Distribution and Forms of Cadmium in Soils Near a Copper Smelter

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Abstract

Despite cadmium is not an essential contaminating metal in soils surrounding a copper smelter, the toxicity of cadmium motivates monitoring of cadmium concentration and mobility in soils. The objectives of this study were therefore (i) to determine vertical distribution and chemical forms of cadmium using sequential extraction procedure in soil profiles exposed to smelter emissions, (ii) investigate the relationship between Cd forms and soil properties, and (iii) assess the potential Cd mobility. Four pedons were sampled near a copper smelter Głogów, in operation since 1972. A sequential extraction selected for this study separate metals into operationally defined fractions: water – soluble (WS), exchangeable (EX), specifically sorbed and carbonate bound (SSC), occluded on Fe/Mn oxides (OX), complexed by organic matter (OM), and residual (RES). Total Cd concentration does not depend on the distance to the smelter, but correlates to clay content and CEC. Relative significance of fractions in non-contaminated soil horizons is as follow: RES >> OX > EX+SSC > OM >> WS. Increasing contamination of soils located close to the smelter manifests in a relative increase of non-residual fractions, the exchangeable Cd in particular. Cd mobility assessed both by single (in 0.01 M CaCl$_2$) and sequential extractions is relatively high in upper soil horizons. There is however little risk of groundwater contamination as the concentration of labile Cd in lower horizons is negligible.

Keywords: cadmium, fractionation, soil, copper smelter

Introduction

Atmospheric fallout from ore smelters can contribute significantly to soil contamination with heavy metals. Consequently, metal concentrations in soils near the smelters may be elevated and may pose a significant health hazard [1, 2]. Total concentrations of heavy metals can be used to estimate the degree of soil contamination and to the pollution monitoring, but they are generally not well-correlated to plant uptake of metals [3, 4]. As bioaccumulation and metal transfer to the food chain or to groundwater are greatly affected by the kind and strength of the toxic metals bonds in soils, it has become evident that the environmental impact of a particular metal species may be more important than the total metal content [5].

Heavy metals in soils are considered to exist in various solid-phase forms which can be operationally divided in the following fractions: easily soluble (water soluble), exchangeable, carbonate bound, oxide bound (Mn and Fe oxides), organic bound, and silicate bound (residual). The easily soluble fractions are of the greatest interest, as their highest mobility, bioavailability or toxicity can influence the quality of environment. Distilled water and several salt solutions (*e.g.* KCl, CaCl$_2$, NH$_4$OAc, NH$_4$NO$_3$, EDTA, and DTPA) have been used to extract the "mobile" or "bioavailable" forms of heavy metals with single extraction procedures [3, 6, 7]. Actual mobility of metals is, however, strongly affected by soil properties and may vary significantly in relation to changes in soil pH,

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organic carbon content or redox potential [8-11]. Unlike the single extraction, sequential fractionation gives information about easily extractable and more stable forms of metals in soil, which provides the most complete description of the general behaviour of metals and good estimate of their potential mobilities [12-14].

In a sequential extraction procedure, the soil sample is treated with a series of progressively harsher reagents to dissolve increasingly refractory forms. Ideally, the reagents are chosen to selectively attack a specific soil compartment with minimal dissolution of nontargeted fractions [15]. In practice, however, the integrity of the sequential extractions and meaningfulness of the results are questioned because of poor reagent selectivity, possible redistribution or re-adsorption of elements during extraction, or poor extraction efficiency [16-18]. Despite these limitations, sequential dissolution techniques furnish more useful information on metal binding and mobility than available with single extractions [19, 20].

Several sequential extraction schemes have been presented by many workers, such as by Ahnstrom and Parker [15], Kuo *et al.* [21], Ma and Rao [22], McLaren and Crawford [23], Shuman [14]. The procedure of Tessier *et al.* [24] is one of the most thoroughly researched and widely used to evaluate trace metals behaviour. However, most of the workers improve the original procedure by replacing reagents, introducing new extractants, or modifying conditions of the extraction [13, 25-28].

Investigation on metal forms focuses mostly on surface soil horizons [3, 9, 22, 29]. Studies on contaminated areas require, however, the whole soil profile characterization. The objectives of this study are therefore (i) to determine the vertical distribution and chemical forms of cadmium using sequential extraction procedure in soil profiles exposed to copper smelter emissions, (ii) investigate the relationship between forms of cadmium and some soil properties, and (iii) assess the potential mobility of cadmium. Despite, in general, cadmium is not an essential contaminating metal in soils surrounding a copper smelter, the environmental risk of contamination with cadmium and its toxicity motivate the monitoring of cadmium concentration and mobility in soils.

Materials and Methods

Sampling Sites

Four pedons (Żukowice, Biechów, Bogomice and Zabiele) were sampled in the surroundings of a copper smelter near Głogów, southwestern Poland. The smelter has been in operation since 1972 and the emission of dust containing heavy metals caused extensive soil contamination [30]. Vegetation, parent material, soil texture, chemical properties and the level of soil contamination vary among pedons. Pedon 1 (Żukowice) is located 1.0 km south-east, and the pedon 2 (Biechów) – 2.5 km south-east of a copper smelter. Both soils are Haplic Luvisols as referred to FAO-WRB classification [31], derived from loess-like silt loam. Pedon 3 (Bogomice), located 2.5 km north-east of smelter is an Arenic Fluvisol developed from alluvial sandy deposits, and the pedon 4 (Zabiele), located 6.0 km north-east of smelter is a Gleyi-Fluvic Cambisol derived from alluvial clay-loamy material. Pedons 1, 2 and 3 are located under poplar plantations (black poplar, *Populus nigra L.* and black Italian poplar, *Populus euroamericana f. serotina Hartig*), and the pedon 4 on arable field. Soils at Żukowice and Bogomice sites are heavily contaminated with copper and lead, while at Biechów, and particularly, Zabiele are relatively uncontaminated [30, 32].

Soil samples were collected at the depths of 5-15 cm, 30-40 cm, 50-60 cm (all four pedons), and additionally at 70-80 cm in pedons Żukowice and Biechów. The sampling depths referred, in general, to soil diagnostic horizons.

Analytical Procedures

Bulk soil samples were air-dried, homogenized, and sieved <2 mm. Particle size distribution was determined by the hydrometer method for silt and clay, and by dry sieving for sand fractions, following pre-treatments to remove organic matter, and chemical dispersion with sodium hexametaphosphorate [33]. Soil pH was measured in a 1:2.5 (w/v) ratio of soil and water suspension. Organic carbon was measured using a Leco EC-12 carbon analyzer, after washing soil samples with 2 M HCl. "Free" iron, bound in amorphous and crystalline oxides and hydrooxides (Fe_d) was extracted by the citrate-bicarbonate-dithionite method [33], and measured in extracts by atomic absorption spectrophotometry. Cation exchange capacity (CEC) was calculated as a sum of basic cations extracted with neutral 1 M NH_4OAc and the extractable acidity. Calcium, magnesium, potassium, and sodium were determined by atomic absorption spectrophotometry or flame emission spectrometry, and soil acidity by back titration with 0.01 M NaOH.

Cadmium Fractionation

The procedure of Salbu *et al.* [27], which is a modified version of Tessier *et al.* [24] method was selected for this study. It is designed to separate heavy metals into six operationally defined fractions: (1) water – soluble metals (WS); (2) exchangeable – extractable with 1 M NH_4OAc at pH 7 (EX); (3) specifically sorbed and carbonate bound – extractable with 1 M NH_4OAc at pH 5 (SSC); (4) metals associated – sorbed or occluded, mainly on iron and manganese oxides – extractable with hydroxylamine (OX); (5) strongly complexed by organic matter – extractable with H_2O_2 in HNO_3 (OM), and (6) residual (RES).

Two grams of soil were placed in a 50-mL polycarbonate centrifuge tube. The following extractions were made sequentially [27, 32]:

(1) Sample extracted with 20 mL of deionized water for 1 h at 20°C.

(2) The residue from (1) extracted with 20 mL of 1 M NH$_4$OAc, pH 7 for 2 h.

(3) The residue from (2) extracted with 20 mL of 1 M NH$_4$OAc, pH 5 for 2 h.

(4) The residue from (3) extracted with 20 mL of 0.04 M NH$_4$OH·HCl in 25% HOAc for 6 h (water bath, 60°C).

(5) The residue from (4) extracted with 15 mL of 30% H$_2$O$_2$ at pH 2 (adjusted with HNO$_3$) for 5.5 h (water bath, 80°C). After cooling, 5 mL of 3.2 M NH$_4$OAc in 20% HNO$_3$ was added, sample was shaken for 30 min, and finally diluted to 20 mL with water.

(6) One gram of the residue from (5), after drying, was digested in a conical flask with 10 mL of 7 M HNO$_3$ on a hot plate for 6 h. After evaporation, 1 mL of 2 M HNO$_3$ was added, and the residue after dissolution was diluted to 10 mL.

All the solid phases (with exception of RES) were washed with 10 mL of water before the next extraction step. The washes were collected and analyzed with supernatant from the previous fraction. To verify the sum of sequential extractions, the total cadmium concentration was determined after digestion with aqua regia.

In order to assess the mobile and potentially bioavailable cadmium, a single extraction was carried out with 0.01 M CaCl$_2$ in a 1:10 (w/v) ratio of soil and extractant. This reagent has been proposed to simulate soil solution concentration and to release amounts of metals well correlated with plant uptake [6]. Two grams of soil were extracted with 20 mL of 0.01 M CaCl$_2$ by shaking for 2 h at 20°C.

Concentration of Cd in all extracts was measured by graphite furnace atomic absorption spectrophotometry (GF-AAS). Extracts were replicated, with mean values reported.

All chemical analyzes were made in labs of the Norwegian University of Life Sciences.

Results and Discussion

Physical and Chemical Soil Properties

Soil textures are related to the origin of soil parent materials, and range among pedons from sand to silt loam and clay loam, with clay contents ranging from 1 to 34% (Table 1). Clay increase in the subsoil relative to surface horizons indicates clay illuviation in the pedons Żukowice

Table 1. Selected physical and chemical properties of soils investigated.

Sampling depth cm	Sand %	Silt %	Clay %	pH (H$_2$O)	OC[1] %	Fe$_d$[2] %	CEC[3] cmol·kg^{-1}	Cd$_t$[4] mg·kg^{-1}	Cd$_{sum}$[5] mg·kg^{-1}	Cd$_t$/Cd$_{sum}$	Cd$_{CaCl2}$[6] mg·kg^{-1}	MF$_{Cd}$[7] %
Site 1 – Żukowice, 1.0 km SE												
5-15	34	58	8	5.96	0.97	0.42	7.04	0.32	0.39	1.22	0.038	44
30-40	31	62	7	5.36	0.44	0.36	5.77	0.21	0.29	1.38	0.042	26
50-60	36	56	8	5.86	0.37	0.37	6.82	0.29	0.32	1.10	0.018	8
70-80	30	51	19	6.60	0.19	0.63	9.89	0.35	0.40	1.14	0.005	9
Site 2 – Biechów, 2.5 km SE												
5-15	38	52	10	6.31	1.48	0.49	9.86	0.40	0.44	1.10	0.012	27
30-40	36	52	12	7.07	0.34	0.52	9.88	0.25	0.27	1.08	0.010	7
50-60	16	57	27	7.39	0.27	0.87	17.16	0.36	0.40	1.11	0.006	0
70-80	25	51	24	8.12	0.16	1.07	21.66	0.39	0.41	1.05	0.004	0
Site 3 – Bogomice, 2.5 km NE												
5-15	95	4	1	7.63	0.39	0.22	4.00	0.30	0.42	1.40	0.022	65
30-40	94	4	2	7.19	0.13	0.29	3.59	0.21	0.27	1.29	0.010	17
50-60	97	2	1	6.91	0.09	0.20	2.02	0.08	0.10	1.25	0.004	5
Site 4 – Zabiele, 6.0 km NE												
5-15	40	31	29	7.68	2.18	5.17	73.54	1.52	1.58	1.04	0.010	4
30-40	43	23	34	7.28	0.90	9.57	77.33	1.55	1.65	1.06	0.005	0
50-60	51	15	34	7.24	0.49	20.47	41.61	1.60	1.77	1.11	0.004	0

[1]OC – organic carbon; [2]Fe$_d$ – citrate-dithionite extractable iron; [3]CEC – cation exchange capacity (sum of basic cations and exchangeable acidity), [4]Cd$_t$ – total (aqua regia soluble) cadmium, [5]Cd$_{sum}$ – total sum of six extracted cadmium fractions; [6]Cd$_{CaCl2}$ – 0.01 M CaCl$_2$ extractable cadmium; [7]MF$_{Cd}$ – cadmium mobility factor

Table 2. Coefficients of correlation between cadmium concentrations and some properties of soils.

Variable (N=14)	Clay fraction	Organic carbon	CEC	Fe_d	Cd_t
Total Cd concentration (Cd_t)	0.80***	0.53*	0.91***	0.88***	-
Residual Cd (RES)	0.85***	0.39	0.89***	0.92***	0.98***
Organically complexed Cd (OM)	0.42	0.65**	0.66**	0.42	-
Oxides – bound Cd (OX)	0.59*	0.75**	0.84***	0.52	-
Mobility factor (MF_{Cd})	-0.64*	-0.07	-0.44	-0.36	-0.33
Cation exchange capacity (CEC)	0.82***	0.60**	-	0.64**	-
Fe_d	0.70**	0.18	0.64*	-	-

*Significant at the 0.05 probability level, **Significant at the 0.01 probability level, ***Significant at the 0.001 probability level

and Biechów, and the alluvial stratification in the pedon Zabiele. Soil reaction is neutral or alkaline, with exception to Żukowice soil, ranging from pH 5.4 to 8.1. It is caused by intense liming (in surface horizons) or natural carbonates presence (in subsoil). Surface horizons of forested Luvisols (Żukowice and Biechów) are more acidic than subsoils (Table 1). Organic carbon concentration is the highest in surface soil horizons (ranging from 0.39 to 2.18%) and gradually decreases with depth in all pedons. Cation exchange capacity varies distinctly among pedons from 2 to 77 cmol(+)·kg⁻¹ of soil (Table 1), and is significantly correlated (P<0.01) to clay, organic carbon and iron oxides contents (Table 2). The concentration of dithionite-citrate-extractable iron (Fe_d) is correlated (P<0.01) to clay content and is considerably higher in clay-rich horizons (Table 1). Particularly high Fe_d amount in subsoil of the pedon Zabiele is related to the redoximorphic features and the presence of iron concretions.

Total Concentration of Cadmium

Despite the significant soil contamination with copper and lead, as reported previously [32], cadmium occurs in relatively low amounts (as referred to the Polish law regulations), generally less than 0.40 mg·kg⁻¹ in pedons Żukowice, Biechów and Bogomice, and up to 1.60 mg·kg⁻¹ in Zabiele (clay loam soil). Cadmium concentration in surface horizons does not depend on the distance to the smelter (Table 1). The concentration ratio (total Cd in surface layer versus Cd in parent material) was 1 or lower, and only in the sandy soil Bogomice it was 3, which may be interpreted as a lack of soil contamination with this metal in pedons 1, 2 and 4, and relative contamination in pedon 3. Vertical distribution of cadmium is related, to some extent, to soil horizonation. Eluvial horizons of Luvisols located close the smelter (Żukowice and Biechów) contain less cadmium than illuvial horizons of these soils, which suggests Cd leaching (eluviation) from surface horizons to subsoil. Consequently, the concentration of cadmium in surface humic horizons, as high as those in par-

ent materials, is probably a dynamic resultant of cadmium leaching and, simultaneously, both cadmium bioaccumulation and air-borne contamination with this metal.

Although a small number of observations, we found positive and statistically significant relation of cadmium concentration to clay, organic carbon, CEC, and Fe_d, with correlation coefficients ("r" values) of 0.80, 0.53, 0.93, and 0.88, respectively (Table 2). This indicates strong influence of primary soil properties and natural soil processes on vertical distribution of cadmium in soil profiles investigated. Clay fraction plays probably a crucial role, since CEC and Fe_d depends significantly on clay content (Table 2).

Fractionation and Distribution of Cd in Soil Profiles

Water-soluble fraction of Cd is below detection limits for all pedons, both in upper horizons and in subsoils. Detectable amount (0.008 mg·kg⁻¹) of water soluble Cd occurs only in the surface layer of Bogomice pedon (Fig. 1 and 2). The same soil contains the highest amount (0.195 mg·kg⁻¹) of an "exchangeable" Cd (NH_4OAc-extractable at pH 7). This is a dominant form of cadmium in this soil horizon (46% of Cd_{sum}). "Exchangeable" Cd fraction is significant as well in surface and subsurface horizons of Żukowice silty soil (up to 30% of Cd_{sum}), less significant in Biechów soil (up to 14% of Cd_{sum}), and negligible in Zabiele soil (up to 1.2% of Cd_{sum}), heavy textured and located at the longest distance of the smelter. The dominance of "exchangeable" Cd in some uncontaminated [9] and, particularly, in contaminated soils [21, 22, 29] was also reported previously. Cadmium found in this fraction is weakly absorbed and can easily be solubilized and become readily available to plants. This may be especially harmful for ecosystem and transfer of Cd in the food chain.

The 1 M NH_4OAc extracted distinctly lower amounts of cadmium at pH 5 than at pH 7 (Fig. 2 and 3), particularly in soils located near a smelter (Żukowice and Bogomice), which may result from prevailing of the non-specific and
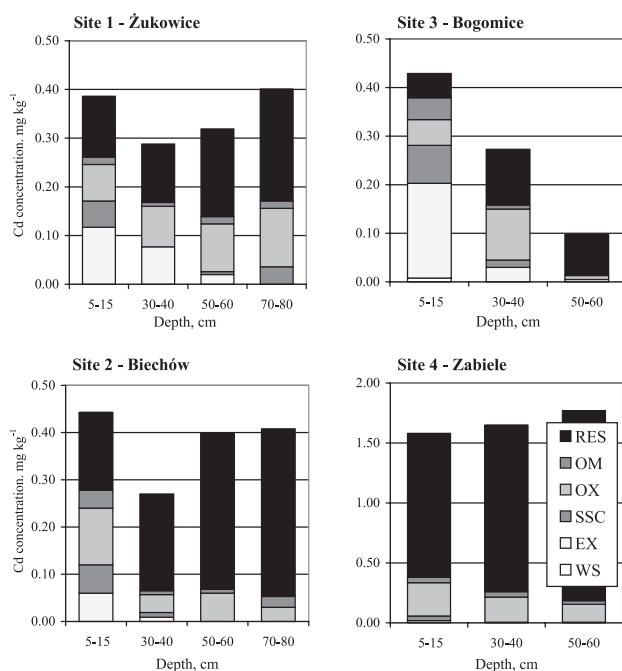
Fig. 1. Distribution of cadmium fractions in soil profiles – absolute Cd concentrations (mg·kg⁻¹). Extractants: WS – distilled water, EX – 1 M NH₄OAc (pH 7), SSC – 1 M NH₄OAc (pH 5), OX – 1 M NH₂OH·HCl in 25% HOAc, OM – 30% H₂O₂ in HNO₃, RES – aqua regia.

Fig. 2. Relative distribution of Cd fractions in soil profiles. Extractants: WS – distilled water, EX – 1 M NH₄OAc (pH 7), SSC – 1 M NH₄OAc (pH 5), OX – 1 M NH₂OH·HCl in 25% HOAc, OM – 30% H₂O₂ in HNO₃, RES – aqua regia.

weak adsorption of Cd in the soils investigated. However, the amount of 0.08 mg·kg⁻¹ Cd in this form found in the upper horizon of a sandy soil Bogomice composes 18% of total Cd. Surface horizons of soils located at greater distances of the smelter (Biechów and Zabiele) contain similar amounts of cadmium in EX and SSC fractions. The occurrence of SSC fraction in surface horizons of soils located near a smelter, and its lack in subsurface horizons and in a whole Zabiele pedon located far of the smelter may suggest atmospheric input of cadmium in the carbonate form. This conclusion is consistent with previous findings that SSC fraction of copper and lead is significant or even dominant in surface horizons of soils located in a close vicinity of the smelter [32].

Cadmium in the "oxide bound" fraction (OX) made a significant contribution, both in surface and subsurface horizons of all the pedons. The percentage of OX fraction in upper horizons of soils located close to the smelter is more than twofold lower than the "exchangeable" form. In all other horizons OX fraction dominates among non-residual fractions. Particularly in Zabiele soil OX fraction makes approximately 79, 81 and 90% of the non-residual Cd (at successive depths from the soil surface). Good relationship between Fe/Mn oxides (as Fe_d) and total Cd content was confirmed in this study by the positive and highly significant correlation coefficient (Table 2) as was also reported by other investigators [13, 20]. Iron and manganese oxides possess specific adsorption sites for divalent cations, which is one of the reasons for the remark-
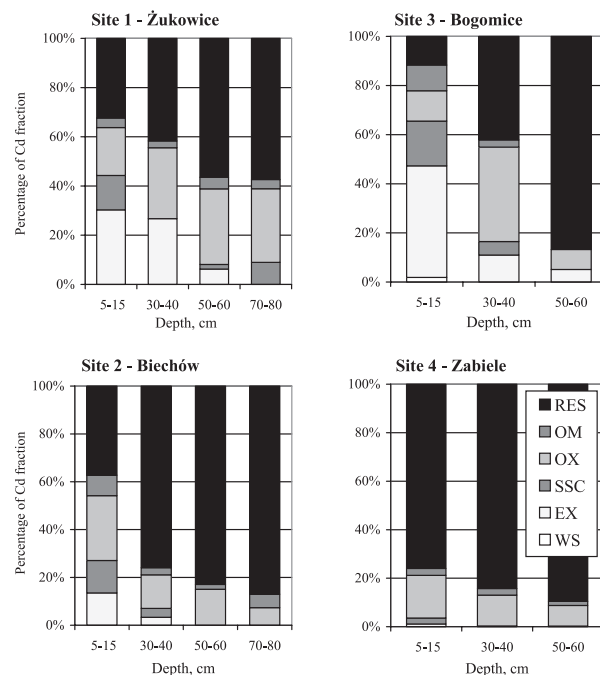
able ability of these oxides to adsorb Cd ions [8]. The relationship between Fe_d and "oxide-bound" Cd fraction is however not significant (Table 2). Kuo *et al.* [21] and Ahnstrom and Parker [15] suggest that extraction of "reducible" fraction prior to organically bound may lead to overestimation of the "oxide-bound" forms of cadmium.

The amounts of "oxidizable" or "organic bound" cadmium (OM) are low in all soils (<5% of total Cd in the subsoils and <11% in the surface horizons). Both total Cd and cadmium in OM fraction are related to organic carbon concentration (Table 2). Low percentage of cadmium in OM fraction of contaminated soils was also reported by Burt *et al.* [25], Chlopecka *et al.* [29], Kuo *et al.* [21], Ma and Rao [22]. Organic matter is considered to play an important role in reducing plant uptake of cadmium from soils due to its high CEC and the influence on soil pH [9, 10, 26]. However the correlations of "exchangeable" Cd forms to organic carbon or CEC are not statistically significant in this study.

Residual fraction of cadmium prevails in subsoils of all pedons, both sandy, silty and loamy textured. Between 83-90% of Cd_{sum} in subsoils of Bogomice, Biechów and Zabiele pedons is in RES fraction, which means, only 10-17% make all non-residual forms of cadmium (Fig. 2). Therefore, the contents of residual fraction decide on total Cd concentrations in these horizons. It is strongly correlated to clay content, CEC and Fe_d, but not correlated to organic carbon (Table 2). The percentage of non-residual Cd fractions increases toward soil surface up to 24%,

68% and 92% of total Cd in Zabiele, Żukowice and Bo-gomice sites, respectively. It suggests that the percentage of non-residual Cd fractions is a function of clay content and other soil properties in subsurface horizons, and, to a large extent, function of the distance to the smelter and the degree of soil contamination in surface layers of soils under investigation.

Cadmium Mobility Assessment

Mobility of cadmium in soil profile may be assessed on the basis of absolute and relative content of fractions slightly bound to soil components. The results of a single extraction with 0.01M $CaCl_2$, imitating a soil solution concentration, show in this study higher amounts of labile cadmium in surface horizons than in subsoils (Table 1). The difference between surface and subsoil horizons is more significant in Żukowice (eight-fold) and Bogomice (five-fold), located near the smelter than in Zabiele pedon, located at greater distance. Somewhat enhanced amounts of 0.01 M $CaCl_2$-soluble Cd in Zabiele soil occur in arable horizon only and rapidly decrease in subsoil (Table 1). In other pedons, in Żukowice soil particularly, the contents of the most labile Cd decrease gradually, and at the depth of 30-40 cm are still visibly elevated. Comparing surface horizons of two similar pedons developed from silt loams, located 1 km of the smelter (Żukowice) and 2.5 km of the smelter (Biechów) we can find, that the percentage of 0.01 M $CaCl_2$-soluble cadmium in total Cd concentration is unexpectedly higher near the smelter (12-20% of total Cd), than at the greater distance (3-4% of total Cd). The percentage of this labile Cd form in Zabiele soil, as well in subsoil of other pedons does not exceeds 0.3-1.5% of total Cd.

The relative index of cadmium mobility was calculated as a "mobility factor" [20, 27] on the basis of the following equation:

$$MF_{Cd} = \frac{(WS + EX + SSC)}{(WS + EX + SSC + OX + OM + RES)} \cdot 100$$

Since some metal forms (extracted as SSC) are relatively less mobile (stronger bound to the soil components than those extracted as WS and EX), the above mentioned index describes the potential mobility [27]. The cadmium mobility factor (MF_{Cd}) has values between 0 and 65%, the highest (44-65%) in upper horizons of soils located close to the smelter, and significantly lower (0-9%) in Zabiele soil and in subsoils of all other soils (Table 1). The high values of MF have been interpreted as symptoms of relatively high potential lability and biological availability of heavy metals in soils [20, 22]. Low values of the factor in the subsoil are however arguments of cadmium stability in these horizons, even if surface layers contain higher concentrations of the metal. The mobility index is negatively correlated with clay content (Table 2). However, statistical coefficients of this expected relation may not be true in present study, as the soil texture changes with the distance of the smelter.

The results of a single and sequential extractions show in this study that mobility of cadmium, determined on the basis of easily soluble Cd fractions is relatively high in surface horizons and determines, to some extent, a vertical redistribution of cadmium in pedons investigated. The levels of labile Cd in subsurface horizons of soils located close to the smelter appear elevated to at least the 40 cm depth, which indicates that this element is more mobile than either Cu or Pb [32]. The lack or trace amounts of labile cadmium in subsoils indicate however negligible leaching to lower soil horizons and little risk of ground-water contamination. Kuo *et al.* [21] made similar conclusions, emphasizing higher vertical mobility of cadmium as compared to copper and zinc in soils located near the 80-year operating ore smelter in Montana.

Conclusions

On the basis of results obtained in this study, only a little influence of the 30 years operating copper smelter on the cadmium concentration in soils is indicated. Total Cd concentration does not depend on the distance of the smelter, but correlates to primary soil properties, including clay content and CEC in particular. Vertical distribution of cadmium is related to soil horizonation and reflects natural differences between Luvisols and Cambisols.

The distribution of chemical forms of cadmium indicates however some symptoms of soil contamination with this metal. Relative significance of cadmium fractions in non-contaminated surface and subsoil horizons of pedons investigated is as follow: Cd residual >> Cd bound in/on Fe-Mn oxides > Cd exchangeable and specifically adsorbed > Cd complexed by organic matter >> water soluble Cd.

Increasing soil contamination with cadmium, visible in surface horizons of soils located near a smelter, manifests in a relative increase of non-residual fractions, the exchangeable and non-specifically adsorbed cadmium in particular.

Mobility of cadmium, assessed as the concentration of 0.01 M $CaCl_2$-extractable metal or the percentage of easily soluble fractions (WS+EX+SSC) is relatively high in upper soil horizons and depends on the distance to the smelter. Simultaneously, it is negatively correlated with clay content. Vertical distribution of labile cadmium indicates higher mobility of this metal as compared to copper and lead. There is however little risk of groundwater contamination with cadmium as the concentration of labile Cd in lower horizons of soil profiles is negligible in spite of the 30-year period of smelter operation.

Acknowledgement

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