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“Acid extractable” metal concentrations in solid matrices: a comparison and evaluation of operationally defined extraction procedures and leaching tests

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Abstract

Different frequently used methods to determine the influence of acid conditions on heavy metal release from soils, sediments and waste materials, namely pH_{stat} leaching tests and acid extractions with acetic acid (0.11 M and 0.43 M) and sodium acetate (1 M)) were compared for 30 samples (soils, sediments and waste materials) with different physico-chemical properties and a different degree of contamination. No distinct relationship was found between physico-chemical sample characteristics, total element concentrations and acid-extractable metal concentrations in the present dataset due to the very different physico-chemical and mineralogical characteristics of the samples and the different contamination history.

pH played an important role in explaining the release of metals from the contaminated soils, sediments and waste materials. The pH-shift after extraction with the different acetic acid solutions (0.11M and 0.43 M) was both explained by the initial pH of the sample and its acid neutralizing capacity. The pH of the NaOAc extract was well buffered and the release of elements from solid matrices by NaOAc was both the result of the complexation with acetate and pH (pH = 5). Generally, a linear correlation was found between the amount of Zn, Cd extracted by HOAc 0.11 M, HOAc 0.43 M and NaOAc 1 M. The amounts of Zn and Cd extracted with acetic acid (0.11 M and 0.43 M) were often comparable with amounts of respectively Zn and Cd released during pH_{stat} leaching at pH 4. However, For Cu, Pb and As, it was often not possible to relate the results of a pH_{stat} leaching tests to the results of single extractions with acetic acid solutions.

Key words: acidification, extractions, leaching, pH_{stat}, pollution

Abbreviations: ANC: acid neutralizing capacity, BCR: Community Bureau of Reference, CEC: cation exchange capacity, CEN: Comité Européen de Normalisation, HOAc: acetic acid, NaOAc: sodium acetate, L/S: liquid/solid ratio, SM&T: Standards Measurements and Testing Program

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1 Introduction

The pH is one of the key parameters that determine heavy metal mobility in soils and sediments. The influence of a pH-decrease on element release from soils, sediments and waste materials can be assessed by means of extractions with acid solutions (for example in single and sequential extractions) or by pH_{stat} titrations. In many respects leaching behaviour as reflected by the single and sequential extractions, pH_{stat} leaching test and related characterisation leaching tests provide a better means of assessing environmental impact than analysis of total composition. Although column tests

give a better simulation of field conditions than batch tests (e.g. more realistic L/S ratio, laminar instead of turbulent flow), column tests require a more sophisticated equipment than batch tests and usually they last much longer than batch tests.

1.1 Single extractions

Single extractions represent a relatively fast, cheap and simple way to assess heavy metal mobility in contaminated soils and sediments. Depending on the objectives of the extraction, water, diluted salt solutions or stronger reagents such as EDTA (ethylenediaminetetraacetic acid) are used. Single extractions are also widely applied in soil science for the quantification of the amount of Fe- and Al-oxides in soils. Within the framework of harmonisation of leaching procedures for risk assessment of heavy metals in soils, the Standards Measurements and Testing Program (SM&T) of the European Commission performed an extensive collaborative study, which resulted in the selection of HOAc 0.43 M ('mobilisable fractions', indicate the 'potential availability') as a soil extractant to estimate the influence of acidifications on element release of soils and sediments [1]. The extraction with **HOAc** 0.43 M allows an estimation of the metal fraction remobilized after acidification of the soil to the pH of the extractant [2].

1.2 Sequential extractions

Sequential extractions provide semi-quantitative information on element distribution between operationally defined geochemical fractions. Therefore, the fractions obtained from sequential extractions 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) [3]. Although leaching techniques such as column leaching 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 the eighties and the beginning of the nineties, the Tessier sequential extraction scheme [4] was probably the best known and most applied extraction scheme. Moreover, numerous modifications have been made to the original procedure ([5],[6],[7]).

Standardisation of sequential extraction procedures is the only way to achieve comparability when using sequential extractions [8]. 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 [9],[10]. 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 [11]. 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.

NaOAc 1 M, acidified to pH 5 and HOAc 0.11 M are the most widely used reagents to determine 'acid extractable metal concentrations in sequential extractions schemes: NaOAc is used to determine the 'carbonate fraction' in the Tessier sequential extraction procedure, whereas the first step of the BCR sequential extraction procedure consists of an extraction with HOAc (0.11 M). In recent years, attempts to improve sequential extractions towards higher selectivity and higher operational efficiency have been made. One of the major parameters that influence the selectivity of reagents during sequential extractions, is the pH of the extracts. CH₃COOH 0.11M (Fraction 1 in the BCR sequential extraction scheme) is supposed to release 'exchangeable' elements and to dissolve some poorly crystalline hydroxy- and carbonate-metal phases [12]. It is of major concern that this extraction is as complete as possible since pH and changes in pH during extractions are key parameters that determine the potential redistribution of trace elements during extractions [13].

1.3 pH_{stat} leaching tests

Different types of test are available to assess pH dependent leaching. In the United States, the TCLP (Toxicity Characteristic Leaching Procedure) is commonly used to determine the toxicity characteristics of a material. The TCLP is a batch test in which the size-reduced material is leached with acetic acid at a L/S ratio of 20 for 18 hours. This test is less suited to estimate metal release over a long period of time, especially since the extraction time for a TCLP is arbitrarily chosen (18 h). Moreover, leaching is addressed at only one pH value.

Although buffer solutions represent a simple way to assess heavy metal mobility as a function of pH (e.g. [14]), buffer components can induce heavy metal complexation, resulting in unusually high leaching [15]. Manual titrations are rather unpractical and require some knowledge of the acid neutralizing capacity of the sample. Cremer and Obermann [16] introduced a computer-based titration system allowing continuous registration and fine-tuning of pH during leaching experiments. In the nineties, the CEN (Comité Européen de Normalisation; [17]) started with the harmonisation of new European leaching tests, partly based on existing leaching tests. The pH dependence leaching test (PrEN 14429), which has been developed by the Network for the Harmonisation of Leaching/Extraction Tests (SMT-CT96-2066) and which is currently being standardized within the CEN framework (CEN-TC292/WG6), consists of parallel extractions of the material at a Liquid/Solid ratio of 10 (L/kg) for 48 h at a series of pre-set pH values. The pH_{stat} test is used for the characterisation of waste materials and building materials.

The aim of this study was to compare and to evaluate different methods to determine the influence of acid conditions on heavy metal release from soils, sediments and waste materials. Therefore, extractions with NaOAc (1 M, pH 5), HOAc (0.11 M), HOAc (0.43 M) and pH_{stat} titrations (at pH 2, 4 and 6) were carried out on 30 samples (soils, sediments and waste materials) with different physico-chemical properties and a different degree of contamination

Our objectives were to

- investigate the mobilization of Cd, Zn, Pb, and Cu from several contaminated soils with different contamination histories in response to acidification
- compare the amounts of heavy metals mobilized by 3 conventional single batch extractions with acid solutions
- compare the amounts of heavy metals mobilized by pH_{stat} leaching experiments with the results of conventional single batch extractions.

2 Experimental

2.1 Sampling and sample pretreatment

Sampling was performed between September 2001 and September 2004. Land-disposed dredged sediments (DR) were sampled along the Leie (samples 1 to 5), Scheldt (samples 6 to 8) and Grote Beek (sample 10) rivers (Flanders, North Belgium) by augering and digging of profile pits. Alluvial soil samples (AS) were taken from overbank sediment profiles along the Grote Beek (North-Belgium, samples 11, 12), Grote Laak (North-Belgium, sample 14) and Geul (East-Belgium, samples 17 to 24) rivers. River sediments (RS) from the Upper Scheldt river (sample 9), the Grote Beek (sample 13) and the Grote Laak (sample 15) were sampled with a Van Veen Grab.

Surface samples from two mine tailings (MT) from the processing of Pb- and Zn-ores (sample 25 and 26) (East-Belgium), from a zinc smelter (North-Belgium) (samples 27 to 29) and from the surrounding of the zinc smelter (sample 30) were taken by augering [18]. The samples were dried in oven at 30 °C during 5 days. For the physico-chemical analysis, part of the sample was disaggregated in a porcelain mortar and sieved (<2 mm).

2.2 General sample characterisation

pH(H₂O) was measured in a soil/water suspension (1/2.5) (pH Hamilton Single pore electrode). Organic carbon was determined according to the Walkley and Black method [19]; effective cation exchange capacity (CEC) was analysed applying the 'silver thiourea method' [20],[21]. CaCO₃ content was measured with the rapid titration method [22]. The sample was treated with HCl 0,2 M, followed by a backtitration of the unreacted HCl with NaOH 0,1 M. Total element concentrations (Al, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn, Fe, Mg, Mn, K and Ca) were determined after dissolution of the samples with a mixture of 3 concentrated acids (4 mL HCl_{conc}, 2 mL HNO_{3conc} and 2 mL HF_{conc}). These solutions were analysed by AAS (Varian® Techtron AA6) for Ca, Fe, K and Al. For As, Cd, Cr, Cu, Mn, Ni, Pb and Zn a multi element analysis by ICP-MS (HP 4500 series) was carried out. A Reference Material (BCR701) and sample duplicates were used for quality assurance of the analytical data.

2.3 Apparatus

An induced Coupled Plasma Mass Spectrometer (ICP-MS, HP4500) was used for the analysis of As, Cd, Cu, Ni, Pb and Zn digests and extracts. Zn- and Pb-concentrations above 1000µg/L were measured with Flame Atomic Absorption Spectrometry (Thermo Electron Corporation S Series AA). The wavelengths selected were 213.9 nm for Zn and 217.0 nm for Pb. Detection limits for As, Cd, Cr, Cu, Ni, Pb and Zn for the different solutions are given in Table 1.

[Table 1]

Total S was determined with the Ströhlein Sulfur Analyzer (model S-mat, Carbolite Co. Ltd., Bamford-Sheffield). Grain size was determined by laser diffraction analysis (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK) after removing carbonates (0.1 M HCl), iron oxides (0,5% oxalic acid, boiling) and organic carbon (35% H₂O₂, 60°C) and applying a peptizing solution (10 g/L sodium polyphosphate, boiling). A mineralogical sample characterisation was conducted by X-ray diffraction (XRD, Philips®, Co-target, $\lambda = 1.79 \text{ \AA}$). A Beckman GS-6 centrifuge was used for the separation of the extracts. A reciprocal shaker (SM) was employed to shake the samples during extractions. For the pH-measurements, a pH Hamilton Single pore electrode was used. pH_{stat} leaching tests were performed with an automatic multititration system (Titro-Wico Multititrator®, Wittenfield and Cornelius, Bochum, Germany).

2.4 Reagents

All reagents used were of analytical grade Suprapur quality: acetic acid (Riedel-de Haën), sodiumacetate (Merck) and nitric acid (Chem-Lab).

Standard solutions for FAAS were made by serial dilution of 1000 µg L⁻¹ standard solutions (Merck) of the appropriate elements. Standard series for ICP-MS were made up starting from the "10 ppm Multi-Element Calibration Standard 2A in 5% HNO₃" from Hewlett Packard®. The spectroscopic interference of ArCl, which has the same m/z as As (75) was corrected according to the recommendations of the US Environmental Protection Agency (EPA) (method 200.8, [23]).

2.5 Extractions

The extraction with HOAc 0.11 M was performed according to the BCR sequential extraction procedure. 40 ml of a 0.11 M HOAc solution was added to 1 g of oven dry sediment. The suspension was shaken for 16 h in a reciprocal shaker, centrifuged (3500 rpm, 10 min), decanted off and filtered (0.45 µm). For the HOAc (0.43 M) extraction the protocol of the SM&T program [8] was followed. 40 ml of a 0.43 M HOAc solution was added to 1 g of oven dry sediment. The suspension was shaken for 16 h in a reciprocal shaker, centrifuged (3500 rpm, 10 min), decanted off and filtered (0.45 µm). After measurement of the pH, the HOAc and NaOAc extracts were acidified with concentrated HNO₃ to bring the pH<2. A Reference Material (CRM 483), certified for its acetic acid (HOAc 0.43 M) extractable content of Cd, Cr, Cu, Ni, Pb and Zn, was also included in quadruplicate.

An overview of the different extractions and leaching test is given in Table 2.

[Table 2]

2.6 pH_{stat} leaching tests

The pH_{stat} experiments were carried out with an automatic multtitration system (Titro-Wico Multititrator®). The samples were dried at 30°C, homogenized and sieved (< 2 mm). 80 g of the < 2 mm fraction was put in an Erlenmeyer flask together with 800 ml of distilled water and placed on a horizontal shaking device. A pH-electrode (pH Hamilton Single pore electrode) and an automatic titration dispenser were attached to each flask. The suspensions were first shaken for 30 min without addition of acid and then the titration was started. Previous experiments performed in our laboratory [24] demonstrated that the rapid addition of acid to the soil-water suspension could lead to an overpassing of the set-point pH. Therefore, the concentration of the titration solution was adapted to the set-point pH (pH 2: HNO₃ 2.5 M; pH 4: HNO₃ 1 M and pH 6: HNO₃ 0.25 M). Based on previous experiments [25], the interval of pH-acquisition was set to 200 s (instead of 1 s). By doing so, after addition of acid to the suspension, the system is given enough time to react and eventually neutralise the acid before more acid is added. After 96 h, the suspension was filtered. Part of the solution was acidified with a drop of concentrated HNO₃, whereas another part of the solution was left unaltered and the solution was put aside for analysis of anions, dissolved organic carbon (DOC) and electrical conductivity.

2.7 Statistical analysis

Statistical analysis consisting of a parametric test (t-test) and linear correlations were performed using EXCEL and SPSS software. An α -value of 0.05 was adopted at the critical level for all statistical testing giving a 95% confidence level. The possible association between variables was investigated using Varimax-rotated Principal component analysis (PCA).

3 Results and discussion

3.1 Quality control of analytical data

The quality of the analytical data was evaluated by analysing certified reference materials. The BCR701 and CRM483 Reference Materials are used for the verification of the 0.11M acetic acid extraction following the BCR extraction protocols [26]. Metal concentrations extracted with 0.43 M acetic acid were analysed for CRM 483. Total metal concentrations were also determined in two Reference Materials (BCR701 and GBW07411 soil).

3.1.1 Total metal concentrations

Total concentrations of Cd, Cr, Cu, Ni, Pb and Zn were determined in Reference Material BCR-701[27] by dissolution with 3 concentrated acids (HF, HCl and HNO₃) (Table 3).

Although the extraction procedure is different from the aqua regia extraction, the own values were within 1 standard deviation of the indicative values, except for Cu.

[Table 3]

3.1.2 Extractions

A very good accuracy was obtained for all elements since the difference between the own results and the certified values was less than one standard deviation (Table 4). It has to be mentioned that a reciprocal shaker was used instead of an end-over-end shaker. This may lead to a difference between our own results and the certified values.

[Table 4]

The Reference Material CRM 483, which was certified for the HOAc extractable contents [9], was also extracted using HOAc 0.11M (first step of the BCR sequential extraction scheme) [10], resulting in

indicative values. A very good agreement between our experimental values and indicative values (Table 3), with a difference of less than 1 standard deviation, was obtained for Cd, Cu, Cr, Ni, Pb and Zn, except for Cu in Step 1. Nevertheless, the result for the latter elements still differed less than 2 standard deviations from the indicative values.

3.2 General sample characteristics

The pH of the samples investigated in this study was in the range 4-8 (Table 5). The calcium carbonate content, which was only determined for samples with a pH above 6, was between 3.8 and 12%.

The grainsize of the samples varied from clayey to sandy and cation exchange capacity (CEC) was between 6 and 36 cmol kg⁻¹. All the samples were polluted with at least one of the following heavy metals: Zn, Cd, Pb, Cu, As and/or Ni.

[Table 5]

The possible association between variables was investigated using Varimax-rotated Principal component analysis (PCA). PCA was first applied to all the data concerning physico-chemical sample properties (pH, clay content, organic carbon content, CEC) and total element concentrations. The variables that showed deviation from normality were log-transformed. 90% of the total variance in the dataset was explained by four principal components: the first component included Zn, Cd, Pb, As and S. The second component included pH; Fe and Al was associated with the third component; and the fourth component included Cu

3.3 Extraction efficiency

In a second run, principal component analysis was applied on the complete dataset, including HOAc (0.11 M and 0.43 M) and NaOAc extractable metal concentrations. The variability in acid-extractable element concentrations, however, could not significantly be explained by total element concentrations or physico-chemical soil or sediment properties.

The lack of a distinct relationship between total and acid-extractable metal concentrations in the present dataset is due to the different physico-chemical and mineralogical characteristics of the samples. In a previous study on land-disposed dredged sediments [30], HOAc (0.11 M) extractable Zn- and Cd-concentrations were linearly correlated with total Zn- and Cd-concentrations. All the samples originated from the same river catchment and were characterised by an elevated clay and organic carbon content.

The HOAc 0.43 M solution extracted 33-94 % of the total Zn-content of the samples and 33-95% of the total Cd-content. The amount of Zn, Cd, Cu, Pb and Ni extracted with HOAc 0.11 M and NaOAc was linearly correlated with the amount of the respective metals extracted with HOAc 0.43 M (Table 6). Generally, The lowest amount of heavy metals (Zn, Cd, Cu, Pb and Ni) was released from the sediments with HOAc 0.11 M.

[Table 6]

For Cd, the highest extraction efficiency was obtained with HOAc 0.43 M, because the final pH of this solution is lower than the pH of the HOAc 0.11 M solution (the final pH of the HOAc 0.43 M solution is 0.1 to 0.8 units lower than the pH of the HOAc 0.11 M solution) and NaOAc solutions. Although Cd and Zn generally display a similar release behaviour towards pH-changes in soils and sediments, NaOAc 0.43 M was a more effective extractant for Zn than HOAc 0.43 M, whereas for Cd, HOAc 0.43 M was able to release more Cd from the samples than NaOAc., despite the fact that the pH of the NaOAc solution is generally lower than the pH of the HOAc 0.43M solution (Figure 1). Probably the more concentrated acetate solution is favourable for the formation of Zn-acetate complexes, which enhances the solubility of Zn. Although the NaOAc-extractable pool of Zn is more important than the NaOAc-extractable pool of Cd, relatively more Cd is released from the sediments when pH decreases.

For Pb, Cu and Ni, the extraction efficiency of HOAc 0.11 M and NaOAc 1 M was comparable, despite the lower pH of the HOAc 0.11 M solution. Since the pH of the NaOAc 1 M solution is well buffered and thus almost constant (on the average pH = 5.15 ± 0.06), acetate-complexation is more important in explaining Pb, Cu and Ni solubility than pH.

[Figure 1]

The high solubility of anglesite (PbSO₄) from sample 4 during the extractions with HOAc is also caused by the formation of easily soluble complexes with acetate ions. PbSO₄ dissolves in concentrated solutions of hydroxide or acetate ions. For example, Calmano et al. [31] also observed the unexpected dissolution of PbSO₄ 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⁻¹ in water (20°C) [32], there was no precipitation of Pb-acetate for this 4 samples. However, in highly contaminated samples, precipitation of species with a good solubility can occur.

3.4 Influence of sediment characteristics and the pH of the extracts on metal extractability

The pH after extractions with HOAc 0.11 M was between 2.83 and 4.41, which is up to 1.6 units higher than the original pH of the HOAc solution. For the more concentrated HOAc solution (0.43 M), this difference was even larger (2.46 to 4.10 pH units). The final pH of the HOAc (0.11 and 0.43 M) extracts was clearly dependent on the acid neutralizing capacity of the sample, since the pH increased with increasing acid neutralizing capacity (Fig. 1). Contrary, the pH of the NaOAc solution remained almost constant (between 5.05 and 5.30) and was not influenced by the acid neutralizing capacity of the samples. The acid neutralising capacity (ANC at pH 4) was related to the initial pH of the samples: samples with a high pH also displayed a higher ANC (at pH 4). Additionally, the ANC (pH 4) was also related to the Ca-content of the samples, because samples with an elevated ANC usually are characterised by a high CaCO₃ content, which is an important contributor to acid neutralizing reactions in soils and sediments.

For none of the reagents, the extractability of the metals was significantly influenced by the original pH of the sample. For a particular heavy metal, the different solubility in different samples could not directly be explained by other physico-chemical sediment characteristics such as the organic matter and clay content of the sample.

3.5 pH_{stat} leaching versus single extractions

For weakly adsorbed metals, such as Cd and Zn, the amounts released in pH_{stat} leaching experiments corresponded well with the amounts extracted. There was a log-linear correlation between the amount of Zn and Cd released at pH 4 during the pH_{stat} leaching test and the amount of respectively Zn and Cd extracted with HOAc (0.11 M and 0.43 M) (Fig. 2). Generally, more Cd was extracted with the acetic acid solutions than by the pH_{stat} leaching test at pH 4, whereas for Zn a comparable quantity was released by both methods.

For Pb and Cu, no trend was observed between the amount of these elements released by extractions with HOAc and pH_{stat} leaching test (pH 4). For most samples, more Pb and Cu was extracted with acetic acid compared to the pH_{stat} leaching test at pH 4, due to the ability of HOAc to complex these metals. In 5 samples from overbank sediments contaminated by mining and smelting activities

(samples 19-23), more was Cu released by pH_{stat} leaching at pH 4 than after extraction with acetic acid 0.11 M, despite the fact that the pH of the acetic acid extract was lower than 4 (between 2.9 and 3.5).

[Figure 2]

3.6 Influence acid neutralizing capacity (ANC)

The relationship between a pH_{stat} test and a single extraction with HOAc is highly dependent on the ANC of the sample. The final pH of the extract can therefore give an indication of the ANC and function as a kind of 'reference value' that allows comparison with a pH_{stat} test. Nevertheless, it has to be taken into account that the single HOAc extraction is performed at a higher L/S ratio than the pH_{stat} test and that HOAc is a weak acid with a certain metal-complexing capacity (especially important for Pb), while HNO_3 is a strong acid and that both acids were used at different concentrations.

In some cases, the mineralogical sample composition can also provide information concerning potential release of heavy metals upon acidification. This is illustrated by the two samples originating from two mine tailings. Sample 26 contains quartz, kaolinite, illite, smectite, calcite, gypsum, siderite and several Pb- and Zn-containing minerals (anglesite, smithsonite and cerrussite). In sample 25 troilite, arsenopyrite, willemite and magnesioferrite were detected by XRD. Because of the occurrence of many carbonate minerals in sample 26, an elevated acid neutralizing capacity could be expected. Sample 26 was characterized by a much higher acid neutralizing capacity (6311, 2368 and 366 mmol kg^{-1} at resp. pH 2, 4 and 6) than sample 25 (1838, 735 and 119 mmol kg^{-1} at resp. pH 2, 4 and 6). This is also reflected in the higher final pH of the acetic acid solutions of sample 26 (pH = 3.1 and 3.6 for the 0.11 M and 0.43 M solutions resp.) (Fig. 3b) compared to sample 25 (pH = 3.3 and 4.2 for the 0.11 M and 0.43 M solutions resp.) (Fig. 3a). The acetic acid solutions and the acetic acid salt could extract much more Pb from sample 26 than could be released in a pH_{stat} leaching test. The time-dependent release behaviour of Pb and Zn in sample 26 during pH_{stat} leaching at pH 4 (Fig. 4a) shows that a decrease in Pb-concentrations occurs after 48 h. This is most likely due to precipitation phenomena, which are not likely to occur during extractions with acetate solutions because of the formation of metal-acetate complexes. It is also clear that kinetic considerations should be taken into account: in sample 25 (Fig. 4a), Pb is released much more slowly than Zn. After 24 h of pH_{stat} leaching (which is comparable to the duration of the extraction time applied for the HOAc extractions, namely 16 h), the double amount of Zn is released compared to Pb. However, after 96h, more or less the same quantity of both elements is released at pH 4.

[Figure 3]

[Figure 4]

3.7 Behaviour of As during pH_{stat} leaching and single extractions

In general, arsenate adsorption on oxides and clays is maximal at low pH and decreases with increasing pH above pH 7 for Fe-oxides and pH 5 for clays [33]. Whereas the dissolution of clay minerals and Fe-(hydroxides) can explain the release of As at pH 2, it is not clear why As is dissolved at pH 4. The speciation of As at pH 4 (dominantly H_2AsO_4^-) and at pH 2 (both H_2AsO_4^- and H_3AsO_4), can explain why the *adsorption* of soluble As decreases as pH decreases from pH 4 to pH 2. Nevertheless, it does not explain why the *desorption* of As increases when pH decreases from pH 4 to pH 2.

Additionally, often more As is extracted by CH_3COOH than in the pH_{stat} test at pH 4 despite the lower final pH of the CH_3COOH extract. The difference between HOAc and HNO_3 as extractant is clearly shown by the behaviour of As (Fig. 5): HOAc is capable of extracting a considerable amount of As.

Even more As is extracted by HOAc than in the pH_{stat} test at pH 4, despite the lower final pH of the HOAc extract (around 3.5). Tokunaga and Hakuta [34] investigated the solubility of As from a contaminated soil with different acids. In similar concentrations, HNO_3 could extract more As from an artificially contaminated soil than HOAc. In the present study, however, the HNO_3 solution was much less concentrated than the HOAc-solutions. Besides differences in concentrations, differences in liquid/solid ratio (L/S) and in duration of the test can also explain for different results between single extractions and the pH_{stat} test. During the pH_{stat} test, the decrease in As-concentrations with time (Fig. 5) indicates that there was clearly readsorption of As, while possible readsorption phenomena during single extractions with acetic acid could not be evaluated.

[Figure 5]

5 Conclusions

- The release of metals from contaminated soils, sediments and waste materials was very variable. No distinct relationship was found between physico-chemical sample characteristics, total element concentrations and acid-extractable metal concentrations in the present dataset is due to the very different physico-chemical and mineralogical characteristics of the samples and the different contamination history.
- Nevertheless, pH plays an important role in explaining the release of metals from contaminated soils, sediments and waste materials. The pH-shift after extraction with the different acetic acid solutions was both explained by the initial pH of the sample and its acid neutralizing capacity. The pH of the NaOAc extract is well buffered. Therefore, only small pH-changes exist between extracts of samples with different ANC's. As a consequence, the extraction of elements from solid matrices by NaOAc is the result of the complexation with NaOAc and pH (pH = 5). Contrary, during HOAc extractions, the extractability of elements mainly depends on the final pH of the extract, which will be different for samples with a different composition.
- Generally, a linear correlation is found between the amount of Zn and Cd extracted by HOAc 0.11M, HOAc 0.43 M and NaOAc 1M. As can be expected, a 0.43 M HOAc solution extracts more metals than a 0.11 M HOAc solution and the pH of the 0.43 M HOAc extracts is 0.5 to 1 pH-unit lower in samples with an elevated acid neutralising capacity. In samples with a lower ANC, this difference only amounts to less than 0.5 pH units
- The amounts of Zn and Cd extracted with acetic acid (0.11 M and 0.43 M) are often comparable with amounts of respectively Zn and Cd released during pH_{stat} leaching at pH 4. Some exceptions are found in samples with a particular composition, such as waste material from mining activities. For Cu, Pb and As, it is not always possible to relate the results of a pH_{stat} leaching test to the results of single extractions with acid solution. The final pH of the CH_3COOH extract is determined by the properties (mainly ANC (acid neutralizing capacity)) of the samples. Consequently, intercomparison of the 'acid extractable fraction' for different samples is very difficult and at least the final pH of the CH_3COOH -extract should be mentioned. Nevertheless, pH_{stat} titrations, in which the pH can be kept at a constant value and in which the composition of the leaching solution (e.g., ionic strength, DOC) is known, allow a better estimation of the influence of pH on the release of heavy metals.

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Figures

Figure 1: Final pH of the different extracts as a function of the acid neutralizing capacity (ANC) of the samples.

Figure 2: Concentrations (in mg kg^{-1}) of Zn, Cd, Cu and Pb extracted with acetic acid versus concentrations released after 96 h pH_{stat} leaching at pH 4. The diagonal line on each graph is the 1:1 line.

—*— pHstat pH 4 ○ NaOAc 1 M △ HOAc 0.43 M ◆ HOAc 0.11 M

Figure 3: Release of Zn and Pb (% of total concentration) as a function of pH (determined with 96h- pH_{stat} leaching tests) compared to the amount of Pb extracted with HOAc 0.11 M, 0.43 M and NaOAc 1 M in a sample with a high (a) and low (b) acid neutralizing capacity

Figure 4: Release of Zn and Pb in samples 25 (a) and 26 (b) as a function of time during pH_{stat} leaching at pH 4

Figure 5: Time-dependent pH_{stat} leaching of As at pH 4, and CH_3COOH extractable concentrations of As in sample 25.

Tables

Table 1 Detection limits (mg L⁻¹) for As, Cd, Cr, Cu, Ni, Pb and Zn metals in different solutions

	HNO ₃ 0.1M	HOAc 0.11 M	HOAc 0.43M	NaOAc 1 M
	$\mu\text{g g}^{-1}$			
As	0.016	0.016	0.012	0.008
Cd	0.004	0.001	0.001	0.006
Cr	0.007	0.007	0.014	0.026
Cu	0.004	0.004	0.005	0.008
Ni	0.003	0.002	0.001	0.005
Pb	0.019	0.010	0.006	0.086
Zn	0.022	0.024	0.033	0.071

Table 2 Overview of the extractions and leaching test applied in this study

Extraction or leaching test	L/S (L kg ⁻¹)	Extraction time	Reference
NaOAc 1 M, acidified to pH 5 with HOAc	40	5 h	[8]
HOAc 0.11 M	40	overnight (16 h)	[28]
HOAc 0.43 M	40	overnight (16 h)	[1]
pH-stat test	10	48 h	[17]

Table 3 Comparison between aqua regia extractable (indicative values) and '3-acids' extractable (this work) concentrations (mg kg⁻¹) of Cd, Cr, Cu, Ni, Pb, Zn and As in reference materials BCR 701 and GBW07411. Mean $\pm$ standard deviation of 3 replicates.

	BCR701			BCR701			GBW07411			GBW07411		
	Indicative values			This work			Certified values			This work		
Cd	11.7	$\pm$	1.0	10.9	$\pm$	0.2	28.2	$\pm$	1.3	25.9	$\pm$	0.8
Cr	272	$\pm$	20	284	$\pm$	5	59.6	$\pm$	5.0	57.5	$\pm$	3.5
Cu	275	$\pm$	13	242	$\pm$	2	65.4	$\pm$	4.7	62.9	$\pm$	3.7
Ni	103	$\pm$	4	99	$\pm$	7	24.2	$\pm$	2.1	22.3	$\pm$	1.5
Pb	143	$\pm$	6	141	$\pm$	3	2700	$\pm$	100	2944	$\pm$	89
Zn	454	$\pm$	19	465	$\pm$	4	3800	$\pm$	300	3665	$\pm$	147
As	-			-			205	$\pm$	11	193	$\pm$	2.0

Table 4 Comparison of the results of the HOAc 0.11M extraction (first step of the BCR sequential extraction) of sample BCR-701[28] and CRM486 [29] and the HOAc 0.43M extraction of sample CRM486 [26] with certified and indicative values. Concentrations in mg kg⁻¹. The number of replicates is given between brackets.

	HOAc 0.11 M	HOAc 0.11 M	HOAc 0.43 M
	BCR701: Certified values	CRM483: Indicative values	CRM483: Certified values
Cd	7.34 ± 0.35	10 ± 0.77	18.3 ± 0.6
Cr	2.26 ± 0.16	9.4 ± 3.5	18.7 ± 1
Cu	49.3 ± 1.7	17 ± 1.5	33.5 ± 1.6
Ni	15.4 ± 0.9	18 ± 2	25.8 ± 1
Pb	3.18 ± 0.21	0.8 ± 0.7	3.1 ± 0.25
Zn	205 ± 6	441 ± 39	620 ± 24
	BCR701: This work (4)	CRM483: This work (4)	CRM483: This work (6)
Cd	7.32 ± 0.04	9.1 ± 0.1	15.2 ± 1.48
Cr	2.11 ± 0.03	7.8 ± 1.6	13.3 ± 1.95
Cu	47.3 ± 0.4	14 ± 0.4	28.1 ± 0.46
Ni	13.2 ± 0.1	16 ± 0.5	21.5 ± 0.77
Pb	2.5 ± 0.1	0.7 ± 0.1	1.7 ± 0.21
Zn	199 ± 0.9	425 ± 14.7	556 ± 23

Table 5 Type (DR = dredged sediment, AS = alluvial soil, RS = river sediment, MT = mine tailing, IS = industrial soil and SS = soil) and origin of the samples analysed in this work. Total concentrations of Zn, Cd, Pb, Cu, As, Ni, Ca, Al, Fe and S , CaCO₃ –content, pH, cation exchange capacity, organic carbon (OC content) and grainsize distribution of the samples. ND = not determined.

Nr.	type	Locality	Zn mg kg ⁻¹	Cd mg kg ⁻¹	Pb mg kg ⁻¹	Cu mg kg ⁻¹	As mg kg ⁻¹	Ni mg kg ⁻¹	Ca %	Al %	Fe %	S g kg ⁻¹	CaCO ₃ %	pH	CEC cmol kg ⁻¹	OC %	clay %	loam %	sand %
1	DR	Ghent	1103	7	132	428	67	20	1,90	3,83	1,97	0,94	4,5	7,6	22	5,1	27	52	21
2	DR	Deinze	767	3	70	168	17	29	2,18	2,99	2,67	2,07	3,8	7,1	36	10,4	27	59	14
3	DR	Deinze	1263	7	122	756	68	51	2,15	4,56	3,19	1,12	7,7	7,7	30	6,3	34	55	11
4	DR	Deinze	2105	19	244	421	36	52	3,33	3,52	3,33	4,94	9,6	7,5	24	5,2	35	59	6
5	DR	Bavikrove	1226	10	177	162	16	56	3,81	3,46	3,09	3,62	8,5	7,3	28	6,6	37	57	6
6	DR	Antwerp	336	6	49	93	31	21	4,30	2,96	4,74	2,78	10,6	7,6	17	2,7	38	28	34
7	DR	Antwerp	406	9	65	95	43	27	4,16	3,63	5,37	4,24	9,8	7,7	22	3,4	51	33	17
8	DR	Antwerp	452	9	66	134	38	27	4,61	3,91	3,93	5,29	12,0	7,7	25	3,9	54	37	10
9	RS	Kluisbergen	1851	8	112	101	12	43	4,26	3,93	3,26	0,76	10,3	7,7	34	8,9	46	47	7
10	DR	Diest	4083	213	54	182	254	84	1,67	1,21	8,2	0,35	ND	6,8	19	8,8	45	42	13
11	AS	Diest	320	40	67	11	196	36	0,51	1,33	14,7	0,57	ND	6,3	31	9,0	21	29	50
12	AS	Diest	545	11	30	26	103	20	0,26	3,38	11,9	0,16	ND	6,4	33	5,3	81	15	4
13	RS	Diest	574	17	214	97	516	29	2,41	1,33	6,3	0,60	ND	6,9	14	3,5	17	13	70
14	AS	Diest	799	19	84	109	161	25	2,62	1,84	12,6	0,23	ND	6,7	30	10,7	35	41	24
15	RS	Laakdal	282	8	92	42	260	14	2,89	0,90	21,3	0,22	ND	6,9	31	14,2	31	33	36
16	AS	Laakdal	433	14	84	68	242	15	2,61	1,31	23,2	0,15	ND	6,3	33	8,9	23	31	46
17	AS	Plombières	8000	21	4788	60	107	29	0,24	1,33	2,33	0,19	ND	6,1	5	1,7	17	46	38
18	AS	Plombières	9832	23	4066	69	84	25	0,39	1,84	2,11	0,02	ND	6,4	8	2,4	17	50	33
19	AS	Plombières	6683	10	1242	15	36	14	0,22	0,90	2,04	0,02	ND	5,5	6	1,5	16	47	37
20	AS	Sippenaken	3625	9	1153	18	40	27	0,38	2,82	1,57	0,04	ND	5,9	7	2,2	14	42	43
21	AS	Sippenaken	2458	4	678	15	38	26	0,19	3,81	1,87	0,01	ND	5,8	6	0,8	14	48	37
22	AS	Sippenaken	702	3	264	17	28	12	0,12	3,46	1,69	0,01	ND	6,1	7	0,5	15	49	36
23	AS	Epen	2735	10	1267	23	50	25	0,22	2,99	1,89	0,04	ND	6,0	10	2,6	17	47	36
24	AS	Epen	1274	4	1274	12	29	18	0,10	3,22	1,82	0,01	ND	5,6	7	0,9	15	49	37
25	MT	Angleur	30900	124	19500	1704	1928	104	2,22	2,45	9,48	ND	2,72	8,0	ND	ND			
26	MT	La Calamine	108108	297	20592	60	1491	71	4,72	3,08	11,77	12,7	ND	6,5	ND	ND			
27	IS	Ruisbroek	1263	10	1477	180	25	37	1,80	2,74	23,5	ND	1,79	7,5	ND	ND	ND	ND	ND
28	IS	Lommel	882	27	4	12,1	4	2	0,21	0,94	0,10	ND	ND	4,0	ND	ND	ND	ND	ND
29	IS	Lommel	561	25	8	10,7	4	216	0,12	0,643	0,19	ND	ND	4,0	ND	ND	ND	ND	ND
30	SS	Lommel	25	4	10	1	4	1	0,02	0,75	0,36	ND	ND	4,0	ND	ND	ND	ND	ND

Table 6: linear relation between HOAc 0.43 M (x)-, HOAc 0.11 M (y)- and NaOAc (z)-extractable Zn-, Cd-, Cu-, Pb- and Ni-concentrations (30 samples)

					R^2
Zn	y =	0.76 x	+	140	0.94
Cd	y =	0.64 x	+	1.3	0.93
Cu	y =	0.59 x	+	3.5	0.98
Pb	y =	0.48 x	+	18	0.77*
Ni	y =	0.74 x	+	0.4	0.85
<hr/>					
Zn	y =	0.48 z	+	111	0.90
Cd	y =	0.89 z	+	1.7	0.91
Cu	y =	0.64 z	+	3.6	0.97
Pb	y =	0.47 z	+	313	0.58*
Ni	y =	0.61 z	+	0.4	0.82

x = HOAc 0.43 M

y = HOAc 0.11 M

z = NaOAc 1 M