1:2.5 (15 g soil + 37.5 cm^3 water), covered and incubated at 5 and 20°C for up to 60 days.

The chosen properties of the collected soil materials were shown in Table 1. They were determined by the standard methods. Process of soils mineralization with use of HNO_3 and H_2O_2 on mineralizer Maxidigest Mx450 was performed. After that the investigated samples were filtered and completed with distilled water to the volume of 50 ml. Soil extracts, (after mineralization) were measured by atomic absorption spectrophotometer Z-8200 Hitachi (Japan), with graphite furnace atomization (GFAAS). Mean values (3 replicates) with standard deviations are presented in figures.

Analysis of variance by the least significant difference test (95% LSD-test) was done to determine whether the significant difference existed ($P<0.05$), between temperature incubation and Eh effect on investigated metals release. All statistical analyses were performed with the Statgraphics 3.0.

RESULTS AND DISCUSSION

The investigations were realized on samples of loess soils which are susceptible to reduction (Gliński and Stępniewska, 2005; Gliński *et al*., 2007). These soils are homogenous in their granulometric composition, however easily undergo erosion processes, which modified their properties in vertical and horizontal plane (Gliński and Dębicki, 1999; Gliński and Turski, 2002). Taking into account homogeneity of the investigated soil samples we stated, that soil materials are very small diversed (Table 1). They are formed from material with a uniform grain size (loess deposits). The fraction of silt (0.05-0.02 mm) is dominated (52%) in granulometric composition. Variations in pH were in the range of 6.4-8.4, however the mean value of pH was 7.66, what is typical (in natural conditions) for loess soil. There is also virtually no information on the effects of soil properties on Pb decomposition, for instance, the effects of soil pH, soil moisture and soil temperature (Rooney *et al*., 2007). Soil pH in particular is known to have a considerable effect on Pb solubility in soils (Badawy *et al*., 2002), and might therefore be expected to affect Pb shot dissolution. Rooney *et al.* (2007)

Table 1. The chosen characteristics of the loess soil materials

Location	Depth (cm)	Granulometric composition (%, dia in mm)						$C_{org.}$ (%)	pH_{H_2O}
		1- 0.1	0.1-0.05	0.05- 0.02	0.02-0.005	0.005-0.002	< 0.002		
Pliszczyn	0-20	1	10	62	19	1	7	2.63	7.55
	20-60	1	13	53	21	1	11	1.85	8.41
Baszki	0-20	6	9	53	21	3	8	2.28	8.11
	20-60	3	13	54	19	4	7	1.16	7.91
Snopków	0-20	7	15	56	3	17	2	3.08	7.86
	20-60	2	10	52	14	15	7	1.80	7.93
Motycz	0-20	27	12	35	13	3	10	1.74	6.56
	20-60	29	10	33	15	4	9	0.92	6.40

observed greater Pb sorption with increasing values of pH. Organic carbon content revealed diversity in the soil profile as well as within the catchments. The highest percent of carbon were found in the surface layers (0-20 cm), its mean values came to 2.63%, and reduced with increasing depth.

During incubation time, both at 5 as at 20°C, the concentration of measured metals (Cd, Ni and Pb) showed changeable tendency ($P<0.05$). At a lower temperature (5°C) the highest level reached Ni, whereas concentration of Cd occurred at a low level. Initial values of measured metals were lower at 5°C and equaled as follows: 0.39, 1.89 and 1.62 μg kg^{-1} for Cd, Ni and Pb, respectively. Growth of Ni content directly after soil samples flooding had a place. An initial Ni content was higher than Cd and meanly amounted 1.89 μg kg^{-1}. Increasing tendency till to 30 day of the experiment (5°C) was observed. Later drop of Ni concentration was registered, till to 60 day of the incubation, when maximum values (3.93 μg kg^{-1}) appeared, at a soil sample taken from Motycz.

Increase of temperature to 20°C resulted in a release of higher quantity of the heavy metals ($P<0.05$). Changes in Cd, Ni, Pb concentrations at different location of measurement and changeable temperature conditions (5 and 20°C) are presented in Fig. 1. At 20°C an initial metals concentrations were much higher, than at 5°C and came to 0.7, 2.13 and 3.71 μg kg^{-1}, for Cd, Ni and Pb, respectively.

Growth of temperature had the great influence on Pb release efficiency ($P<0.0001$), inasmuch the Pb content were twice as high, than at 5°C, ($P<0.0001$). Among metals investigated Pb concentration displayed the highest diversity during incubation period ($P<0.0001$). At a higher temperature (20°C), run of Pb concentration dynamic was more violent. Both its growth as decrease were noted. Mean value equaled 3.34 μg kg^{-1} and oscillated between 0.38 to 9.79 μg kg^{-1} during 60 days. High level of Pb concentration was reached between 10-60 days.

The highest Cd content at a started days of the study were noted. This trend were similar at every measured points (Pliszczyn, Baszki, Snopków and Motycz). After 10 days of the incubation (5°C) Cd maximum were registered on the level of 1.92 μg kg^{-1}, later its concentration systematically dropped. For the incubation at 20°C, Cd presence ranged between 0.05-3.38 μg kg^{-1}, maximum at 7th day was observed, whilst at 60 day equaled 0.48 μg kg^{-1}.

Similarly, at 20°C, at the beginning of the study increase of Ni content was noted. This trend till to 4th day of the experiment was present, after that significant drop of Ni concentration was stated. In contrast to 5°C, decreasing trend to the end of the study had a place.

Equations describing the mentioned fluctuations at metals release at different temperatures are presented in Table 2, whereas significance fluctuations at metals concentration at 5 and 20°C are displayed in Fig. 2. As a consequence of performed ANOVA test it is possible to state, that at 5°C the highest concentration reached Ni, whereas the lowest Cd ($P<0.0001$). Meanwhile at 20°C the maximum metal concentration was observed with Pb, little lower for Ni whilst the lowest for Cd ($P<0.0001$).

Changes in Cd, Ni, Pb concentration at different depth and temperature combination are shown in Fig. 3. Similar tendency for Cd, Ni, Pb concentration in the soil profile (0-20 and 20-60 cm) were registered, what is connected with homogeneity of the investigated loess materials. Slightly higher values of metals content at surface layer (0-20 cm) were stated. These results are agreed with work of Gąsior *et al.* (1999) and Reszel *et al.* (2004), who observed stronger accumulation of Cd and Pb at the surface layer of the Bieszczady, Beskid Niski and Podkarpacie Region soils.

In order to confirm the significant impact of temperature on heavy metals release, statistical analyses were performed. Its effects are presented in Fig. 4. The highest fluctuations at metals release phenomenon as a result of temperature factor (5 and 20°C) was stated for Pb ($P=0.0000$) and Cd ($P=0.0003$), meanwhile little lower was found for Ni ($P=0.0091$).

Presented the effect of temperature (5 and 20°C) on heavy metals release from loess soils needed some investigation about Eh dynamics (Table 3). During experiment time drop of Eh values was noted. At 5°C Eh fluctuated from +380 to +457 mV (1st day), but at last day of the experiment decrease to +280 mV. At 20°C drop of redox potential was

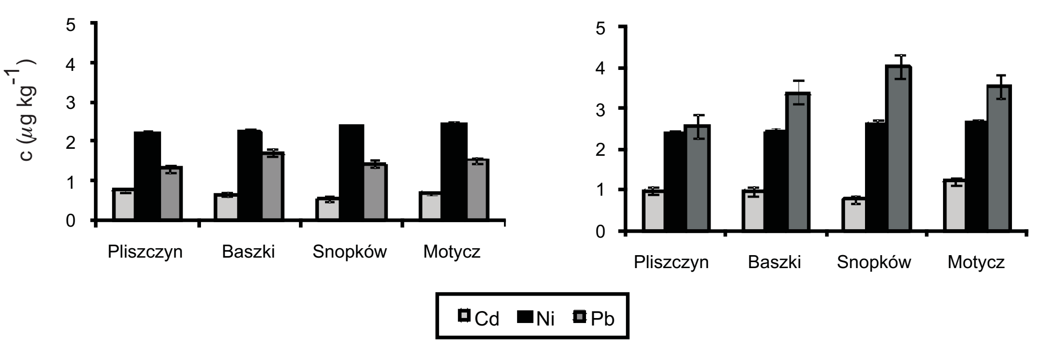

Fig. 1. Changes in Cd, Ni, Pb concentration (c) due to 5 and 20°C incubation (for 60 days and 4 sites). Averaged values of three replicates with standard deviations.

T a b l e 2. Regression equations and correlation coefficient (R^2), describing relationship between metals release and temperature of incubation

Temperature	Metal	Equations	R^2
5°C	Cd	y = 0.067x2-0.378x+1.117	0.83
	Ni	y = 0.099x+2.085	0.95
	Pb	y = -0.075x2+0.411x+1.04	0.32
20°C	Cd	y = 0.115x2-0.531x+1.45	0.62
	Ni	y = 0.114x+2.24	0.92
	Pb	y = -0.332x2+2.017x+0.837	0.96

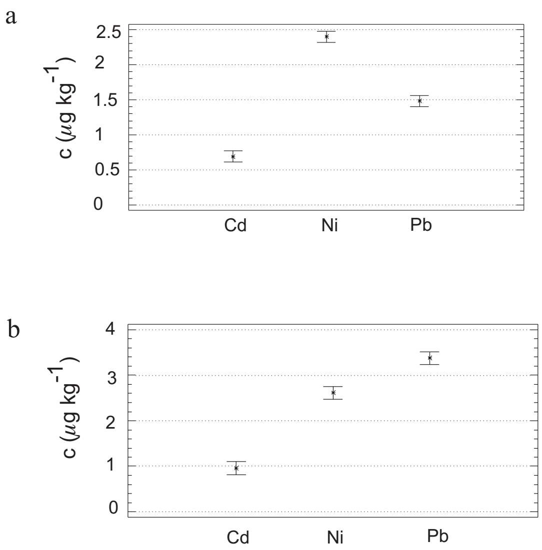

Fig. 2. Significant differences at metals concentrations (c) at: a – 5, and b – 20°C (n=36, *P*<0.0001).

much quicker than at 5°C. An initial redox potential registered at 20°C came to +485 mV, meanwhile at 60 day of the laboratory study this value fall to +191 mV. Rapid decrease of Eh noted at higher temperature is probably connected with soil microorganisms activity, which are more efficient and active at 20°C.

Performed ANOVA test confirmed, that every change of Eh value during 60 days of incubation were significant (*P*<0.0001). Results, including temperature (5 and 20°C) and depth of the soil profiles (0-20, 20-60 cm) are presented in Fig. 5. At 5°C linear drop of Eh value till to 40 day of incubation was stated, then an increase of redox potential at 60 day was noted. Meanwhile at 20°C linear and significant decrease of Eh value from 1 to 60 day was observed.

Kashem and Singh (2001), performed an experiment to assess the effects of flooding and organic matter application on changes in Eh, pH and solubility of Cd and Ni in contaminated soils. They observed decreasing trend of Eh values with flooding time, what is compatible with results presented at this study. Correlation coefficient calculations also showed, that metal solubility decreased with drop of Eh value (from 200 to -350 mV) and increased pH (from 4 to 7) in the soil solution (Kashem and Singh, 2001).

Metal transport from catchments and metal distribution in lake sediments have been studied for Nordic forest lakes. In those context the main issue has often been to asses the effects of large scale atmospheric pollution of lakes unaffected by local pollution sources (Lindstrom, 2001).

The differences in the Cd, Ni and Pb content in the soils of environmentally protected and unprotected areas of the Podkarpacie Region, were studied by Reszel *et al.* (2004). They found that Cd concentration ranged from 250 to 260 µg kg^{-1}, for protected and unprotected territory, respectively. Ni content was higher and they estimated it on the level from 750 to 1270 µg kg^{-1}, whereas Pb fluctuated from 1390 to 1480 µg kg^{-1} at protected and unprotected areas, respectively (Reszel *et al*., 2004). Comparing mentioned values with results presented at this study it is possible to state, that in the Ciemięga catchment the contamination with metals is low and has a local character.

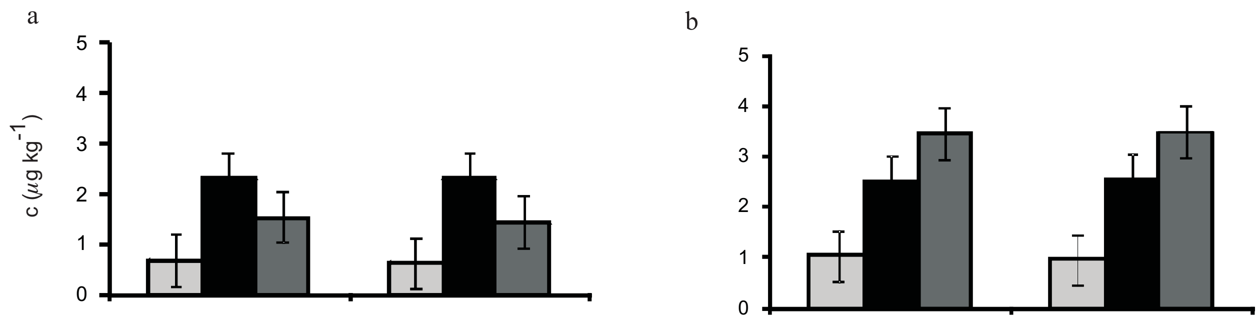

Fig. 3. Changes in Cd, Ni, Pb concentration (c) at two depth (cm) at: a – 5 and b – 20°C incubation. Legend as in Fig. 1.

Table 3. Changes of Eh (mV) values during 60 days, incubation at 5 and 20°C

Location	Depth (cm)	Temperature 5/20°C Incubation time (days) 1	10	20	30	40	60
Pliszczyn	0-20	391/406	406/351	407/310	323/318	341/354	481/301
	20-60	380/381	359/392	386/275	343/277	316/258	285/298
Baszki	0-20	399/390	359/333	305/302	234/315	160/267	280/191
	20-60	386/418	366/368	361/313	310/291	284/265	313/282
Snopków	0-20	402/401	366/295	336/288	250/229	175/236	321/214
	20-60	395/382	367/281	357/231	298/271	260/280	357/273
Motycz	0-20	440/386	344/320	316/338	315/306	218/188	253/191
	20-60	457/485	423/391	390/373	448/355	310/220	303/212

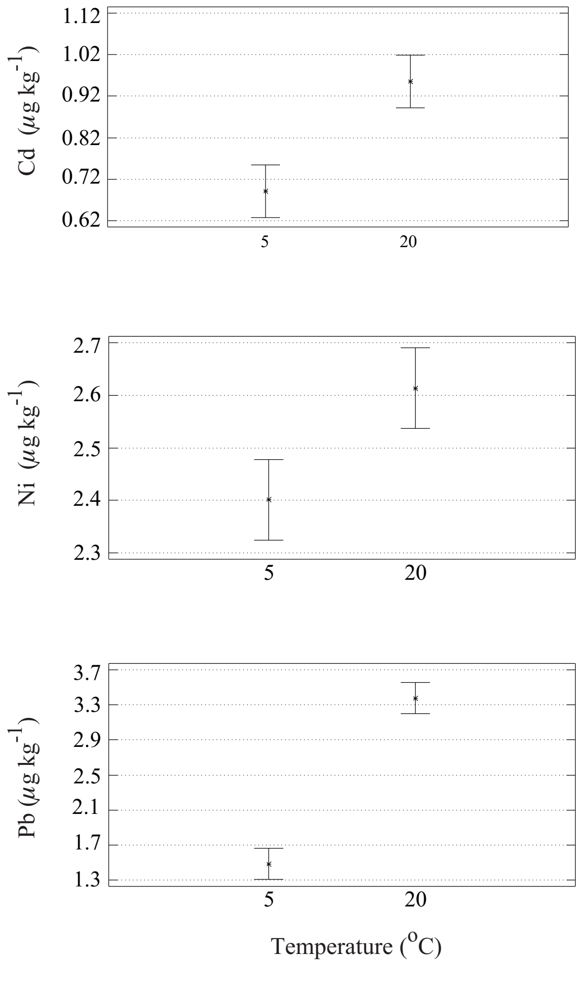

Fig. 4. Significant differences at metals (Cd, Ni, Pb) release at 5 and 20°C (n=24, *P*<0.01).

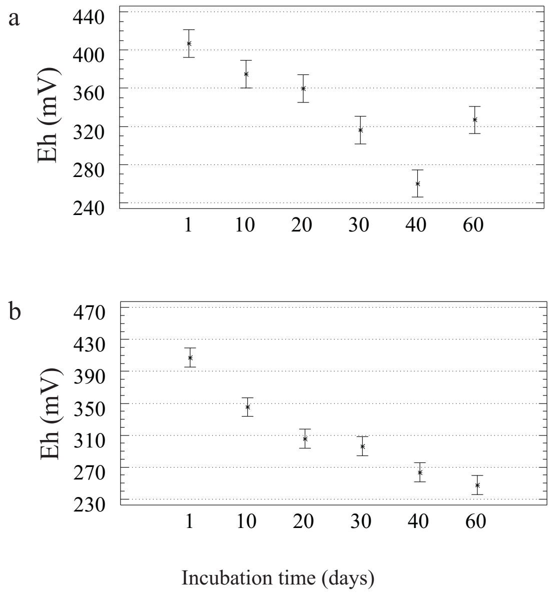

Fig. 5. Significance fluctuations of Eh values during 60 days of incubation at: a – 5 and b – 20°C (n=144, *P*<0.0001).

CONCLUSIONS

1. An increase of temperature (to 20°C) cause release of higher content of heavy metals (Cd, Ni, Pb).

2. The ability of metals to perform into aquatic form is dependent from temperature as follows:
5°C: Ni > Pb > Cd
20°C: Pb > Ni > Cd.

3. The maximum concentration of metals during incubation period were registered after: 10 days for Cd, 60 days – Ni and 10-60 days for Pb.

4. Diversification at heavy metals release between analyzed depth (0-20 cm) and (20-60 cm) were not found. The reason of that is homogeneity of the loess materials used for the experiment.

5. Water action *eg* as a result of water erosion could cause the surface run-off and performation of Cd, Ni, Pb into aquatic form and drop of Eh value due to the small sorption capacity of loess soils. Increase of temperature could enhance the mentioned process.

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