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Application of the BCR sequential extraction scheme to dredged pond sediments contaminated by Pb–Zn mining: A combined geochemical and mineralogical approach

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Abstract

The modified BCR sequential extraction procedure [Rauret, G., López-Sanchez, J., Sauquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to certification of new soil and sediment reference materials. J. Environ. Monit. 1, 57–60.] was applied to 4 sediments from a mine tailing pond in La Calamine (East-Belgium). The results showed a very different behaviour of different samples towards the same extraction scheme. In samples with an elevated acid neutralizing capacity, a significant increase in the pH of the extracts was measured after the first two extraction steps. Other artefacts, such as readsorption of metals and precipitation could be deduced by comparing X-ray diffraction patterns after different extraction steps. For example, anglesite was effectively dissolved during the acid extraction step (step 1) but relatively low Pb concentrations were measured in the CH_3COOH extract because of the readsorption of Pb. Mineralogical analysis of the sediments after each extraction step also indicated the incomplete oxidation of sulphides by H_2O_2. Besides a mineralogical analysis, the monitoring of the pH of the extracts and the analysis of major elements (Fe, Ca, Al, Mn) can be helpful for the interpretation of the results of the sequential extraction.

The combination of sequential extractions with mineralogical sample investigation provided information on the reactivity and solubility of minerals in the samples. This improved the interpretation, at least within the detection limits of the mineralogical analysis applied. Besides the improved interpretation of the results of the sequential extractions for sediments in which minerals are identified, the information concerning the reactivity of minerals is an important tool to evaluate the risk associated with contaminated sediments.

Keywords: Acid neutralizing capacity; Mine tailing; Mineralogy

1. Introduction

Sequential extractions provide semi-quantitative information on element distribution between operationally defined geochemical fractions in soils, sediments and waste materials. Whereas sequential extractions are often used to infer the speciation of heavy metals, the fractions obtained from sequential extraction do not necessarily reflect true chemical speciation.

The different extractions in a sequential extraction scheme often intend to simulate processes in nature such as acidification or oxidation. However, the physico-chemical conditions in sequential extraction experiments (strong reagents and rapid reactions) differ from natural conditions (weak reagents and slow reactions)

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(Nirel and Morel, 1990). Although leaching techniques such as column leaching tests and lysimeter tests are probably more realistic to field conditions, sequential extractions can give an indication of the 'pools' or 'sinks' of heavy metals that are potentially available under changing environmental conditions.

In recent years, attempts to improve sequential extractions towards higher selectivity and higher operational efficiency have been made. With respect to this more problem-orientated approach, Maiz et al. (1997) proposed a short extraction scheme only considering mobile ('exchangable': $CaCl_2$), mobilisable (DTPA) and residual forms. Gómez Ariza et al. (2000a) developed an improved extraction scheme for heavily contaminated and iron-oxide rich sediments, using repetitive extractions with $NH_2OH.HCl$ 0.4 M.

The most common problems with sequential extractions are the non-selectivity of reagents and readsorption phenomena (Rendell et al., 1980; Howard and Vandenbrink, 1999). Sometimes a bad recovery is also observed when total metal concentrations are compared with the sum of concentrations associated with the individual phases. This is often encountered for heavily contaminated samples (e.g. Davidson et al., 2000; Van Herreweghe et al., 2003), and is partially due to sample heterogeneity.

Besides the measurement of elements in the extracts, the analysis of the solid phase (X-ray diffraction, energy dispersive spectroscopy, microprobe analysis) after extraction with a reagent, can give information on the selectivity of the reagent and the completeness of reaction (Tipping et al., 1985; Tessier and Campbell, 1988; Gruebel et al., 1988; Tessier and Campbell, 1991; Dhoum and Evans, 1998; La Force and Fendorf, 2000). The sequential extraction of model solid phases can also yield information of the selectivity and efficiency of reagents in the different steps of a sequential extraction scheme (e.g. Gómez Ariza et al., 2000a,b; Van Herreweghe et al., 2003). La Force and Fendorf (2000) concluded that sequential extractions should not be universally applied to all soils but need to be evaluated on a site basis for a given soil. Therefore, optimisation of a given extraction (concentration of reagents, sequence and reaction time) is required. On the other hand, standardisation of these procedures is the only way to achieve comparability when using sequential extractions (Quevauviller, 1998). In the past decade, much effort has been made to evaluate sequential extraction schemes. The best example is the BCR sequential extraction scheme, a simple 3-stage procedure that was thoroughly tested by interlaboratory trials. The original procedure (Ure et al., 1993) consisted of 3 extractions which separated 'acid extractable' (CH_3COOH 0,11 M), 'reducible' ($NH_2OH.HCl$ 0,1 M, pH 2) and 'oxidisable' (H_2O_2 15%) fractions. During the certification of Reference Materials (Rauret et al., 1999; Sahuquillo et al., 1999), the reducing extraction ($NH_20H.HCl$) in the BCR sequential extraction scheme was found to suffer from a lack of reproducibility. After testing different reaction conditions (concentration of the reagent, pH), the $NH_2OH.HCl$ concentration was changed to 0.5 M and the pH of the reagent was adjusted to 1.5 by addition of a fixed volume of HNO_3.

Finally, different extraction procedures, applied on the same sample, are often compared to select the procedure that is most suited for the soil or sediment of concern (e.g. Gómez Ariza et al., 2000a; Joksi et al., 2005). However, the direct comparison between methods is difficult to carry out, especially when different reagents are applied to extract a specific phase or when reagents with different concentrations are used in the methods to be compared.

The objectives of the present study were to apply the (modified) BCR sequential extraction scheme to dredged pond sediments contaminated by Pb–Zn mining and to investigate mineral reactivity in sediments with a different mineralogical and physico-chemical composition by combining data of sequential extractions and mineralogical analysis (XRD).

2. Materials and methods

2.1. Sampling

Thirty samples of a tailing consisting of dredged mine pond sediments were collected in September 2004. The mine pond tailing, which is located in village of La Calamine (East-Belgium), contains dredged material from a sedimentation pond, which was used to store waste waters from the former Pb–Zn mine (Cappuyns et al., 2006a). In the centre of the tailing, a profile was excavated until a depth of 4 m and samples were taken every 10 to 20 cm. After determination of total element concentrations and mineralogy, 4 samples were selected for a more detailed investigation with sequential extractions.

2.2. Physico-chemical and mineralogical sample characterisation

For the physico-chemical analysis, the samples were air-dried and part of the sample was disaggregated in a porcelain mortar and sieved (2 mm). Grain size was analysed by laser diffraction analysis (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK). Total metal concentrations (Al, As, Ba, Ca, Cd, Co, Cr, Cu,

Fe, K, Mn, Ni, Pb and Zn) were determined in all the samples. The term 'total' is used here as the amount of metals dissolved according to the 3 acid dissolution method. Therefore, one gram of each sample was dissolved in a 3-acid mixture (4 mL HCl_{conc}, 2 mL HNO_{3conc} and 2 mL HF_{conc}) in a Teflon beaker. The mixture was gently heated on a hot plate until half dry and subsequently reattacked with the same three acids and heated until completely dry. The residue was redissolved with 20 ml 2.5 N HCl and filtered (Whatman 45). Finally, the solution was diluted to 50 ml with distilled water. A Certified Reference Material (Montana Soil 2710) and sample duplicates (all the samples were analysed in duplicate, for the reference materials 4 replicates were analysed) were used for quality assurance of the analytical data. Values (in mg/kg) obtained were: for Cd 19.1 (certified value 21.8), Zn: 6612 (certified value 6952), Pb: 5069 (certified value 5532), As: 608 (certified value 626), Fe 2.87 % (certified value: 3.38%) and Ca 1.03 % (certified value 1.25%).

Total S and C were determined with the CHNS element analyser (Interscience CHNS Analyser). Mineralogy was studied combining X-ray diffraction (XRD, Philips®, Co-target, $\lambda = 1.79$ Å) and optical petrography. Diffractometer settings were 30 kV, 30 mA, 10–75° 2θ, step size 0.04° 2θ and 2 s counting per step. Preconcentration was achieved by separating different fractions of the waste material according to magnetic properties (Franz isodynamic separator, McAndrew, 1957) and grainsize. Clay mineralogy was determined on orientated clay preparates. The pH of the samples was measured in a solid-water suspension (liquid/solid ratio of 1/10) that was shaken for 24 h on a reciprocal shaker. After measurement of the pH, the solution was centrifuged, decanted off and filtered (0.45 μm). One half of each sample was acidified with a drop of concentrated HNO_3 and put aside for analysis of major and trace cations. Another part of the sample was put aside for sulphate analysis by turbidimetry (Vogel, 1961).

2.3. Sequential extractions

The optimised BCR sequential extraction procedure (Rauret et al., 1999) was applied to assess heavy metal fractionation in the samples. This extraction procedure consists of three extraction steps, namely: Step1: extraction with acetic acid (0.11 M, 16 h); Step2: extraction with hydroxylamine hydrochloride (0.5 M, pH = 1.5, 16 h); Step3: extraction with H_2O_2 8.8 M (2 × 1 h, 85 °C) followed by an extraction with ammonium acetate 1.0 M. Additionally, a fourth step was added by dissolving the final residue by using the same three acids as for determination of total element content (Step4). The quality of the analytical data for the sequential extraction procedure was assessed by carrying out analyses of the certified reference materials BCR-701 and CRM483. BCR-701 is a lake sediment certified for extractable metal contents in the three steps of the modified BCR sequential extraction procedure and indicative values for aqua regia extraction (Pueyo et al., 2001). CRM483 is a sewage sludge amended soil that has indicative values for Cd, Cr, Cu, Ni, Pb and Zn in the 3 steps of the BCR extraction procedure. Additionally, the BCR sequential extraction procedure was also applied to the reference soil SRM 2710 (Gillis, 1997), which is certified for its total element concentrations. Although no certified values are available for the BCR sequential extraction procedure for this material, a few authors published their results of the BCR sequential extraction procedure.

The reference materials (BCR-701, CRM483 and SRM 2710) were included in quadruplate and blanks of the different extractants were also analysed. Calibration solutions were made up with the appropriate extraction solutions. The pH of the extracts was also determined (after each extraction) with a combined glass electrode (Hamilton Single pore electrode).

Four different samples and 3 reference materials were subjected to the sequential extraction procedure and extractions were performed in quadruplate, yielding 4 series of 7 samples = 28 samples. After each extraction step, one sample of each series was put aside for XRD-analysis (except the reference materials).

2.4. Analysis

The solutions were analysed by AAS (Thermo Electron Corporation S Series AA) for Pb, Zn, Fe and Al. The analytical wavelenghts were: 217.0 nm for Pb, 213.9 nm for Zn, 372.0 nm for Fe and 309.3 nm for Al. For As, Cu and Cd, a multi element analysis by ICP-MS (HP 4500 series) was carried out. The samples were diluted just before analysis with 5% HNO_3 (ultrapure). Standard series were made up starting from the '10 ppm Multi-Element Calibration Standard-2A in 5% HNO_3' from Hewlett Packard®. An Indium (In) internal standard was applied to both samples and standards. The spectroscopic interference of ArCl, which has the same m/z as As (75) was corrected according to the recommendations of the EPA (method 200.8, Brockhoff et al., 1999). Each ICP-MS measurement was carried out with three repetitions holding relative standard deviations below five percent. All reagents used for analysis were of analytical grade. All glassware was

Table 1
pH, element concentrations, grain size, mineralogy and insoluble residue (IR), of the samples

	pH	S g/kg	C g/kg	Fe g/kg	Ca g/kg	K g/kg	Al g/kg	Mg g/kg	Mn mg/kg	<2 µm	2><63 µm	>63 µm
LC1	3.4	33.5	31.1	29.7	50.8	13.3	40.3	1.5	20	31	28	41
LC2	7.5	25.7	23.9	28.1	55.7	15.3	27.9	3.0	3264	11	20	69
LC3	6.4	127.1	37.6	117.7	47.2	10.6	30.8	4.8	872	58	38	4
LC4	3.6	68.2	25.4	63.9	16.5	15.0	54.8	2.3	77	60	33	7

	Zn g/kg	Pb g/kg	Cd g/kg	As mg/kg	Cu mg/kg	IR %	Mineralogy [a]
LC1	2.5	39.1	5	180	6	13.4	Q, ka, ill, sme, ang, gyp, jar
LC2	67.7	4.2	367	249	15	4.9	Q, ka, ill, sme, ang, cal, sid, smi, cer, gyp
LC3	108.1	31.5	305	2294	69	3.9	Q, ka, ill, sme, ang, cal, cer, gal, mar, pyr, sph
LC4	24.4	37.2	307	1196	35	6.4	Q, ka, ill, sme, ang, gal, pyr, sph

[a] ang = anglesite, cal = calcite, cer = cerussite, gal = galena, gyp = gypsum, ill = illite, jar = jarosite, ka = kaolinite, mar = markasite, sid = siderite, sme = smectite, smi = smithsonite, sph = sphalerite, pyr = pyrite, Q = quartz.

thoroughly cleaned with HNO_3 0.2 M. Reagent blanks were determined for each new batch of reagent.

3. Results

3.1. Chemical and mineralogical sample composition

The tailing consists of diverse types of sediments, which is also reflected in the different composition, mineralogy and grainsize of the samples (Table 1). Although more elements were analysed, the discussion will mainly focus on Zn, Pb, Cd, As, Fe, Ca and S. The 4 samples contained elevated concentrations of Zn, Pb, Cd, and As (Table 1).

The pH of samples LC1 and LC4 was acid, while LC2 and LC3 displayed a near-neutral pH. Samples LC1 and LC2 were characterised by a coarser grainsize than samples LC3 and LC4. Quartz, kaolinite, illite, smectite and anglesite ($PbSO_4$) were detected in all the samples. Samples LC1, LC2 and LC3 contained larger concentrations of Ca than sample LC4. This reflects the occurrence of calcite and gypsum in these samples. Gypsum also occurs as white precipitate on the tailings' surface and indicates that neutralizing minerals are present in the tailing. Sample LC2, with the highest pH, contained several carbonate minerals: calcite ($CaCO_3$), smithsonite ($ZnCO_3$), cerussite ($PbCO_3$) and siderite ($FeCO_3$). The minerals found in the mine tailing partly

Table 2
Comparison of the results of the modified BCR sequential extraction of sample BCR-701 and CRM483 (mean ± standard deviation of 4 replicates) with certified (BCR-710: Rauret et al., 2001) and indicative (CRM 483: Ruaret et al., 2000) values

	BCR701			CRM483		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
Certified values				*Indicative values*		
Cd	7.34±0.35	3.8±0.28	0.27±0.06	10±0.77	25±2.3	1.22±0.48
Cr	2.26±0.16	46±2	143±7	9.4±3.5	654±108	2215±494
Cu	49.3±1.7	124±3	55.2±4	17±1.5	141±20	132±29
Pb	3.18±0.21	126±3	9.3±2	0.8±0.7	379±21	66.5±22
Zn	205±6	114±5	45.7±4	441±39	438±56	37.1±9.9
Fe(*)	71±1	7698±106	1079±53	36±2	6691±198	1058±11
This work				*This work*		
Cd	7.32±0.04	3.8±0.04	0.23±0.01	9.1±0.1	23±0.5	1.02±0.17
Cr	2.11±0.03	39±1	128±7	7.8±1.6	470±13	1988±135
Cu	47.3±0.4	120±1	59.1±3	14±0.4	135±3	126±11
Pb	2.5±0.1	121±11	7.9±0.3	0.7±0.1	271±4	51.6±4.1
Zn	199±1	94±2	47.7±2	425±15	392±14	38.2±2.9
Fe	62±1	8804±221	808±37	40±2	6174±177	1101±33

For Fe, the values of Kubová et al. (2004) were taken as indicative values. Concentrations in mg/kg.

Table 3
Comparison of the results of the modified BCR sequential extraction of sample SRM 2710 (mean ± standard deviation of 4 replicates) with the results from other authors

Reference [a]		Step 1	Step 2	Step 3	Step 4	Total [b]	Recovery
[1]	Zn	1290±6	1510±13	758±33	2760±48	6952±91	91
[2]	Zn	1226±25	1625±16	705±19	2874±18	6952±91	92
[3]	Zn	1320±80	1510±16	738±19	2283±46	6952±91	84
[1]	Pb	677±2	4240±75	250±13	458±29	5532±80	102
[2]	Pb	677±2	3966±23	263±14	457±4	5532±80	97
[3]	Pb	618±4	4030±78	239±7	349±2	5532±80	95
[1]	Cu	912±32	1230±22	349±9	323±5	2950±130	95
[2]	Cu	955±3	1205±11	326±3	279±3	2950±130	94
[3]	Cu	912±10	1182±32	288±5	202±1	2950±130	88
[1]	Fe	16±1	4510±311	1080±49	25400±720	33800±1000	92
[2]	Fe	16±1	5820±64	1050±10	23804±1244	33800±1000	91
[3]	Fe	19±1	4328±2	611±22	31167±44	33800±1000	107
[3]	As	13±2	445±2	23±1	95±2	626±5	92
[3]	Cd	11±0,2	5,9±0,03	1,1±0,01	2,0±0,01	21,8±0,6	93

Concentrations in mg/kg, recovery in %.
[a] [1] = Sutherland and Tack (2002), [2] = Kubová et al. (2004), [3] = This work.
[b] Certfied total concentrations.

reflect the mineralogy of the ore deposits around the village of La Calamine, which mainly consist of calamine (a mixture of smithsonite, willemite (Zn_2SiO_4) and hemimorphite ($Zn_4(Si_2O_7)(OH)_2.H_2O$) hold together with Fe-oxides and clay minerals (Dejonghe and Jans, 1983)). Samples LC3 and LC4 contained more Fe and S than LC1 and LC2 (Table 1), which is also indicated by the occurrence of Fe- and sulphide-minerals in these samples. Pyrite (FeS_2) was only detectable in the lower part of the tailing (samples LC3 and LC4), which contained enough S for all the Fe to occur as FeS_2 (pyrite and/or marcasite). Here heavy metal containing sulphides, namely sphalerite (ZnS) and galena (PbS) were also found. XRD analysis indicates that siderite

Table 4
Amount of Zn, Pb, Cd and As released in the different steps of the BCR sequential extraction procedure

	Zn	Pb	Cd	Ca	Fe	As	pH
Step 1 (n = 4)							
LC1	438±39	124±4	3±0.1	24299±468	1003±24	4±0.07	2.98
LC2	40982±940	333±8	263±4.6	46813±338	862±37	1±0.07	4.66
LC3	8166±89	1475±19	43±1.0	40871±239	2783±68	2±0.1	4.02
LC4	3345±53	177±7	92±1.4	14969±182	1900±55	5±0.1	3.03
Step 2 (n = 3)							
LC1	86±3	16278±866	0.2±0.1	1283±138	1731±50	18±0.1	1.44
LC2	6888±163	1090±64	41±0.4	6068±374	5582±342	15±0.4	1.60
LC3	8025±510	21516±3782	48±0.8	7849±1068	14303±1249	111±11	1.85
LC4	2185±102	17149±956	41±1.0	1615±32	9652±177	47±1	1.97
Step 3 (n = 2)							
LC1	1013±17	10276±220	3±4	98±15	119±9	22±1.0	ND
LC2	6397±33	16±1	20±3	451±217	7800±256	28±9.2	ND
LC3	46267±951	1793±562	154±23	1868±456	49983±516	709±1.7	ND
LC4	16020±309	1991±71	65±3	256±182	22503±279	231±49	ND
Step 4 (n = 1)							
LC1	1063	11901	1	985	12214	154	ND
LC2	2278	2148	5	689	9919	184	ND
LC3	52152	8770	118	1260	11884	1691	ND
LC4	4149	21136	5	559	28842	944	ND

The number of replicates is given between brackets. 'pH' is the pH of the extract after extraction.

and (jarosite $(KFe_3SO_4)_2(OH)_6$) , a common product of pyrite oxidation (Larsson et al., 1990), are the most abundant Fe-minerals in sample LC2 and LC1 respectively. Sulphate minerals such as anglesite and gypsum are often present in mine tailings as the result of wet-dry processes (Jambor et al., 2000).

Considering the contaminants in the mine pond sediments, Zn and Pb are the most abundant heavy metals. Very high Cd-concentrations were detected in samples LC2, LC3 and LC4, whereas the Cd-content of sample LC1 was significantly lower. No As-containing minerals could be detected with XRD-analysis, but the elevated As concentrations in samples LC3 and LC4 are most likely related with the occurrence of pyrite (Saunders et al., 1997).

3.2. Distribution of elements among the geochemical fractions

3.2.1. Certified reference materials

The BCR extraction procedure was applied on the reference materials BCR-701 and CRM483, which are characterized by relatively low total metal concentrations. Since the sediments investigated in this paper are characterized by very high total heavy metal concentrations, a certified reference material with a higher metal load, namely SRM2710, was also analysed. Metal concentrations in the last extractions step (Step 4) and recovery were only determined for SRM2710. The distribution of Zn, Pb, Cd, Ca, Fe and As among the different geochemical fractions from the BCR sequential extraction procedure is given in Tables 2 and 3.

3.2.2. Samples of the dredged mine pond tailing

Between 79% and 91% of total Ca-concentrations were released in the first extraction step (Table 4). For Fe and As, the residual fraction prevailed since more than 50% and 40% of the total Fe- and As-content respectively was released during the last step (residual fraction, step 4). In samples LC2, LC3 and LC3, a considerable amount of Fe was also extracted in step 3. Cd and Zn displayed the highest solubility. In sample LC2, more than 70% of the total Zn-content was extracted with acetic acid, whereas this was less than 20% for the other samples. Cd and Zn displayed a similar distribution between different geochemical fractions, which is usually the case in soils and sediments (e.g. Cappuyns et al., 2006b). However the acid-extractable fraction of Cd and Zn was very variable for different samples: between 11 and 80% of the total Cd-content and 13–72% of the total Zn content was extracted with acetic acid (Table 4). Pb was less soluble than Zn and Cd and mostly recovered in the residual and reducible fractions.

3.3. pH of the extracts

The pH of the extracts was measured after each extraction step to assess the influence of pH on the mobilisation of heavy metals from the sediments (Table 4). The original pH of the acetic acid solution (before extraction) was 2.3. For all the samples a significant increase in pH of the acetic acid solution was noticed, going from 0.6 pH unit for sample LC1 to 2.3 pH unit for sample LC2. The pH of the acetic acid extract was clearly related to the original pH of the sediment, since a higher sediment-pH resulted in a higher pH of the acetic acid extract and vice versa. The (partial) dissolution of carbonate phases in samples LC2 and LC3 explains for the very important increase in pH. In the second extraction step ($NH_2OH.HCl$), the increase in pH was only significant for samples LC2 and LC3 (Table 4). This pH increase was most likely caused by the dissolution of carbonate phases that were not completely dissolved in step 1.

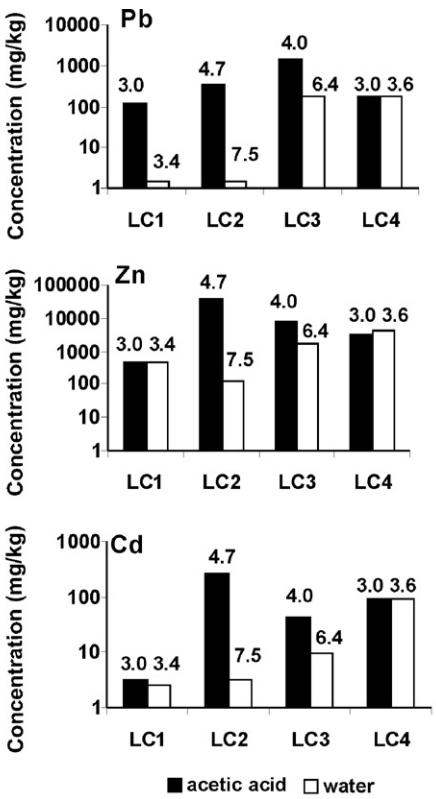

Fig. 1. Comparison of the amount of Pb, Zn and Cd extracted with water and with acetic acid. The pH of the extract is indicated on top of each graph.

3.4. Solubility of Pb, Zn and Cd in water and acetic acid

In samples with a low pH (LC1 and LC4), the amount of Zn and Cd extracted with acetic acid was only slightly higher than the amount of Zn and Cd extracted with water (Fig. 1). pH played on important role here, since the pH of the acetic acid solution is only slightly lower than the pH of the water extract (Fig. 1). In general, the release of Pb in acetic acid is much more important than in water, except for sample LC4.

4. Discussion

4.1. Quality control of the data of sequential extractions

4.1.1. Certified reference materials

4.1.1.1. Accuracy and precision. In the certified reference materials developed for the BCR sequential extraction procedure (BCR-701 and CRM483) the experimental precision was very satisfactory, with relative standard deviations for all elements below 10%. Accuracy was also satisfactory, since the values obtained in this study differed less than 2 standard deviations from certified (BCR-701) or indicative (CRM483) values (Table 2).

For the certified reference material with a higher total metal content (SRM 2710), no certified values are available for the BCR sequential extractions procedure. Therefore we will compare our results with the results of Sutherland and Tack (2002) and Kubová et al. (2004), who applied the modified BCR sequential extraction procedure to this reference material. Although As and Cd were not investigated by these authors, the results for As and Cd are also reported because it are very important contaminants in many soils and sediments. It has to be mentioned that several authors published the results of other sequential extraction schemes (Li et al., 1995; Hall et al., 1996) or from the original BCR sequential extraction scheme (Ho and Evans, 1997) for SRM 2710. Although Hall et al. (1996) tried to compare the results of different extraction schemes for SRM 2710, it is clear that intercomparison between different researchers is only possible when exactly the same extraction procedure is followed.

As can be seen from Table 3, a reasonable agreement is found between our results and the results of Sutherland and Tack (2002) and Kubová et al. (2004).

4.1.1.2. Recovery. The recovery was calculated by dividing the sum of the concentrations of an element in the 4 extractions steps by the total concentration. The recovery for the reference materials (Table 3) is sometimes too low because the metals in Step 4 were determined by the 3-acid dissolution method, in which a small part of the sample (few %) is not dissolved. When the recovery is calculated with total concentrations obtained with our method, a recovery around 100% is obtained.

For the samples from La Calamine (Table 5), the recoveries were in the range 90–110% ([step 1 + step 2 + step 3 + step 4]/total concentration × 100) In 75% of the cases. A poor recovery can be explained by the washing with water between two extraction steps. It is likely that the water (from washing with water between two extractions), which is discarded after extraction, can contain a significant amount of metals. This could explain why, in the present study, the recovery was systematically too low for Ca. Another reason for inferior extraction variability and recovery, especially in made-up materials such as contaminated ground from industrial sites could relate to subsample heterogeneity (Van Herreweghe et al., 2003).

4.2. Extractability of major- and trace elements from sediment samples

4.2.1. Influence of the pH and acid neutralizing capacity on the extractability of elements

Sahuquillo et al. (1999) showed that pH was of paramount importance for the extractability of heavy metals in the second step of the BCR sequential extraction scheme. Whereas Cd and Zn are less sensitive to pH-variations, the extractability of Pb, Cu and Cr dramatically decreases when the pH of the extract increases. Sample LC2 is characterized by an elevated acid neutralizing capacity, which results in a relatively high pH (almost 5) for the (first) acetic acid extract (Fig. 2). After 3 consecutive extractions with acetic acid, the pH decreased to a value of approximately 3 (Fig. 2), which is comparable with the pH of the acetic acid solutions of samples LC1 and LC 4 after 1 extraction (Table 4). For sample LC3, even 5 extractions with acetic acid were necessary to reach a pH of 3. Repetition

Table 5
Recovery (%) of Zn, Pb, Cd, Fe, Ca and As. (Recovery = ([step 1 + step 2 + step 3 + step 4]/total concentration) × 100)

	Zn %	Pb %	Cd %	Fe %	Ca %	As %
LC 1	103	99	94	52	51	111
LC 2	83	85	90	97	86	92
LC 3	106	106	119	110	67	110
LC 4	105	109	94	106	98	103

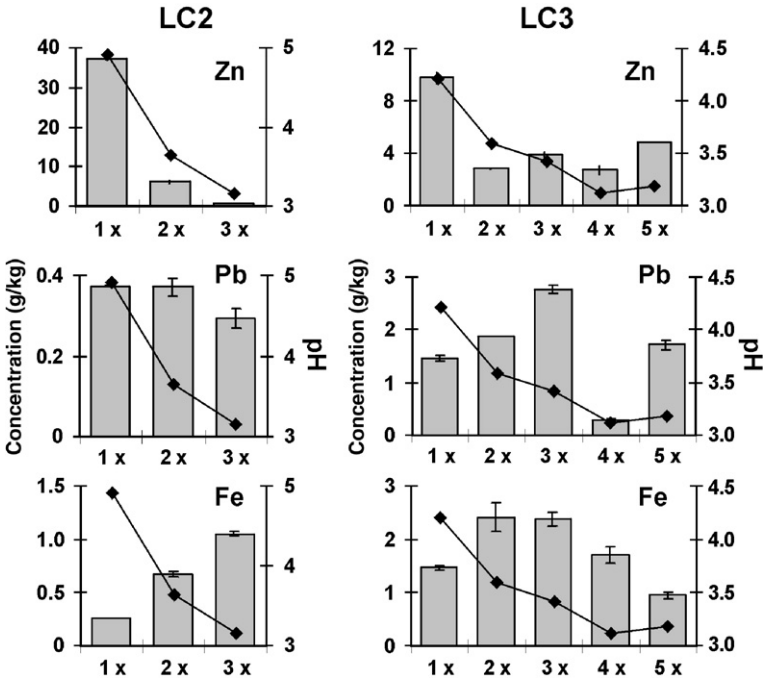

Fig. 2. Release of Zn, Pb and Fe during the 3 (sample LC2) or 5 (sample LC3) successive extractions with 0.11 M acetic acid and pH of the extracts.

of the acetic acid extraction is especially important for Pb and Fe (Fig. 2). It may indicate that Pb-minerals were not completely dissolved after the first extraction with acetic acid, and/or that there was a redistribution of Pb as a consequence of binding to other matrix components. Similar observations were made in carbonate-rich dredged river sediments (Cappuyns et al., 2004, 2006b).

4.2.2. Dissolution of mineral phases: geochemical versus mineralogical data

The dissolution of mineral phases from the disposed pond sediments was assessed by X-ray diffraction analysis of sediments after different extraction steps and by taking into account (thermodynamic) data concerning the solubility of minerals. Since almost all the minerals that were identified in the four samples are represented in samples LC2 and LC3, only the X-ray diffraction patterns of samples LC2 and LC3 are given (Figs. 3 and 4). Notice that some of the minerals in Table 1 were present in heavy mineral concentrates and their presence can not be deduced from the X-ray diffraction pattern of the bulk samples in Figs. 3 and 4.

4.2.2.1. Sulphate minerals. After the first extraction step, *gypsum* is completely dissolved in all the samples (Fig. 3). Since *anglesite* is easily soluble, the first extraction is often the most important fraction for Pb in anglesite. For example, water or diluted salt solutions are capable to extract anglesite from dust particles and roadside soils (Harrison et al., 1981; Clevenger et al., 1991). However, the first step of the BCR extraction procedure (HOAc 0.11M) seems less effective in extracting anglesite from the La Calamine samples. Relatively small Pb-concentrations (between 124 and 1475 mg/kg) were released from the four samples and anglesite was still detected with XRD after the first extraction step (Fig. 4 for sample LC3). Giordano (1989) measured the solubility of anglesite in buffered acetate solutions (pH ≈ 5) and found that, above free acetate concentrations of 0.01 M, anglesite solubility sharply increases to concentrations near 1000 mg/L. However, the pH of the acetate solution used in the BCR sequential extraction is 2.3, which explains for the low solubility of anglesite. In sample LC1, anglesite was further removed after the reducing extraction step. In an investigation of Fonseca and Martin (1986), part of the anglesite was also dissolved during the reducing extraction because of the relative high acidity of the $NH_2OH.HCl$ solution. Nevertheless, in sample LC3, anglesite and gypsum appeared again after oxidation with H_2O_2 (Step 3). Possibly sulphate was generated by the oxidation of sulphur and precipitated as $PbSO_4$ (anglesite) and $CaSO_4.2H_2O$ (gypsum).

Jarosite is formed by precipitation from acid mine drainage solutions at pH < 2.8 (Bigham et al., 1996) and is only stable below pH 7 (Welham et al., 2000).

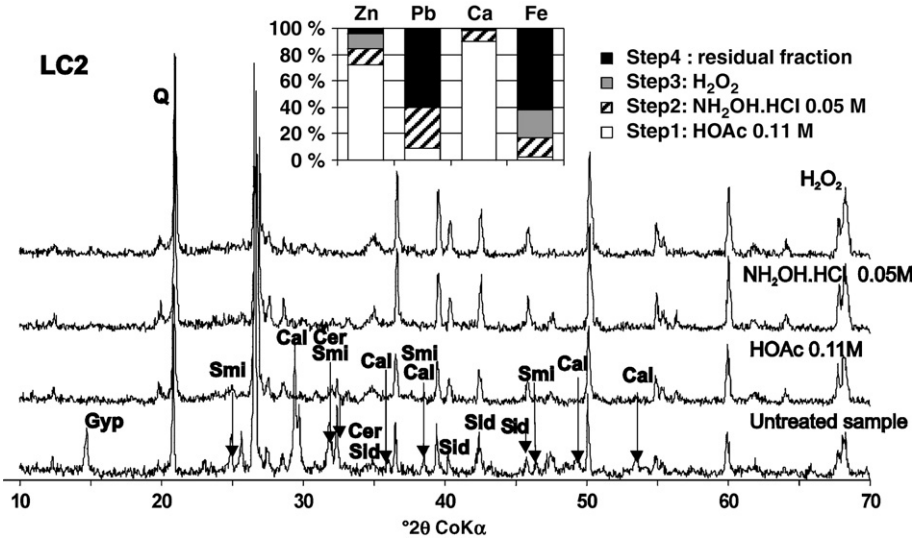

Fig. 3. Fractionation of Zn, Pb, Ca and Fe in sample LC2 and XRD spectrum of sample LC2 after the different steps of the BCR sequential extraction. Gypsum (gyp), calcite (cal), smithsonite (smi) and cerussite (cer) are dissolved in step 1 (HOAc), but siderite (sid) is still present after extraction with H_2O_2. Q = quartz.

However, jarosite can dissolve at low pH (pH 2) in the presence of sulphuric acid (Smith et al., 2006). In the present study, the pH of the acetic acid extract was higher than 2 (Table 4) and XRD analysis showed that jarosite disappeared from sample LC 1 after extraction Step 2 ($NH_2OH.HCl$). The reducing conditions created by this reagent seem to have contributed to the dissolution of jarosite. In a study of Dold (2003), jarosite was also dissolved from Cu-bearing waste after reduction with ammonium oxalate.

4.2.2.2. Carbonate phases. In sample LC2, *calcite* and *smithsonite* are almost completely dissolved in the first extraction step (Fig. 3). None of the reagents used in the BCR sequential extraction is capable of completely dissolving *siderite* (Fig. 3). Thermodynamic calculations with the speciation code MINTEQA2 (Allison et al., 1999) indicate that the solubility of siderite sharply increases at pH-values below pH 3.5. Whereas the limited dissolution of siderite in Step 1 (acetic acid extraction) can be attributed to the too high pH (pH 4,

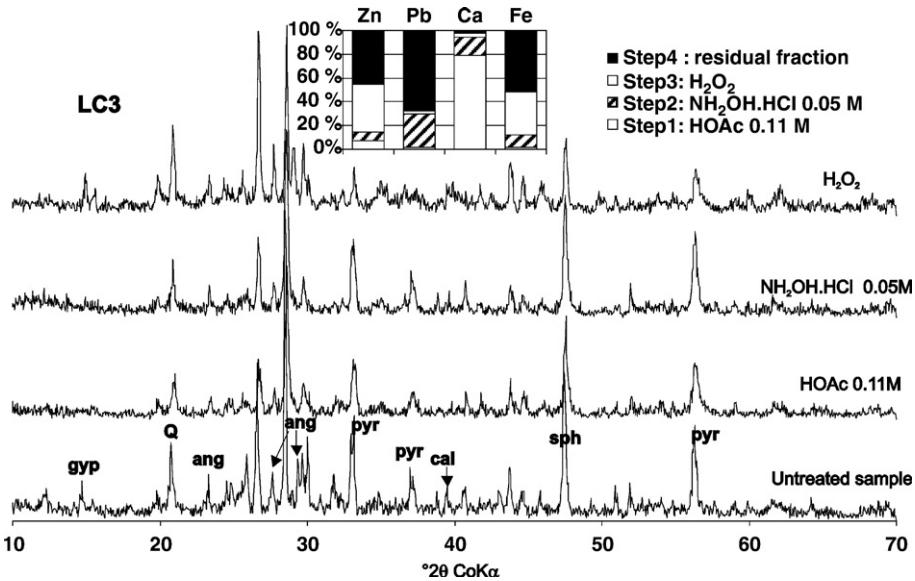

Fig. 4. Fractionation of Zn, Pb, Ca and Fe in sample LC3 and XRD spectrum of sample LC3 after the different steps of the BCR sequential extraction. Gypsum (gyp) and calcite (cal) are dissolved in step 1 (HOAc), but anglesite (ang), pyrite (pyr) and sphalerite (sph) are still present after extraction with H_2O_2.

Table 4) of the solution, this is not the case for extraction step 2, where pH is 1.4. Even during the oxidising step (Step 3), siderite is not completely dissolved. Kinetic limitations might explain the limited solubility of siderite. Skousen et al. (1997) mentioned that the determination of the neutralizing potential of siderite samples especially requires H_2O_2 treatment to accelerate iron oxidation, and may require more H_2O_2 and retitration to reach a stable endpoint. In the study of Fanfani et al. (1997), most of the siderite from a mine tailing material was recovered in the reducible fraction (extracted with a 0.04 M $NH_2OH.HCl$ solution in 25% acetic acid).

4.2.2.3. Sulphidic phases. The important amount of Fe released in the oxidisable fraction (H_2O_2, Step 3) and in the residual fraction (Step 4) is consistent with the occurrence of Fe-sulphides (pyrite, marcasite) in samples LC3 and LC4 (Table 4). The X-ray diffraction pattern of sample LC3 (Fig. 4) indicates that *sphalerite* (ZnS), *pyrite* (FeS_2) and *marcasite* (FeS_2) are not completely dissolved by H_2O_2. This is consistent with the results of Fonseca and Martin (1986), who performed sequential extractions on pure Pb- and Zn-minerals.

Nevertheless, the intensity of the peaks of pyrite and sphalerite decreases after the H_2O_2 extraction and a considerable amount of Zn and Fe is released during Step 3 (Fig. 4), indicating a partial dissolution of these minerals. Both in samples LC3 and LC4, *galena* (PbS) is dissolved after the oxidizing extraction step (Fig. 4). However, almost no Pb was found in the solution after the H_2O_2 extraction. The precipitation of Pb as $PbSO_4$ is a potential artefact that might explain why almost no lead is found after oxidation with H_2O_2, despite the fact that galena has disappeared from the sample.

For all the samples, the dissolution of Fe in Step 2 ($NH_2OH.HCl$) was also relatively low (Table 4). Davidson et al. (2004) investigated the use of ammonium oxalate as an alternative for the hydroxylammoniumchloride ($NH_2OH.HCl$) in step 2 of the BCR sequential extraction. Although ammonium oxalate provides a more complete dissolution of Fe-bearing phases than hydroxylammoniumchloride, it is not an adequate reagent for the samples of the present study because of the potential rapid precipitation of Ca- and Pb-oxalates.

4.2.3. Solubility of Pb, Zn and Cd in water and acetic acid: geochemical versus thermodynamic data

Since anglesite displays a lower solubility at acid pH-values than at neutral and alkaline pH, it was interesting to compare the solubility of Pb in acetic acid and water. Thermodynamic calculations with MINTEQA2 indicated that the water extracts of sample LC4 was only slightly oversaturated with respect to $PbSO_4$ (anglesite), suggesting equilibrium conditions between soluble and solid phase. The water extract of sample LC2 was supersaturated for several Pb-containing minerals. Anglesite (SI = 0.743, SI = saturation index), hydrocerussite (SI = 6.066) and cerussite (SI = 1.911) are often involved in the precipitation of Pb from aqueous solutions (Marani et al., 1995).

Other Pb-sulphate and Pb-hydroxide minerals with a positive saturation index were $Pb_4(OH)_6SO_4$ (SI = 2.063), $Pb_3O_2SO_4$ (SI = 1.869), $PbSO_4.PbO$ (SI = 3.169) and $Pb(OH)_2$ (SI = 1.558). According to literature data, $PbSO_4.PbO$ and $Pb(OH)_2$ (SI = 1.558) are difficult to form by direct precipitation from solution at room temperature, due to kinetic limitations (Marani et al., 1995).

Normally the release of Pb in acetic acid is much more important than in water, except for sample LC4. When acetic acid is added to sample LC4, only a small decrease in pH is observed (From 3.6 to 3.0, Tables 1 and 4) and a slight increase in the release of Pb. On the one hand, anglesite precipitates when pH decreases, on the other hand, the formation of acetate and sulphate complexes keeps Pb in solution.

Calmano et al. (2001) also observed the unexpected dissolution of $PbSO_4$ from a soil extracted with ammonium acetate and Na acetate (pH 5), due to the formation of easily soluble complexes with acetate anions of the extractant. Since Pb-acetate has a solubility of 44.3 g/L in water (20 °C) (Lide, 2005), there was no precipitation of Pb-acetate for any of the 4 samples.

4.3. Implications for reactions in mine environments

From an environmental point of view, data obtained with sequential extractions can be helpful to assess the risk associated with the heavy metal burden in the mine tailing. Since the dredged mine tailing pond sediments contain significant amounts of sulphide-bearing minerals, they represent a potential source of acid mine drainage, which would increase the release of heavy metals into the environment. The physico-chemical conditions and reactions occurring during sequential extractions can be considered as a worst-case simulation of physico-chemical processes (acidifications, oxidation, …) in nature. The very limited and incomplete oxidation of sulphides by H_2O_2 indicates that the minerals in the mine tailing of La Calamine are not likely to cause acid mine drainage. Moreover, in some parts of the tailing, the carbonate minerals can buffer the acidity produced by the oxidation of sulfidic minerals.

5. Conclusions

5.1. A combined geochemical-mineralogical approach

The modified BCR sequential extraction procedure was applied to dredged sediments from a mine tailing pond. A very different behaviour of different samples in front of the same scheme was observed. Although the BCR sequential extraction procedure was no meant to study trace metal binding to mineralogical fractions, the combination of sequential extractions with mineralogical sample investigation provided information on the reactivity and solubility of minerals in the samples. This improved the interpretation of the results of the sequential extractions for sediments in which minerals were identified, at least within the detection limits of the mineralogical analysis applied. Besides the enhanced effectiveness of the BCR scheme in providing a geochemical–mineralogical comparison, the information concerning the reactivity of minerals is an important tool to evaluate the risk associated with contaminated sediments.

5.2. Certified reference materials

Although much effort has been made to provide certified reference materials for the BCR sequential extraction procedure, only reference materials with relatively low total heavy metal concentrations are yet available. Certified reference materials with higher total metal concentrations would be a better reference for soils and sediments with a higher metal load, as was the case in the present investigation. Although several authors published results of sequential extractions for the certified reference material SRM 2710 (NIST), which contains elevated Cu-, Pb- and Zn-concentrations, the same procedure is not always followed, making intercomparison difficult. There is clearly a need of certified values for this (or another highly contaminated) reference material. A certification campaign, in which the BCR extraction procedure is tested in an interlaboratory exercise would therefore be very useful.

According to the official BCR sequential extraction procedure, only the element concentrations released in the different extraction steps have to be mentioned. However, our results show that other parameters, such as the (final) pH of the extract can have a paramount influence on the results. Therefore, we would recommend to mention the pH of the CH_3COOH extract and eventually also of the $NH_2OH{\cdot}HCl$ extract. Additionally, the release of major matrix elements such as Ca and Fe can provide information concerning the dissolution of matrix-components. These parameters (pH, major elements) could also be included in the development of a new certified reference material for the BCR sequential extraction scheme.

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References

Allison, J.D., Brown, D.S., Novogradac, K.J., 1999. MINTEQA2/PRODEFA2, a Chemical Assessment Model for Environmental Systems: Version 4.0 User's Manual. Environmental Research Laboratory Office of Research and Development, US-EPA, Athens.

Bigham, J.M., Schwertmann, U., Pfab, G., 1996. Influence of pH on mineral speciation in a bio-reactor simulating acid mine drainage. Appl. Geochem. 11, 845–849.

Brockhoff, C.A., Creed, J.T., Martin, T.D., Martin, E.R., Long, S.E., 1999. EPA Method 200.8, Revision 5.5: Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, EPA-821R-99-017, October 1999. 61 pp.

Calmano, W., Mangold, S., Welter, E., 2001. An XAFS investigation of the artefacts caused by sequential extraction analysis of Pb-contaminated soils. Fresenius' J. Anal. Chem. 371, 823–830.

Cappuyns, V., Swennen, R., Verhulst, J., 2004. Assessment of acid neutralizing capacity and potential mobilisation of trace metals from land-disposed dredged sediments. Sci. Total Environ. 333 (1–3), 233–247.

Cappuyns, V., Swennen, R., Vandamme, A., Niclaes, M., 2006a. Environmental impact of the former Pb–Zn mining and smelting in East-Belgium. J. Geochem. Explor. 88, 6–9.

Cappuyns, V., Swennen, R., Verhulst, J., 2006b. Assessment of heavy metal mobility in dredged sediments: porewater analysis, single and sequential extractions. Soil Sediment Contam. 15 (2), 169–186.

Clevenger, T.E., Saiwan, C., Koirtyoham, S.R., 1991. Lead speciation of particles on air filters collected in the vicinity of a lead smelter. Environ. Sci. Technol. 25, 1128–1133.

Davidson, C.M., Duncan, A.L., Littlejohn, D., Ure, A.M., Garden, L.M., 2000. A critical evaluation of the three stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially contaminated land. Anal. Chim. Acta 363, 45–55.

Davidson, C.M., Hursthouse, A.S., Tognarelli, D.M., Ure, A.M., Urquhart, G.J., 2004. Should acid ammonium oxalate replace hydroxylammonium chloride in step 2 of the revised BCR sequential extraction protocol for soil and sediment? Anal. Chim. Acta 5058 (2), 193–199.

Dejonghe, L., Jans, D., 1983. Les gisements plombo-zincifères de l' Est de la Belgique. Cron. Rech. Min. 470, 3–24 BRGM, Orléans.

Dhoum, R.T., Evans, G.J., 1998. Evaluation of uranium an arsenic retention by soil from a low level radioactive waste management site using sequential extraction. Appl. Geochem. 13 (4), 415–420.

Dold, B., 2003. Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulphide mine waste. J. Geochem. Explor. 80, 55–68.

Fanfani, L., Zuddas, P., Chessa, A., 1997. Heavy metal analysis as a tool for studying mine tailings weathering. J. Geochem. Explor. 58, 241–248.

Fonseca, E.C., Martin, H., 1986. The selective extraction of Pb and Zn in selected mineral and soil samples, application in geochemical exploration (Portugal). J. Geochem. Explor. 26 (3), 231–248.

Gillis, T.E., 1997. Certificate of Analysis Standard Reference Material 2710 Montana Soil (highly elevated trace element concentrations). National Institute of Standards and Technology, Gaithersburg, MD. 5 pp.

Giordano, T.H., 1989. Anglesite ($PbSO_4$) solubility in acetate solutions: the determination of stability constants for lead acetate complexes to 85°C. Geochim. Cosmochim. Acta 53 (2), 358–366.

Gómez Ariza, J.L., Giráldez, I., Sánchez-Rodas, D., Morales, E., 2000a. Comparison of the feasability of three extraction procedures for trace metal partitioning in sediments from south-west Spain. Sci. Total Environ. 246, 271–283.

Gómez Ariza, J.L., Giráldez, I., Sánchez-Rodas, D., Morales, E., 2000b. Selectivity assessment of a sequential extraction procedure for metal mobility characterization using model phases. Talanta 52, 545–554.

Gruebel, K.A., Davis, J.A., Leckie, J.O., 1988. The feasibility of using sequential extraction techniques for arsenic and selenium in soils and sediments. Soil Sci. Soc. Am. J. 52, 390–397.

Hall, G.E.M., Gauthier, G., Pelchat, J.C., Pelchet, P., Vaive, J.E., 1996. Application of a sequential extraction scheme to ten geological certified reference materials for the determination of 20 elements. J. Anal. At. Spectrom. 11, 787–796.

Harrison, R.M., Laxen, D.P.H., Wilson, S.J., 1981. Chemical association of lead, cadmium, copper and zinc in street dust and road side soils. Environ. Sci. Technol. 15, 1378–1383.

Ho, M.D., Evans, G.J., 1997. Operational speciation of Cadmium, Copper, Lead and Zinc in the NIST standard reference materials 2710 and 2711 (Montana Soil) by the BCR sequential extraction procedure and flame atomic adsorption spectrometry. Anal. Commun. 34, 363–364.

Howard, J.L., Vandenbrink, W.J., 1999. Sequential extraction analysis of heavy metals in sediments of variable composition using nitrilo-triacetic acid to counteract readsorption. Environ. Pollut. 106, 285–292.

Jambor, J.J., Nordstrom, D.K., Alpers, C.N., 2000. Metal-sulfate salts from sulphide mineral oxidation. In: Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (Eds.), Sulphate minerals: Chrystalography, Geochemistry and environmental Significance, vol. 40. Mineralogical Society of America and Geochemical Society, Washington, D.C., pp. 303–350.

Joksi, A.S., Katz, S.A., Horvat, M., Radmila Milacic, R., 2005. Comparison of single and sequential extraction procedures for assessing metal leaching from dredged coastal sediments. Water Air Soil Pollut. 162 (1–4), 265–283.

Kubová, J., Streško, V., Bujidoš, M., Matúš, P., Medveď, J., 2004. Fractionation of various elements in CRMs and in polluted soils. Anal. Bioanal. Chem. 379, 108–114.

La Force, M.J., Fendorf, S., 2000. Solid-phase iron characterization during common selective sequential extractions. Soil Sci. Soc. Am. J. 64, 1608–1615.

Larsson, L., Olsson, G., Holst, O., Karlsson, H.T., 1990. Pyrite oxidation by thermophilic archaebacteria. Appl. Environ. Microbiol. 56 (3), 697–701.

Li, X., Coles, B.J., Ramsey, M.H., Thornton, I., 1995. Chemical partitioning of the new national institute of standard reference materials (SRM 2709-2711) by sequential extraction using inductively coupled plasma atomic emission spectrometry. Analyst 120, 1415–1418.

Lide, D.R., 2005. In: Lide, D.R. (Ed.), Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data. CRC press, Boca Raton.

Marani, D., Macchi, G., Pagano, M., 1995. Lead precipitation in the presence of sulphate and carbonate: testing of thermodynamic predictions. Water Res. 29 (4), 1085–1092.

Maiz, I., Esnaola, V., Millán, E., 1997. Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. Sci. Total Environ. 206, 107–115.

McAndrew, J., 1957. Calibration of a Franz isodynamic separator and its application to mineral separation. Proc. Australas. Inst. Min. Metall. 181 (1957), 59–73.

Nirel, P.M.V., Morel, F.M.M., 1990. Technical note: pitfalls of sequential extractions. Water Res. 24 (8), 1055–1056.

Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, Ph., López-Sánchez, J.F., 2001. Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimized three-step sequential extraction procedure. J. Environ. Monit. 3, 243–250.

Quevauviller, Ph., 1998. Operationally defined extraction procedures for soil and sediment analysis: I. Standardization. Trends Anal. Chem. 17 (5), 289–298.

Rauret, G., López-Sanchez, J., Sauquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to certification of new soil and sediment reference materials. J. Environ. Monit. 1, 57–60.

Ruaret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, A., Muntau, H., Quevauviller, Ph., 2000. Indicative values for extractable contents (mass fractions) of Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge amended soil (CRM 483) following the modified BCR-sequential extraction procedure (addendum to EUR-report 17127 EN). European Commission, BCR information, Reference materials. EUR 19503 EN. 22 pp.

Rauret, G., Lopez-Sanchez, J.F., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, Ph., 2001. The certification of the extractable contents (mass fractions) of Cd, Cr, Cu, Pb and Zn in freshwater sediment following a sequential extraction procedure BCR-701. European Commission, BCR information, Reference materials. EUR 19775 EN. 82 pp.

Rendell, P.S., Batley, G.E., Cameron, A.J., 1980. Adsorption as a control of metal concentrations in sediment extracts. Environ. Sci. Technol. 14 (3), 314–318.

Sahuquillo, A., López-Sanchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., Ure, A.M., 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. Anal. Chim. Acta 382, 317–327.

Saunders, J.A., Pritchett, M.A., Cook, R.B., 1997. Geochemistry of biogenic pyrite and ferromanganese coatings from a small watershed: A bacterial connection? Geomicrobiol. J. 14 (3), 203–217.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., Ziemkiewicz, P., 1997. Neutralization potential of overburden samples containing siderite. J. Environ. Qual. 26, 673–681.

Smith, A.M.L., Hudson-Edwards, K.A., Dubbin, W.E., Wright, K., 2006. Dissolution of jarosite [Kfe3(SO4)2(OH)6] at pH 2 and

8: insights from batch experiments and computational modeling. Geochim. Cosmochim. Acta 70, 608–621.

Sutherland, R.S., Tack, F.M.G., 2002. Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. Anal. Chim. Acta 454, 249–257.

Tessier, A., Campbell, P.G.C., 1988. Comments on the testing of the accuracy of an extraction procedure for determining the partitioning of trace metals in sediments. Anal. Chem. 60, 1475–1476.

Tessier, A., Campbell, P.G.C., 1991. Comment on 'pitfals of sequential extractions' by P.M.V. Nirel and F.M.M. Morel. Water Res. 24, 1055–1056.

Tipping, E., Hetherington, N.B., Hilton, J., Thompson, D.W., Bowles, E., Hamilton-Taylor, J., 1985. Artifacts in the use of chemical extraction to determine distributions of metals between oxides of manganese and iron. Anal. Chem. 57, 1944–1946.

Ure, A., Quevauviller, Ph., Munteau, H., Griepink, B., 1993. Improvements in the determination of extractable contents of trace metals in soils and sediments prior to certification. Community Bureau of reference, Commission of the European Communities.

Van Herreweghe, S., Swennen, R., Vandecasteele, C., Cappuyns, V., 2003. Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. Environ. Pollut. 122 (3), 323–342.

Vogel, A.I., 1961. Nephelometric determination of sulfate. Quantitative Inorganic Analysis, pp. 850–851.

Welham, N.J., Malatt, K.A., Vukcevic, S., 2000. The stability of iron phases presently used for disposal from metallurgical systems—A review. Miner. Eng. 13 (8–9), 911–931.