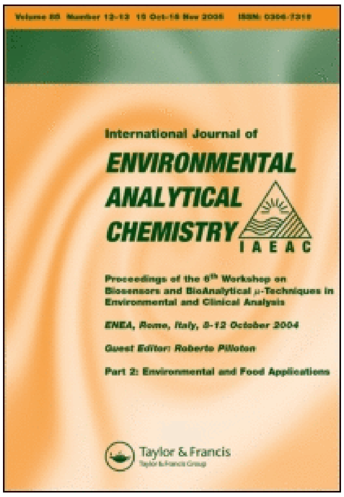

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A critical evaluation of the 0.05 M EDTA extraction of Pb from forest soils

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A critical evaluation of the 0.05 M EDTA extraction of Pb from forest soils

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Among many single-step extraction procedures proposed, 0.05 M EDTA (ethylenediaminetetraacetic acid) extraction is widely used. Although it has been often criticised, this protocol remains an effective and simple approach for a fast determination of the potential availability of several metals (e.g., Pb, Cd, Cu, Zn, etc.). However, other metallic elements present in soils at high concentrations such as Ca and Fe can possibly influence the extraction of the target metal due to competition for the EDTA ligand. The aim of this study was to evaluate the role of these metals during the 0.05 M EDTA extraction procedure. Furthermore, sequential extraction and Pb isotope analyses ($^{206/207}$Pb) were used in order to obtain more detailed information. The results of this study showed that especially the concentration and crystallinity of Fe play a very important role during the extraction of the target metals from low to moderately contaminated soils and this fact should be taken into account during result interpretation.

Keywords: single extraction; EDTA; soil; lead; Pb-isotope ratio; contamination

1. Introduction

For the evaluation of soil contamination with Pb, methods based on extraction/digestion procedures are used, often combined with Pb isotope ratio determination for tracing Pb origin. In the case of forest soils a combination of total digestion and 0.05 M EDTA (ethylenediaminetetraacetic acid) extraction is strongly recommended for Pb isotopes analysis [1]. The sequential extraction procedure first designed by Tessier *et al.* [2] and consequently modified and simplified, e.g., by Quevauviller [3] allows a detailed study of Pb distribution in contaminated soils.

Earlier studies dealing with soils in smelting areas showed that Pb is predominantly associated with the ‘‘potentially mobilisable’’ and thus EDTA-extractable fractions. While Komárek *et al.* [4] and Ettler *et al.* [5] found that the majority of Pb was bound to the reducible (Mn, Fe (hydr)oxides) fraction especially in deeper mineral soil horizons, Tawinteung *et al.* [6] determined more than 50% of Pb in the exchangeable fraction of a heavily polluted soil, however, in a less-polluted soil, the dominant fraction of Pb was

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found to be in Fe, Mn (hydr)oxides and/or organic matter. Both the single 0.05 M EDTA and sequential BCR-extraction procedures (proposed by the Commission of the European Communities Bureau of Reference, BCR programme followed by the Standards, Measurement and Testing programme) are reference methods for soil and sediment analyses [3]. EDTA presents an interesting extracting agent with a high affinity to form soluble EDTA-complexes, e.g., the stability constant of PbEDTA was found to be log $K_{PbEDTA} = 18.0$ [7] and this value has been used by many authors in different studies [8–10]. Other elements present in soils at high concentrations can lower the extraction efficiency of the target metal (e.g., Pb) due to the formation of more stable complexes with those metals. EDTA extraction efficiencies are to a great extent influenced by the stability constant of the formed complex and the concentrations of the chelating agent and the metals [10,11]. For example, the formed Fe(III)EDTA complexes are more stable (log $K_{Fe(III)EDTA} = 25.1$) [7] than complexes with Pb. Moreover, the addition of EDTA to soils leads to dissolution of Fe-(hydr)oxides [11–13]. The possible formation of Fe(III)EDTA complexes thus depends on physicochemical properties of the studied soils, e.g., amount of Fe-(hydr)oxides, their crystallinity, soil pH, Eh etc. [12,13].

In order to determine the content of Fe, Mn-(hydr)oxides, the hydroxylamine hydrochloride-acetic acid extraction (HA–AA) was proposed as a suitable reducing procedure [14]. It was suggested that HA–AA dissolves not only amorphous Fe (hydr)oxides but also a significant amount of Fe-oxides in crystalline form (such as goethite) by the mechanism based on a combination of: (i) non-selective oxide dissolution; (ii) preferred crystal orientation; and (iii) partial quartz dissolution. On the other hand, ammonium oxalate extraction (NH_4–OX) dissolves mainly high amounts of poorly crystalline phases (such as ferrihydrite) [14]. Semiquantitive methods (e.g., XRD or SEM-BSE), which would provide additional information about Fe, Mn and Al phases, are often not available in common laboratories. On the other hand, simpler methods based on chemical extraction procedures allow full quantification of each operationally defined form and reflect better behaviour integrity of the studied material itself.

The aim of this study is to evaluate the influence of selected metals (Fe, Ca, Mn, Al) present in soils on the efficiency of the single 0.05 M EDTA extraction procedure used for the determination of potentially mobilisable Pb in low- and highly contaminated soils.

2. Method

2.1 *Soil sampling, sample preparation and basic soil characteristics*

Two localities with different Pb contamination levels were chosen. The first forest soil profile (N 49°42.310′; E 13°59.440′) was sampled at a locality with prevailing Pb atmospheric deposition originating from a secondary Pb-smelter operational for more than 200 years [15,16]. The soil is classified as a Gleyic Cambisol developed on basalt veins in clastic sediments. Information available from other works [1,16] shows that Pb concentrations in superficial soil horizons reach more than 30,000 mg Pb kg^{-1}. The second forest soil profile (N 48°58.489′; E 14°15.218′) correspond to an unpolluted area with limited industry and therefore with small atmospheric depositions of metals [15]. This relatively shallow soil profile is classified as a Haplic Cambisol developed on Proterozoic porphyric granodiorites. Forest soils were chosen because of their variability of physico–chemical properties throughout the profile.

Soil horizons and bedrock samples were collected from 1 × 1 m pits dug down to the mineral soil horizons. The surface layer (~1 cm) containing fresh litter was removed. The bedrock samples were collected from the deepest soil horizons at both localities and were subsequently finely ground prior to analyses. Soil samples were stored in plastic bags which were leached prior to use in the solution of 10% HNO_3 for 24 h. Then, the samples were air dried to constant weight, sieved through a 2 mm stainless sieve and well homogenised. An aliquot amount of soil sample (from 0.2 to 5 g; according to the extraction procedure used) was obtained by quartation.

Soil pH was determined using a 1 : 2.5 ratio (w/v) of soil and deionised water. The cation exchange capacity (CEC) was computed as a sum of basic cations and Al determined in 0.1 M $BaCl_2$ solution. Total organic carbon (TOC) was determined by catalytic oxidation (1250°C) using an ELTRA (Neuss, Germany) Metalyt CS1000S analyser. Clay content was determined by the hydrometer method. Acid oxalate extraction (NH_4–OX) was carried in order to determine the amount of crystalline Fe, Mn and Al (hydr)oxides [14]. An aliquot of 0.4 g of dried soil sample was put into a polyethylene bottle and 80 mL of 0.2 M ammonium oxalate (modified by oxalate acid to pH 3) were added. The suspension was shaken in the dark for 2 h and centrifuged at 1500 rpm. Fe, Mn and Al concentrations were measured using FAAS. Hydrous amorphous Fe oxides were determined using the pyrophosphate extraction procedure. Approximately 1 g of each soil sample was put into a plastic bottle and 60 mL of 0.1 M $Na_4P_2O_7 \cdot 10H_2O$ was added. The suspension was shaken overnight and centrifuged at 1500 rpm [17]. Amorphous and some crystalline forms of Fe oxides were determined using the hydroxylamine hydrochloride extraction procedure [14]. An aliquot amount of 4 g of each soil sample was put into a plastic bottle with 200 mL of 0.25 M $NH_2OH \cdot HCl$ (in 25% (v/v) acetic acid) added. The suspension was shaken for 2 h and centrifuged. Iron concentrations in the extracts were determined using FAAS.

2.2 *EDTA and BCR-sequential extraction procedures*

In order to define the geochemical position of Pb in the studied soils, a modified version of the sequential extraction procedure by Quevauviller [3] was used. The extraction solutions were prepared from chemicals of analytical grade (Analytica Prague, Czech Republic and Merck, Darmstadt, Germany) and deionised water (Milli-Q Element, Millipore, France). The fractions defined by given operational steps were as follows: (i) Fraction A (F_A) – exchangeable and acid-extractable (0.11 M CH_3COOH); (ii) Fraction B (F_B) – reducible (0.5 M $NH_2OH \cdot HCl$); (iii) Fraction C (F_C) – oxidisable (8.8 M H_2O_2/1 M CH_3COONH_4); and (iv) Fraction D (F_D) – residual (total digestion of the residue using a mixture of concentrated $HF/HClO_4/HNO_3$). The residual fraction, defined by Quevauviller [3] as an *aqua regia*-extractable content, does not include metals bound to silicates. The potentially available or 'labile' pool of Pb used for further evaluation process was determined using the 0.05 M EDTA extraction. An aliquot amount of 5 g of a soil sample was extracted with 50 mL 0.05 M EDTA (pure acid of analytical grade, Fluka, Germany) at pH 7 adjusted using ammonium hydroxide according to a standardised method [3]. The obtained mixture was shaken for 1 hour on an end-over-end shaker at 30 rpm, centrifuged and analysed using ICP–MS. Detailed procedures are given elsewhere [3,18].

2.3 *Analytical and quality control procedures*

All the measurements of metals concentrations with the exception of Pb were performed using a flame atomic absorption spectrophotometer (FAAS – SpectraAA 640, Varian, Palo Alto, USA). The determination of Pb concentrations and $^{206/207}$Pb ratios were performed using an inductively coupled plasma mass spectrometer (ICP–MS – PQ ExCell, ThermoElemental, Winsford, UK) under standard analytical conditions. Calibration against the Pb isotope reference material NIST 981 (common lead) after every two samples was used in order to correct mass bias and dead time effects. The standard error for $^{206/207}$ Pb isotope ratio did not exceed 0.4% RSD (based on 10 replicates of each sample). During analyses of Pb concentrations, quantification was performed using an aqueous multi-element solution MERCK VI (CertiPUR, Merck, Darmstadt, Germany).

The quality control procedures consisted of measuring sample replicates and certified reference materials (CRM). Due to the well known higher variability of the sequential extraction scheme, triplicate samples of each step were carried out. The variabilities within triplicate samples are given in Figure 1 as error bars. The accuracies of the results of the sequential extraction procedures and EDTA-extractions were evaluated using CRM BCR 483 Sewage-Sludge-Amended Soil (Institute for Reference Materials and Measurements, Belgium). The relative standard error between found and certified means was less than 20%. In order to evaluate the precision of the total digestion, the CRM Light Sandy Soil (Analytica, Prague, Czech Republic) was used. The relative standard error between found and certified means for total digests was less than 15%.

3. Results

3.1 *Soil properties*

Basic physical and chemical characteristics of the studied soil profiles are given in Table 1. The pH of studied soils reached a maximum of 4.7 (horizons C, smelting and unpolluted area). The surface horizons were generally more acidic (Table 1). The CEC values were similar at both soil profiles. Generally, higher values were found in surface and subsurface soil horizons (Table 1). At both localities, a similar TOC content was found in the appropriate soil horizons. The highest TOC content was found in superficial soil horizons (40 and 41% in smelting and unpolluted area, respectively). With increasing depth, the TOC content dropped rapidly (Table 1).

Oxalate-extractable contents of Fe, Mn (Table 2) and Al corresponded to amorphous and poorly crystalline Fe, Mn and Al (hydr)oxides. The two superficial soil horizons at the locality near the smelter had two times higher oxalate-extractable contents of Fe compared to the same horizons at the unpolluted site. The Mn oxalate-extractable contents (NH_4–OX) at both localities were relatively lower (Table 2). In the smelting area, the maximum was reached in the mineral horizon ($0.37\,g\,kg^{-1}$) and at the unpolluted site in the superficial horizon ($0.55\,g\,kg^{-1}$). The amount of oxalate-extractable Al concentration was relatively constant at both localities and all soil horizons (the highest values found were 1.58 and $1.35\,g\,kg^{-1}$ in the Bw soil horizons from the unpolluted and smelting area, respectively).

Sodium pyrophosphate-extractable Fe content, corresponding approximately to the organic and hydrous amorphous Fe oxide fraction [17], is shown in Table 2. At the locality of the unpolluted area, the highest value was found in the Bw soil horizon whereas at the locality in the smelting area the concentrations of Fe in the first two soil horizons were similar.

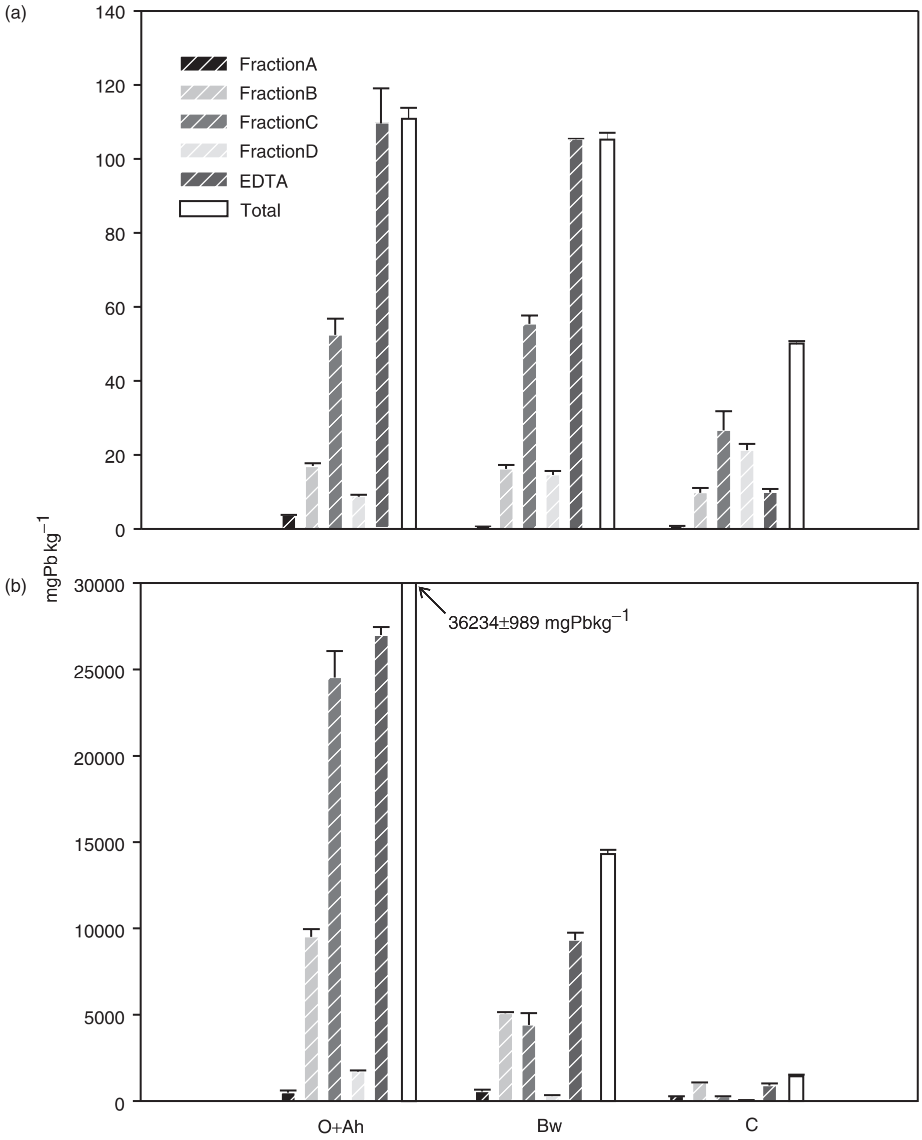

Figure 1. Total concentrations and Pb fractionation in separate horizons of soils originating from the unpolluted (a) and smelting area (b).
Notes: Each bar corresponds to mean ± SD ($n = 3$).

The hydroxylamine hydrochloride acetic acid-extractable Fe had a similar trend as the oxalate-extractable Fe content at both studied localities. However, it is a weaker reducing agent than NH_4–OX (Table 2) and therefore defines a more easily reducible fraction [19].

The EDTA-extractable fraction at both localities followed a different pattern. In the smelting area, the EDTA-extractable Fe concentration increased with sample depth, but remained almost constant in the Bw and C soil horizons in the unpolluted area. It is thought that during Pb extraction from soils using EDTA, the dissolution of Fe, Mn (hydr)oxides occurred which leads to a release of Pb [20].

Table 1. Basic physico-chemical characteristics, total Pb, Fe and Ca concentrations in the studied soils.

Soil horizon (depth, cm)	pH (H_2O)	CEC (cmol kg^{-1})	TOC (%)	Clay content (%)	$Pb_{TOT.}$ (mg kg^{-1})	$Fe_{TOT.}$ (g kg^{-1})	Pb/Fe ratio	Ca $_{TOT.}$ (g kg^{-1})
Unpolluted area								
O + Ah (1–5)	4.1	22.8	41.4	n.d.	111 ± 3	4.16 ± 0.21	2.6×10^{-5}	2.58 ± 0.04
Bw (5–16)	4.5	16.0	21.9	6.3	107 ± 2	7.45 ± 0.23	1.4×10^{-5}	2.33 ± 0.02
C (16–x)	4.7	8.68	1.60	7.6	48.7 ± 0.6	11.4 ± 0.3	0.4×10^{-5}	1.41 ± 0.03
Smelting area								
O + Ah (1–6)	4.4	20.8	40.0	n.d.	36234 ± 989	9.14 ± 0.11	3.9	2.11 ± 0.07
Bw (6–23)	4.4	11.9	15.4	6.1	14306 ± 497	13.7 ± 0.4	1.0	1.98 ± 0.04
C (23–x)	4.7	9.20	2.91	7.2	1232 ± 103	10.6 ± 0.4	0.1	1.33 ± 0.06

The total content of Fe (Table 1) in the unpolluted area increased very rapidly with sampling depth (from approx. 4.2 to 11 g kg^{-1} in superficial and mineral soil horizons, respectively). In the case of the smelting area, the Fe concentration first increased (from approx. 9 to 14 g kg^{-1} for O + Ah and Bw soil horizons, respectively) and then decreased in mineral soil (Table 1). This finding compared with much lower values of organic, amorphous and poorly crystalline forms of Fe (Table 2) could be explained by the fact that with increasing depth, Fe is present in more crystalline forms.

Similar values of separate Fe-extractions form were obtained in the unpolluted area between Bw and C soil horizons while in the smelting area between O + Ah and Bw soil horizons with the only exceptions of EDTA-extractable content (Table 2). The total content of Ca was very similar at both studied localities in comparable soil horizons (Table 1).

3.2 *Total Pb concentration and Pb isotopic composition*

Total Pb concentration at the two localities decreased with decreasing soil depth. In the soil of the smelting area, total concentrations of Pb reached 36.2 ± 1; 14.3 ± 0.5 and 1.23 ± 0.1 g kg^{-1} (in horizons of O + Ah, Bw and C, respectively). The total amount of Pb in soil in the unpolluted area was significantly lower and Pb concentration in horizons of O + Ah and Bw were very similar (111 ± 3 and 107 ± 2 mg kg^{-1}, respectively, Table 1). Lead isotopic composition obtained from total digests varied between separate soil horizons at both the smelting and unpolluted area. In the smelting area, the highest $^{206/207}$Pb ratio (1.169 ± 0.001; Table 3) was found in the superficial soil horizons O + Ah which is in a good agreement with earlier findings [4,16] and which reflects the predominant influence of the smelter-derived air pollution control (APC) residues from ore and secondary battery processing as the main contaminant in the area [16]. The $^{206/207}$Pb ratio of the Bw soil horizon was slightly lower (1.164 ± 0.0001, Table 3). This finding corresponds well to the fact that "older" Pb from the former processing can migrate downwards the soil profile [16]. In mineral soil horizon C, the isotopic ratio $^{206/207}$Pb found was much lower than in the previous horizons (1.158 ± 0.001, Table 3). This fact can be explained by mixture of the geogenic Pb source originating from the bedrocks (1.160 ± 0.003) with anthropogenic Pb which slowly migrated down to the mineral horizon.

Table 2. Chemical forms of Fe and Mn in the studied soils.

Soil horizon (depth, cm)	Oxalate-extractable Fe ($g\,kg^{-1}$)	Oxalate-extractable Mn ($g\,kg^{-1}$)	Pyrophosphate-extractable Fe ($g\,kg^{-1}$)	Pyrophosphate-extractable Mn ($g\,kg^{-1}$)	HA-AA-extractable Fe ($g\,kg^{-1}$)	HA-AA-zextractable Mn ($g\,kg^{-1}$)	EDTA-extractable Fe ($g\,kg^{-1}$)	EDTA-extractable Mn ($g\,kg^{-1}$)
Unpolluted area								
O + Ah (1–5)	1.66 ± 0.02	0.55 ± 0.08	0.62 ± 0.01	0.28 ± 0.01	0.40 ± 0.01	0.46 ± 0.03	1.08 ± 0.06	0.67 ± 0.05
Bw (5–16)	2.35 ± 0.03	0.20 ± 0.07	1.14 ± 0.10	0.09 ± 0.01	0.71 ± 0.01	0.13 ± 0.01	1.84 ± 0.10	0.22 ± 0.07
C (16–x)	2.39 ± 0.03	0.04 ± 0.001	0.99 ± 0.05	0.02 ± 0.01	0.81 ± 0.02	0.03 ± 0.002	1.71 ± 0.08	0.01 ± 0.003
Smelting area								
O + Ah (1–6)	3.97 ± 0.06	0.22 ± 0.03	2.28 ± 0.04	0.09 ± 0.01	1.35 ± 0.04	0.10 ± 0.01	0.29 ± 0.03	0.14 ± 0.03
Bw (6–23)	3.98 ± 0.05	0.21 ± 0.01	2.28 ± 0.04	0.02 ± 0.01	1.72 ± 0.03	0.02 ± 0.001	0.64 ± 0.02	0.03 ± 0.001
C (23–x)	2.48 ± 0.01	0.37 ± 0.05	1.38 ± 0.03	0.09 ± 0.01	1.03 ± 0.02	0.12 ± 0.005	1.62 ± 0.10	0.04 ± 0.001

Table 3. Isotopic composition ($^{206/207}$Pb) of Pb in total digests, EDTA extracts and separate fractions obtained from the sequential extraction procedure. Each isotope ratio corresponds to mean ± SD ($n = 3$).

	Total digest	Fraction A	Fraction B	Fraction C	Fraction D	EDTA-extract
Unpolluted area						
O + Ah	1.156 ± 0.001	1.165 ± 0.003	1.155 ± 0.001	1.155 ± 0.002	1.170 ± 0.002	1.156 ± 0.001
Bw	1.161 ± 0.001	1.167 ± 0.005	1.157 ± 0.001	1.158 ± 0.002	1.168 ± 0.001	1.161 ± 0.001
C	1.178 ± 0.001	1.179 ± 0.002	1.174 ± 0.001	1.172 ± 0.004	1.164 ± 0.001	1.179 ± 0.0001
Smelting area						
O + Ah	1.169 ± 0.001	1.172 ± 0.005	1.171 ± 0.003	1.170 ± 0.0001	1.168 ± 0.003	1.166 ± 0.001
Bw	1.164 ± 0.0001	1.170 ± 0.006	1.170 ± 0.003	1.166 ± 0.001	1.169 ± 0.004	1.167 ± 0.001
C	1.158 ± 0.001	1.158 ± 0.003	1.166 ± 0.003	1.166 ± 0.0001	1.171 ± 0.0001	1.158 ± 0.0001

Table 4. Pb concentration extractable by EDTA and recovery calculation for sum of fractions A, B, C compared with EDTA and total concentration.

Soil horizon (depth, cm)	EDTA-extractable concentration (mg kg^{-1})	Σ fractions A, B, C (mg kg^{-1})	Recovery to EDTA-extraction (%)	Recovery to total concentration (%)
Unpolluted area				
O + Ah (1–5)	109 ± 9	66.9	61.4	60.3
Bw (5–16)	105 ± 0.2	72.2	68.6	68.8
C (16–x)	9.81 ± 0.83	37.1	378	76.2
Smelting area				
O + Ah (1–6)	31589 ± 468	34521	109	95.3
Bw (6–23)	9315 ± 433	10032	108	70.1
C (23–x)	889 ± 126	1551	174	126

An opposite trend in the isotopic composition was found in soil horizons at the locality of the unpolluted area. The highest $^{206/207}$Pb ratio (1.178 ± 0.001) was detected in the digest of the mineral soil horizon C (Table 4). This value corresponds again to a mixture of an anthropogenic and geogenic source of Pb, where the $^{206/207}$Pb ratio of the bedrock was much higher (1.221 ± 0.003). This finding is in a good agreement with the results from the sequential extraction procedure, mentioned below, and shows that some amount of anthropogenic Pb is able to migrate down the mineral horizons and significantly influences the isotopic composition of Pb.

3.3 *Sequential and EDTA extraction and isotopic composition of Pb*

The results of the sequential extraction procedure for concentration and isotopic composition are given in Figure 1 and Table 3, respectively. The comparison of the extraction efficiency of EDTA and the sum of fractions A, B and C in separate soil horizons are summarised in Table 4.

In the unpolluted area, the highest concentration of Pb was present in fraction C (Figure 1) in all soil horizons and decreased with increasing sampling depth. The most mobile fraction (fraction A) contained the lowest Pb concentration which further decreased down to the mineral soil horizon C (Figure 1). The $^{206/207}$Pb ratio determined in separate fractions of the surface and subsurface soil (O + Ah, Bw) showed a similar trend. The $^{206/207}$Pb ratio in fraction A is relatively high (Table 3) and rapidly decreased in fraction B and C. Fraction D has a higher $^{206/207}$Pb ratio (1.170 ± 0.002 and 1.168 ± 0.001 in soil horizons O + Ah; Bw, respectively). This fact can be attributed to a mixing of Pb originating from leaded petrol (1.135 ± 0.001) [16] and coal combustion in the potentially available soil fractions (A, B, C). Fraction D (residual fraction) contained Pb of geogenic origin and thus had a higher $^{206/207}$Pb ratio as it is evident from earlier works [1,16]. The determined concentration of Pb in EDTA extracts in the surface and subsurface soil horizons reached the total Pb concentration (109 ± 9 and $105 \pm 0.2\,\mathrm{mg\,kg^{-1}}$ in O + Ah and Bw horizons, respectively, Figure 1, Table 4). The relatively higher EDTA extraction efficiencies were achieved due to the lower pH of the studied soil [21]. Almost the whole amount of Pb was present in the first three soil fractions A, B and C and is to a great extent EDTA-extractable, moreover, a small amount of Pb was bound to silicates and thus certain amount of Pb present in silicate matrices (fraction D) must be EDTA-extractable as well (Figure 1, Table 4). These facts are in a good agreement with earlier studies by Barona *et al.* [21]. The isotopic composition of Pb in total digests and EDTA extracts was identical in appropriate soil horizons O + Ah; Bw and C (Table 3). Furthermore, in mineral soil horizons, the amount of Pb extractable by EDTA was much smaller compared to the total digestion or even to the amount of Pb in fraction C. It is evident that the extraction efficiency of EDTA in mineral soil horizon was lower. The oxalate-extractable Fe was similar in horizons Bw and C, the amount of Mn decreased from the superficial down to the mineral soil horizon. It can be assumed that down to the mineral soil horizon, the composition and crystallinity of Fe, Mn (hydr)oxides changed and thus lowered the EDTA extraction efficiency. This situation is well documented in Table 4. The sum of fractions A, B and C were compared to total Pb and EDTA-extractable Pb concentration. In the superficial soil horizons O + Ah the sum of the first three fractions represented approximately 61% of EDTA-extractable and 60% of the total Pb amount (Table 4). In the second soil horizon Bw, the same comparison showed similar results, 69% of EDTA extract and 68% of the total Pb. In the mineral soil horizon C, the sum of the first three fractions (76% of the total Pb amount) was almost 4-fold higher than Pb concentration extractable by EDTA (Table 4). The decreasing of EDTA efficiency can be attributed to a change in the composition of Fe, Mn (hydr)oxides (Table 2).

While the highest content of Pb in soils originating from the smelting area was present in fraction C of the two superficial soil horizons O + Ah and Bw, in the mineral soil horizon C, the highest Pb content was present in fraction B (Figure 1). The isotopic composition of the two superficial soil horizons (O + Ah and Bw) was very homogenous due to the wide contamination with anthropogenic Pb originating from industrial depositions (Table 3). It was found that Pb can migrate from the superficial soil horizon down to the Bw horizon. The downward migration of Pb in forest soils has been already documented in other works [16,22]. The first two soil horizons could serve as a trap for Pb because Pb has a large affinity to organic matter and Fe (hydr)oxides, both present in increased concentrations here ([Tables 1 and 2]). It has been reported that Pb has a greater affinity for Mn oxides [23]; however, in the studied soils the Mn oxide content is low compared to Fe oxides (Table 2) and the latter will thus play a more important role in Pb sorption.

The majority of Pb in all three soil horizons was extractable by EDTA (Figure 1, Table 4). The isotopic composition of total Pb content in separate soil horizons was in a good agreement with those obtained from the EDTA extraction procedure (Table 3). The sum of fractions A, B and C represented about 109% of Pb extractable by EDTA and about 95% of the total Pb content in superficial soil horizon O + Ah (Table 4). In the second soil horizon Bw, the sum was about 108% of EDTA-extractable Pb and 70% of the total Pb content. In the mineral soil horizon C, the EDTA extraction efficiency was lower, thus the sum of the three fractions represented about 174% of EDTA-extractable Pb while it was about 126% of the total Pb content.

4. Discussion

From the results presented it can be concluded that at both studied localities the Pb extraction efficiency of EDTA rapidly decreased in mineral soil horizons and the amount of Pb was not comparable to the sum of the first three steps in the BCR-sequential extraction scheme. In the smelting area, Pb in soil was present at high concentrations which were higher compared to Fe (high Pb/Fe ratio) (Table 1). It is important to note that during the EDTA extraction not only the log K of the forming complex influences the speciation but also the concentrations of metals and ligand (EDTA) [12]. In the superficial soil horizons (O + Ah and Bw), EDTA complexed not only Fe but even Pb at a high level. This was well documented by low Fe concentrations in EDTA extracts of O + Ah and Bw soil horizons. In the mineral soil horizon, the Pb/Fe ratio changed, and more Fe was present as Fe(III)EDTA which is the predominant species. Because 1 h of extraction time was not sufficient to reach full equilibrium, the Pb content in the EDTA extract was much lower.

A different situation could be observed in the unpolluted area. The amount of Fe was much higher compared to Pb (low Pb/Fe ratio). While the total Fe concentration rapidly increased down the soil profile (Table 1), there were no such large differences in Fe forms throughout the profile (Table 2). The amount of Fe extractable by EDTA was also constant in Bw and C horizons. The different EDTA extraction efficiency could be explained here by the fact that most Pb in the mineral soil horizon must be present in highly crystalline Fe (hydr)oxides and/or in occluded forms, which are not EDTA extractable, nor dissolved by a reducing agent because these can be surrounded by organic matter present in high concentrations in forest soils [24]. This fact can be proven by the highest Pb concentration in the oxidisable fraction (fraction C) of the mineral soil horizon (Figure 1a). Besides Fe, Ca is another important metal able to compete for the EDTA ligand, especially due to its high concentrations in some soils. However, due to the fast exchange kinetics of CaEDTA [20], the low log K_{CaEDTA} value (12.4) and a lower Ca concentration in the studied soils compared to Fe (Table 1), Ca will probably not compete to such an extent as Fe during the EDTA extraction of Pb. Another factor influencing Pb extractability using EDTA is ''ageing''. Older Pb is bound more strongly to the soil matrix, which is the case especially for the unpolluted area, while in the smelting area; the vast majority of Pb is originating from recent anthropogenic activities and is more available (Figure 1; [Tables 1 and 2]).

5. Conclusions

The 0.05 M EDTA extraction presents a fast and efficient tool for evaluation of metal availability in soils. However, there are several drawbacks involved during the extraction procedure. Other cations present in soils at high concentrations (especially Fe and Ca) can influence the extraction efficiency of the target metals. Due to the fact that EDTA proved to dissolve Fe (hydr)oxides, the subsequent remobilisation of sorbed metals and complexation of Fe significantly influences the extraction procedure. The knowledge about the concentrations and forms of the competing cations in soils is, therefore, indispensable because, for example, in low- to moderately contaminated soils with high concentrations of amorphous Fe, the extraction efficiency will be significantly influenced. Nevertheless, despite being often criticised, the 0.05 M EDTA extraction is sufficient for the determination of the potentially mobilisable metals (fractions A, B, C) and the isotopic composition of anthropogenic Pb in soils and, due to its simplicity, it presents an important analytical procedure in environmental soil analyses.

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References

[1] M. Komárek, V. Chrastný, V. Ettler, and P. Tlustoš, Anal. Bioanal. Chem. **385**, 1109 (2006).

[2] A. Tessier, P.G.C. Campbell, and M. Bisson, Anal. Chem. **51**, 844 (1979).

[3] Ph. Quevauviller, Trac Trends Anal. Chem. **21**, 774 (2002).

[4] M. Komárek, V. Chrastný, and J. Štíchová, Environ. Int. **33**, 677 (2007).

[5] V. Ettler, A. Vaněk, M. Mihaljevič, and P. Bezdička, Chemosphere. **58**, 1449 (2005).

[6] N. Tawinteung, P. Parkpian, R.D. DeLaune, and A. Jugsujinda, J. Environ. Sci. Health Part A **40**, 385 (2005).

[7] J.W.W. Huang, J. Chen, W.R. Berti, and S.D. Cunningham, Environ. Sci. Technol. **3**, 800 (1997).

[8] Z.G. Shen, X.D. Li, C.C. Wang, H.M. Chen, and H. Chua, J. Environ. Qual. **31**, 1893 (2002).

[9] B. Kos and D. Leštan, Environ. Sci. Technol. **37**, 624 (2003).

[10] A.E. Martell, R.M. Smith and R.J. Motekaitis, NIST critically selected stability constants of metal complexes, Version 6.0. (NIST, Gaithersburg, MD, USA, 2001).

[11] B. Nowack, R. Schulin, and B.H. Robinson, Eniron. Sci. Technol. **40**, 5225 (2006).

[12] B. Nowack, Environ. Sci. Technol. **36**, 4009 (2002).

[13] M. Komárek, P. Tlustoš, J. Száková, V. Chrastný, and J. Balík, Plant. Soil Environ. **53**, 216 (2007).

[14] D.K. McCarty, J.N. Moore, and W.A. Marcus, Appl. Geochem. **13**, 165 (1998).

[15] J. Sucharová and I. Suchara, Sci. Total Environ. **223**, 37 (1998).

[16] V. Ettler, M. Mihaljevič, and M. Komárek, Anal. Bioanal. Chem. **378**, 311 (2004).

[17] C.L. Bascomb, Eur. J. Soil Sci. **19**, 251 (1968).

[18] M. Pueyo, G. Rauret, D. Lück, M. Yli-Halla, H. Muntau, Ph. Quevauviller, and J.F. Lopéz-Sánchez, J. Environ. Monitor. **3**, 243 (2001).

[19] T. Koeckritz, J. Thöming, Ch. Gleyzes, and K.E. Ødegård, Acta Hydrochim. Hydrobiol. **29**, 197 (2001).

[20] B. Nowack, F.G. Kari, and H.G. Krüger, Water, Air, Soil Pollut. **125**, 243 (2001).

[21] A. Barona, I. Aranguiy, and A. Elías, Env. Poll. **79**, 113 (2001).

[22] H. Puchelt, U. Kramar, G.L. Cumming, D. Krstic, T. Nölttner, M. Schöttle, and V. Schweikle, Appl Geochem. Suppl. **2**, 71 (1993).

[23] D.M. Dong, Y.M. Nelson, L.W. Lion, M.L. Shuler, and W.C. Ghiorse, Water Res. **34**, 427 (2000).

[24] W.A. Maher, Bull. Environ. Contam. Toxicol. **32**, 339 (1984).