

## THE ROLE OF FREE IRON OXIDES IN THE ASSOCIATION OF LEAD AND CADMIUM IN GLEYIC PHAEOZEMS (BLACK EARTHS)

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**A b s t r a c t:** Twelve samples, collected from four pedons of cultivated soils (black earths) were analyzed by sequential extraction to characterize the role of free iron oxides in the association of lead and cadmium.

Amounts of lead and cadmium retained varied from 11 to 89.3% of the total Pb and from 4.8 to 48.7% of the total Cd. Metals associated with amorphous Fe oxides are at least ten times higher than with crystalline Fe forms. Under the existing soil conditions (high pH and CaCO<sub>3</sub> content) free iron oxides are components of great importance in the Pb and Cd binding process. However, the results may indicate a stronger association of Pb than Cd with iron oxides in the studied black earths.

**K e y w o r d s:** iron oxides, adsorption, lead, cadmium, soils.

### INTRODUCTION

Increased amounts of heavy metals originating from anthropogenic sources have drawn attention to their chemistry in the soils. The capacity of each individual soil component, i.e. organic matter, clay minerals and free hydrous oxides to retain highly toxic metals like lead and cadmium is of particular interest. Important constituents are iron oxyhydroxides and oxides, which contribute to the high specific surface area and influence soil properties and its efficiency as a sorbent [9,14]. Jenne [6] reported that sesquioxide surfaces control metal activity in the soil solution. In numerous studies, surface sorption of heavy metals either on colloidal suspension of pure synthetic iron oxide [5,9,17], rocks [11] or isolated soil clay fractions [18] were examined. Since little is known about the role of natural iron oxyhydroxides which are formed during pedogenesis in the soils, investigation on the contribution of free Fe oxides to lead and cadmium retention in particular soil types were undertaken.

Black earths (Gleyic Phaeozems) from the Kujawy region were chosen for the study. These soils were formed on a glacial till and are used primarily for

the intensive crop production. In natural conditions, they generally contain low levels of lead and cadmium. However, considerable amounts of metals can be introduced to them with commercial fertilizers, pesticides or during sewage sludge application [1,8].

#### MATERIALS AND METHODS

Soil samples were taken from each horizon of the selected sites located in the cultivated land of the Kujawy region with black earths. In the laboratory, the samples were thoroughly mixed and left to dry. After a week the soils were hand crushed with a mortar and passed through a 1 mm sieve. Total content of metals was determined after wet mineralisation of the samples in the concentrated HF and HClO<sub>4</sub>. Each sample was analyzed in triplicate. In the tables below, mean values are presented.

An effective method of determining the role of free iron oxides in heavy metal associations is by chemical extraction. The method of sequential chemical extraction described by Miller *et al.* [12] with Shuman's modification [16] was used in the study. For the analysis, only extraction with ammonium oxalate in the darkness (noncrystalline iron oxides, associated metals and ascorbic acid) and extraction with ammonium oxalate under VV-Vis radiation (crystalline Fe oxides and the retained cations) were used. More mobile fractions [4] were discarded.

Total content of lead and cadmium was determined with a flame atomic absorption spectrometer (Philips PU 9100 X) using diluted Merck's stock solutions as standards.

The content of lead and cadmium in the filtered extracts (fractions of metals) were analyzed using a differential pulse method of anodic stripping voltametry (DPASV) on a Polarograph PP-04 instrument.

Physico-chemical properties of the soils were determined by common geochemical methods. Soil pH was measured in a 1:5 soil:water suspension, using a Radiometer model PHM62 pH meter with a radiometer combined glass electrode. Organic C was determined by the Tiurin's method. Carbonate content was determined according to the Scheibler's method. Particle size distribution was performed according to the Bouyoucose-Cassegrande's method.

#### RESULTS AND DISCUSSION

Selected soil properties are presented in Table 1. The analyzed soils are neutral or alkaline (pH 6.92-8.37) and contain from 11 to 24% of clay fraction, the

content of  $\text{CaCO}_3$  is in the range of 0.6-17.0% and the content of organic carbon range is between 0.21 and 1.86 % (Table 1).

Among free iron compounds, crystallized forms predominated in the studied soils. The contents of amorphous oxides was ten to one hundred times lower than crystalline compounds. The maximum amount of amorphous iron oxides was found in the humus horizons (Table 2).

Concentration of crystalline Fe oxide fraction ranged between 2833.4 and 6297.2  $\text{mg kg}^{-1}$ . The maximum content of this component was detected in the B horizons of the soils (Table 2) where accumulation of iron hydroxyoxides during braunification processes may occur.

Total lead and cadmium concentrations were in the range of 18.5-39.0  $\text{mg kg}^{-1}$  and 0.4-1.9  $\text{mg kg}^{-1}$ , respectively (Table 1), while the background levels for the Polish soils are 18.0  $\text{mg kg}^{-1}$  for Pb and 0.2  $\text{mg kg}^{-1}$  for Cd [8]. Thus, the elevated levels of lead were detected only in the surface soil horizons of the studied soils. Lead is far less mobile than cadmium and is accumulated in the top horizon. This is because even at  $\text{pH}=4$ , Pb is still strongly retained by iron oxides [10].

Amounts of lead and cadmium retained by free iron oxides varied from 2.9 to 23.0  $\text{mg kg}^{-1}$  for Pb and from 0.03 to 0.26  $\text{mg kg}^{-1}$  for Cd. (Tables 3 and 4). Iron oxides that bound lead ranged between 11.0-89.3 % of the total Pb and Fe-oxide bound cadmium were in the range of 4.8-48.7% of the total metal content, respectively.

**Table 1.** Selected physicochemical properties of the soils

No.	Site	Horizon	Depth (cm)	$C_{\text{org}}$	$N_{\text{tot}}$	$\text{CaCO}_3$ <2 $\mu\text{m}$		pH $\text{H}_2\text{O}$	Total Pb	Total Cd
						(%)			(mg $\text{kg}^{-1}$ )	
1	Kruśliwiec	Ap	0-28	1.55	0.17	0.9	17.0	7.52	35.8	1.9
2		A <sub>1</sub> /C	40-60	0.21	0.01	3.0	14.0	8.31	19.4	1.2
3		Cg	>120	n.d.	n.d.	7.7	20.0	8.30	22.4	1.3
4	Płowce	Ap	0-24	1.86	0.11	0.8	17.0	7.30	28.9	1.8
5		A <sub>1</sub> /C	36-52	0.62	0.01	2.7	16.0	8.13	23.6	1.1
6		Cg	>92	n.d.	n.d.	12.1	23.0	8.37	21.5	1.0
7	Rzepiszyn	Ap	0-28	1.05	0.07	0.6	11.0	6.92	39.0	0.7
8		B <sub>br</sub>	43-53	0.43	0.03	0.6	24.0	7.47	24.7	0.6
9		C <sub>ca</sub>	>120	n.d.	n.d.	13.0	14.0	8.25	20.5	0.4
10	Gnojno	Ap	0-30	1.63	0.13	0.7	16.0	7.31	31.6	0.7
11		B <sub>Br</sub>	47-62	0.46	0.03	0.6	20.0	7.83	23.7	0.4
12		C <sub>ca</sub>	>80	n.d.	n.d.	17.0	24.0	8.14	18.5	0.5

Table 2. Contents of free iron oxides in the soils

Site	Horizon	Fe <sub>free</sub>	Fe amorphous	Fe crystalline
		mg/kg		
Kruśliwiec	Ap	3272.7	32.5	3240.2
	A <sub>1</sub> /C	2920.9	87.5	2833.4
	Cg	4270.8	164.4	4106.4
Płowce	Ap	3832.2	307.7	3524.5
	A <sub>1</sub> /C	5120.4	227.3	4893.1
	Cg	4810.8	231.0	4579.8
Rzepiszyn	Ap	4040.8	552.2	3488.6
	B <sub>br</sub>	6783.4	486.2	6297.2
	CCa	4035.8	347.1	3688.7
Gnojno	Ap	4098.0	312.4	3785.6
	B <sub>Br</sub>	5296.9	264.0	5032.9
	CCa	4042.0	247.4	3794.6

Table 3. Cd associated with amorphous (Fe<sub>a</sub>) and crystalline (Fe<sub>cryst.</sub>) iron oxides in black earths

Site	Horizon	Cd-Fe <sub>a</sub>		Cd-Fe <sub>cryst.</sub>		Σ Cd Fe <sub>a</sub> +Cd-Fe <sub>cryst.</sub>	
		mg/kg <sup>a/</sup>	% <sup>b/</sup>	mg/kg	%	mg/kg	%
Kruśliwiec	Ap	0.011	0.6	0.184	9.7	0.19	10.2
	A <sub>1</sub> /C	0.004	0.3	0.125	10.6	0.13	10.9
	Cg	0.000	0.0	0.103	8.1	0.10	8.1
Płowce	Ap	0.011	0.6	0.170	9.5	0.18	10.1
	A <sub>1</sub> /C	0.017	1.5	0.241	22.3	0.26	23.8
	Cg	0.007	0.7	0.039	4.1	0.05	4.8
Rzepiszyn	Ap	0.049	7.0	0.113	16.4	0.16	23.4
	B <sub>br</sub>	0.063	3.8	0.280	17.4	0.35	21.3
	CCa	0.012	2.7	0.018	4.0	0.03	6.7
Gnojno	Ap	0.034	5.1	0.056	8.3	0.09	13.4
	B <sub>br</sub>	0.080	20.0	0.115	28.7	0.19	48.7
	CCa	0.006	1.3	0.080	17.4	0.09	18.7

<sup>a/</sup> in mg per kg of soil; <sup>b/</sup> percent of total Cd in soil.

In the cambic horizons where accumulation of free iron oxides due to the release of Fe from primary minerals occurred, the observed amounts of retained Pb were higher than in other horizons [2].

In almost all A horizons of the studied soils, the ratio of metals accumulated by iron oxides is smaller than in the subsurface horizons. The difference in the contents of Cd and Pb associated with Fe-oxides in the surface and subsurface horizons

**Table 4.** Pb associated with amorphous ( $Fe_a$ ) and crystalline ( $Fe_{cryst.}$ ) iron oxides in black earths

Site	Horizon	Pb - $Fe_a$		Pb - $Fe_{cryst.}$		$\Sigma$ Pb $Fe_a$ +Pb $Fe_{cryst.}$	
		mg/kg <sup>a/</sup>	% <sup>b/</sup>	mg/kg	%	mg/kg	%
Krušliewiec	Ap	4.8	13.5	8.6	23.9	13.4	37.4
	A <sub>1</sub> /C	2.5	12.7	7.1	36.8	9.6	49.5
	Cg	9.8	43.7	2.1	9.3	11.9	53.0
Płowce	Ap	5.7	19.9	12.3	42.6	18.0	62.5
	A <sub>1</sub> /C	10.4	44.3	8.4	35.6	18.8	79.9
	Cg	1.5	7.1	1.4	6.6	2.9	13.7
Rzepiszyn	Ap	7.5	19.3	15.5	39.7	23.0	59.0
	B <sub>br</sub>	15.6	63.1	6.5	26.2	22.1	89.3
	CC <sub>a</sub>	1.2	5.8	2.8	13.5	4.0	19.3
Gnojno	Ap	3.1	9.8	11.1	35.2	14.2	45.0
	B <sub>br</sub>	10.7	45.1	7.4	31.2	18.1	76.3
	CC <sub>a</sub>	0.0	0.3	2.0	10.7	2.0	11.0

<sup>a/</sup> in mg per kg of soil; <sup>b/</sup> percent of total Pb.

can be explained by the presence of the most important binding component for Cd and Pb, i.e. organic matter in the A horizon, which plays a dominant role in heavy metals retardation [19].

The iron oxide surface had different selectivity to Pb and Cd with the preference for lead adsorption [10]. In studied soils, pedogenic iron oxides may exhibit the same properties, since the Pb fraction associated with iron oxides is larger than the Cd fraction in the studied black earths.

Jeng and Singh [7] found that oxide bound Cd in the cultivated soils of Norway, 33% of total Cd on the average with range of 25-47%.

According to Jenne [6] and Pickering [13], iron oxide surfaces strongly adsorb metals in the cation forms, particularly divalent cations.

At high pH ranges (pH>7), commonly found in the studied soils, adsorption of such heavy metals as Pb and Cd to iron oxide surfaces is high, due to high negative surface charge of Fe hydroxyoxides. Iron oxides have a p.z.c. of 7.8 [14]; therefore they play an important role in the sorption processes of cations in the studied black earths.

With decreasing pH and surface groups which lost protons, oxide surface with variable charge iron become less negative and less ready to adsorb metals (cations). At low pH iron oxides have a positive charge. Consequently, a decrease of pH influences the sorption of heavy metals like Pb and Cd on Fe oxide surface.

Wilkens and Loch [19] reported that adsorption of cadmium on iron oxides appears to be of minor importance at low pH (<5.5).

The amounts of Pb and Cd associated with amorphous Fe oxyhydroxides are at least ten times higher than with crystalline Fe oxides in the studied soils. According to Schwertmann [15], amorphous Fe oxides (mainly ferrihydrite) have large specific surface area (200 m<sup>2</sup>/g). Such component is a good adsorbent. The average particle size of ferrihydrite is unusually small (~30Å). Because of it, the surface constitutes a considerable fraction of the total volume (>30 % of the total volume) [20].

The calculated specific surface areas of free iron oxides in the studied black earths, were in the range of 35.54-103.91 m<sup>2</sup>/g [3]. Relatively low values compared to literature [15] are due to the dominance of crystalline forms of Fe oxide over the amorphous. Large differences in specific surface areas of free iron oxide and the ability to retain lead and cadmium may indicate different iron oxides mineralogy in the studied black earths.

Iron oxides embracing oxides, oxyhydroxides and hydrated oxides due to their different crystal size, crystallinity and mineralogical form may vary in their susceptibility to cation adsorption. Thus, crystal properties are of great significance as they modify surface properties [15].

Since data on Fe oxide structure and properties in the soils are rather scarce, effects of iron hydroxyoxide mineralogy on heavy metal adsorption in the soils need to be quantified.

## CONCLUSIONS

Data from the studies indicate that a significant proportion of lead and cadmium are bound in the Fe oxyhydroxides in black earths formed from a glacial till. The highest amounts of metals associated with iron oxides were detected in the cambic horizons where free oxides are accumulated. The results indicate stronger association of Pb than Cd with iron oxides due to different selectivity of oxide surfaces to these metals. This is in full agreement with Jenne [6] and Cole and Rose [2] investigations who stated that Fe-hydrous oxides bound significant amounts of heavy metals, particularly lead.

Under the existing conditions (high pH, CaCO<sub>3</sub> content) free iron oxides are the components of great importance in lead and cadmium binding processes. Thus, adsorption of lead and cadmium by Fe oxyhydroxides acts like a relative permanent sink for these metals in the studied soils.

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