

The application of pH_{stat} leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials

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Abstract

pH is one of the key parameters that determines heavy metal mobility in soils, sediments and waste materials. In many respects leaching behaviour as reflected by the pH_{stat} leaching tests provide a better means of assessing environmental impact than analysis of total elemental composition. This paper discusses the use of pH_{stat} leaching tests as a tool to assess the potential mobilisation of trace metals from soils, sediments and waste materials. The possibilities of pH_{stat} leaching tests are illustrated by means of different examples.

The mathematical fitting of metal leaching behaviour from soils and sediments enabled a distinction between 5 groups of elements with a different leaching behaviour, which could be related to ‘pools’ with different reactivity. Contrary to single and sequential extractions, where pH is difficult to control, the reactivity and mobility of metals at a user-defined pH can be investigated. Moreover, the potential buffering capacity of the sample and its sensitivity to pH changes as a result of external stresses (e.g. soil acidification, liming) can be estimated.

A multidisciplinary approach combining mineralogical analysis (X-ray diffraction) with chemical analysis, pH_{stat} leaching tests and geochemical modelling (MINTEQA2) can provide information on the solid-phase speciation and reactivity of heavy metals in soils, sediments and waste materials. Besides the influence of pH on heavy metal leaching behaviour, additional information on heavy metal leachability and retention by the solid matrix was obtained from the kinetics of metal release during a pH_{stat} test.

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1. Introduction

1.1. Assessment of pH-dependent leaching behaviour

pH is one of the key parameters that determines heavy metal mobility in soils and sediments. In many respects leaching behaviour as reflected by the pH_{stat} leaching test and related characterization leaching tests provide a better means of assessing environmental impact than analysis of total elemental composition

[1]. A pH_{stat} test allows to assess how the solubility changes if *in situ* pH changes occur. Moreover, information is obtained on the potential buffering capacity of the sample and its sensitivity to pH changes as a result of external stresses (e.g. soil acidification, liming). Different types of tests are available to assess pH-dependent leaching. In the United States, the toxicity characteristic leaching procedure (TCLP [2]) 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 h. 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. [3]), buffer components can induce heavy metal complexation, resulting in unusually high leaching [4]. Kaupenjohann and Wilcke [5] presented a pH_{stat} titration in which ion exchange resins were used to remove reaction products. Cation-exchangers provide protons

Abbreviations: ANC, acid neutralizing capacity; BNC, base neutralizing capacity; CEC, cation exchange capacity; DOC, dissolved organic carbon; DIC, dissolved inorganic carbon; EC, electrical conductivity; L/S, Liquid/solid ratio; RC, release capacity; XRD, X-ray diffraction.

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to the suspension while cations are released by pH-buffering of the soil. Manual titrations are rather unpractical and require some knowledge of the acid neutralizing capacity of the sample. Cremer and Obermann [6] introduced a computer-based titration system allowing continuous registration and fine-tuning of pH during leaching experiments. This system was used by Gäbler [4] and Paschke et al. [7], who performed pH_{stat} leaching tests for 24 h. After 24 h, the suspended matter was removed from the liquid phase by centrifugation and filtration. Some standardized leaching tests also rely on pH_{stat} titrations. In the German standard leaching experiment (DIN 38 414-4), pH is kept at a preset value (pH 4–11). The L/S ratio is 10 (L/kg) and the duration is 24 h [8]. The standardized availability test NEN 7341 [9] uses pH_{stat} titrations at pH 7 and pH 4. To obtain a larger degree of dissolution, particle size is reduced to $<125 \mu\text{m}$ and a solid/liquid ratio of 1/50 is used. The total extraction time amounts to only 3 h. The latter test intends to examine the availability for leaching of inorganic compounds in solid materials (waste materials, building materials, soils). The aim is to determine the amount of a component that can leach out of a material upon exposure of the material in aerobic conditions to extreme conditions (e.g. disintegration of the material or complete consumption of ANC). This test has been criticized for not promoting complete dissolution or equilibrium. Since only the final leachate is analysed and because of the short duration of the availability test, slow buffering reactions are not taken into account. The pH dependence leaching test (PrEN 14429 [10]), which has been developed by the Network for the Harmonisation of Leaching/Extraction Tests (SMT-CT96-2066) consists of parallel extractions of the material at an L/S = 10 (L/kg) for 48 h at a series of pre-set pH-values. In addition, the test provides a measure of acid–base neutralization capacity (ANC/BNC). The most important difference between the above mentioned pH_{stat} tests and the pH_{stat} test used in our laboratory (see also Ref. [11]), is the longer duration of the test (96 h, because a plateau phase was often not reached after 24 or 48 h) and the monitoring of metal release during test. Additionally, the pH_{stat} leaching test was further optimised by adapting the concentration of the titration agent and by adjusting the interval of pH-acquisition (see Ref. [12]).

1.2. Application of pH_{stat} leaching tests

During the last few decades, pH_{stat} leaching tests have been applied to assess the pH-dependent leaching behaviour of heavy metals in different types of matrices, for example: soils [4], samples from industrially contaminated sites [11], waste materials [13], dredged sediments [12,14], overbank sediments [3,15] and anoxic river sediments [16]. An overview of the applications of pH_{stat} leaching tests described in literature is given in Table 1. Furthermore, pH_{stat} leaching tests have been evaluated as a tool to measure the weathering rates in soils [17]. pH_{stat} experiments are less suited to directly estimate weathering rates in soils since the continuous abrasion of mineral particles during stirring or shaking cause an overestimation of weathering rates [17]. In the nineties, the Comité Européen de Normalisation (CEN) started with the harmonisation of new European leaching tests, partly based on existing leaching tests. One of these

tests is the pH_{stat} test, which is used for the characterization of waste materials and building materials. Although pH_{stat} leaching tests have mostly been applied to study the leaching of heavy metals, Hirner et al. [18] used pH_{stat} leaching tests to study the leaching behaviour of organic contaminants. Besides for soils, sediments and waste materials, pH_{stat} leaching tests are also frequently used in medical research, for example to simulate the conditions in the digestive tract. This paper discusses the use and the possibilities of pH_{stat} leaching tests as a tool to assess the potential mobilisation of heavy metals from contaminated soils, sediments and waste materials.

2. Materials and methods

2.1. Samples

Three sediment and soil samples with different physico-chemical characteristics and 1 waste material were selected for analysis. The soil and sediment samples originate from the floodplain of the Grote Beek river in Central Belgium, a small river contaminated by industrial activities. Sample GB(dr) is a dredged sediment, disposed on land more than 12 years ago. Samples GB(fo) and GB(cl) were sampled in a regularly inundated floodplain. Sample GB(cl) is a green clay-rich soil, sampled in the upper part (0–20 cm) of an overbank profile at a distance of 20 m from a river. Sample GB(fo) was taken from the same overbank profile, between 20 and 35 cm depth. This sample was characterised by red-brown and black colours because of the abundant occurrence of Fe-oxides and organic matter. Sample LC is a waste material from the mine tailing pond of La Calamine, in the mining district of Plombières-La Calamine (East-Belgium), where extensive Zn–Pb mining and smelting was carried out from the Middle Ages until the beginning of the 20th century.

Samples GB(cl), GB(dr) and GB(fo) were used to illustrate the pH-dependent and time-dependent leaching behaviour of elements, while sample LC will mainly be used to illustrate the approach combining pH_{stat} leaching tests with mineralogical analysis and thermodynamical modelling.

2.2. Physico-chemical and mineralogical sample characterization

pH 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 [37]; effective cation exchange capacity (CEC) was analysed applying the ‘silver thiourea method’ [38,39]. 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 $\text{HNO}_{3\text{conc}}$ and 2 mL HF_{conc}). A certified reference material (GBW07411 soil) and sample triplicates were used for quality control. Values (in mg/kg) obtained were for Cd 25.9 (certified value 28.2 ± 1.3), Zn: 3630 (certified value 3800 ± 300), Ni: 22.3 (certified value: 24.2 ± 2.1), Cu: 62.9 (certified value 65.4 ± 4.7), Pb: 3010 (certified value 2700 ± 100), Cr: 57.5 (certified value: 59.6 ± 5.0)

Table 1
Application of pH_{stat} leaching test for soils, sediments and waste materials (ordered by year of publication)

Reference	Material	Elements analysed	L/S	Duration of the test	pHs investigated
[18]	Soil, tar coke, waste, shredder material	<i>n</i> -Alkanes, PAHs, PCBs	50	1 h	pH 4 and pH 10
[17]	Soil	K, Na, Ca, Mg, Al, Si, Cl, SO ₄ , NO ₃	6	10 days	pH 3
[5]	Soil	Al, Fe, Ca, Mg, K	10	96 h	pH 3
[19]	Waste material: slag and ashes	Na, Ca, S, Ba, Cr, Pb, As, Ni, V, Cd, Al	2, 10	24 h	pH 10–11
[3]	Floodplain soils	Pb, Cu, Zn and Cd	10	24 h	
[20]	Solid waste materials and waterwork sludges	Fe, Mn, As, Cu, Zn, Ni	10	24 h	pH 4 and pH 11
[21]	Incinerator bottom ash	Mo, Cu, Zn, Cd, Pb	5	24 h	pH 4–12
[22]	Soils (A-horizons)	Cd, Pb, Cu, Zn, Ni, Cr	10	10 to 96 h	pH 3
[7]	Waste of copper mining, topsoils, sediments	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	10	24 h and >170 h	pH 4
[23]	Floodplain soils	Pb, Cd, Zn, Cu	10		pH 3.5, 5, 6.2
[24]	Bricks	Mg, Ca, V, Cr, Mn, Ni, Cu, Zn, As, Sr, Cd, Ba, SO ₄ , K and Mo	10	24 h	pH 4, 5, 6, 7 and 11
[25]	Synthetic aggregates	Al, B, Ca, K, Li, Mg, Mb, P, S, Si, Sr	10	48 h	pH 4–13
[26]	Concrete mortars, cement-stabilized waste	Al, Ba, Ca, Cd, Cl, Cr, K, Mb, Pb, S, Si, V, Zn	10	24 h	pH 2–10
[11]	Soils of heavily contaminated sites	Mg, Ca, Mn, Fe, Al, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Pb	10	0 to 96 h	pH 1,3,5,7,9,11
[27]	MSWI fly ash	Pb, Zn, Cd, Cr, Cu, Ni, Mn, Al, Mg, Ba, As	40	12 h	pH 4.5 and pH 8.3
[28]	Residue from brick industry	Zn, Se, F, Cl, SO ₄ , Br electrical conductivity	10	24 h	pH 4–12 (8 values)
[12]	Dredged sediments	Mg, Ca, Mn, Fe, Al, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Pb, DOC, DIC, SO ₄ ²⁻ , PO ₄ ³⁻	10	0 to 96 h	pH 2,4,6,8,10
[29]	Contaminated soils	Ni, Cu, Zn, Cd, and Pb	10	24 h	pH 0.4–12
[30]	MSWI bottom ash	Al, Ca, SO ₄ , Mg, Si, Fe, Na and DOC	10	3,6,24,48, 168 h	pH 4,6,8,10,12
[31]	Bottom ash used in road construction	Cd, Cr, Cu, Nu, Pb, Zn, DOC, Cl-	10, 50	NM	pH 7 and pH 10
[32]	Incinerator bottom ash	DOC, Ca, Al, Si	100	2 h	pH 4,6,7,8,9,11
[13]	Mine waste	Mg, Ca, Mn, Fe, Al, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Pb	10	0 to 96 h	pH 2,4,6,8,10
[33]	Stabilized waste samples	EC, Mo, Cd, Zn, Cu, Pb, V, Ca, K, SO ₄ ²⁻ , P, CO ₃ ²⁻	10	48 h	pH 2–13
[34]	Vitric andosols	Al, Si, Ca, Mg, Na, DOC	10	24 h	pH 3
[35]	Cd- and Zn-contaminated podzols	DOC, Al, Ca, Fe, Zn, Cd	10	0 to 96 h	pH 2,3,5,8
[36]	Slags reused in road construction	V, Cr	30	47 days	pH 5

NM, not mentioned; EC, electrical conductivity.

and As: 193 (certified value 205 ± 11). Some measured values for the certified material are out of the certified range because the method used in this study (acid attack followed by ICP-MS measurement) is different from the method used to obtain the certified values (X-ray Fluorescence).

All reagents used for analysis were of analytical grade. All glassware was acid rinsed with HNO₃ 0.2 M before usage.

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 characterization 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.

2.3. pH_{stat} leaching

The pH_{stat} experiments were carried out with an automatic multititration system (Titro-Wico Multititrator, Wittenfeld and Cornelius, Bochum, Germany). Eighty grams of material (<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 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 [11] demonstrated that the rapid addition of acid to the soil/water suspension could lead to an exceeding of the set-point pH. Therefore, the concentration of the titration solution was adapted to the set-

point pH (pH 2: 2.5 M, pH 4: 1 M and pH 6: 0.25 M). The choice of the concentration of the titration agent was based on a rapid potentiometric titration, which was carried out to deduce the acid neutralizing behaviour of the sample. The interval of pH-acquisition was set to 200 s (instead of 1 s) to give the system enough time to react and eventually neutralise the acid before more acid was added [12].

At regular time intervals (0, 0.5, 1, 3, 6, 12, 24, 48, 72 and 96 h), a sample of the suspension was taken over a filter (0.45 μm Acrodisc, Pall, East Hills, NY) by means of a syringe attached to a flexible tube (for more details see also Van Herreweghe et al. [11]). Immediately after sampling, the sample was acidified with a drop of concentrated HNO_3 (ultrapure) to bring the pH < 2. Subsequently the sample was kept in a refrigerator until analysis.

2.4. Analysis of leachates

The solutions (digests from the 3-acid attack and the pH_{stat} leachates) were analysed by Flame Atomic Absorption Spectrometry (Thermo Electron Corporation S Series AA) for Ca, Fe, K and Al. For As, Cd, Cr, Cu, Mn, Ni, Pb and Zn a multi-element analysis by induced coupled plasma mass spectrometry (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 ' (Hewlett Packard, Palo Alto, CA). 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, [40]). Each ICP-MS measurement was carried out with three repetitions holding relative standard deviations below 5%. Accuracy was also checked by measuring standard solutions as unknown samples. In the final leachates, dissolved organic carbon (DOC) was measured with a TOC analyser (Skalar Formacs^{HT} TOC analyser, Breda, The Netherlands); sulphate was measured by turbidimetry [41] and chloride and phosphate by colorimetry [42]. Electrical conductivity (18.34 EC-meter, Eijkelkamp,

The Netherlands) and redox potential (Mettler Toledo Pt 4805-S7/165 Combination redox electrode, Zaventem, Belgium) were also determined.

3. Theory and calculation

3.1. Mathematical and geochemical modelling

ANC and leaching of metals as a function of time was described mathematically by the use of MATLAB software (The Mathworks, Natick, MA).

ANC curves obtained in the pH_{stat} tests with continuous set-point titration were described according to Schwarz et al. [22]. The proton buffering capacity of soils during pH_{stat} experiments can be described as the sum of two independent first-order reactions, i.e.:

$$H_b(t) = BC_1(1 - \exp(-k_1t)) + BC_2(1 - \exp(-k_2t)) \quad (1)$$

where $H_b(t)$ (mmol/kg) corresponds to the buffered protons at time t , BC_i (mmol/kg) is the buffering capacity of system i , k_i (h^{-1}) is the rate coefficient of the buffer system i and t (h) is the time after starting the titration.

Analogously, the cumulative release of an element m at time t is given by:

$$RL_m(t) = RC_1(1 - \exp(-r_1t)) + RC_2(1 - \exp(-r_2t)) \quad (2)$$

With RC_i (mg/kg) is the release capacity of buffer system i , r_i (h^{-1}) is the rate coefficient of the buffer system i and t is the time after starting the titration. The release capacities of the two buffer systems (RC_1 and RC_2) can be considered as two dominant sinks for heavy metals from which elements are released with a different rate. It has to be noticed that the two 'buffer systems' or 'pools' are only operationally defined and that they are not automatically related to classical waste or sediment components. Mathematically, it is possible to fit the cumulative release of an element with more exponential equations, but this does not result in a significantly better fit. Additionally, since a clear

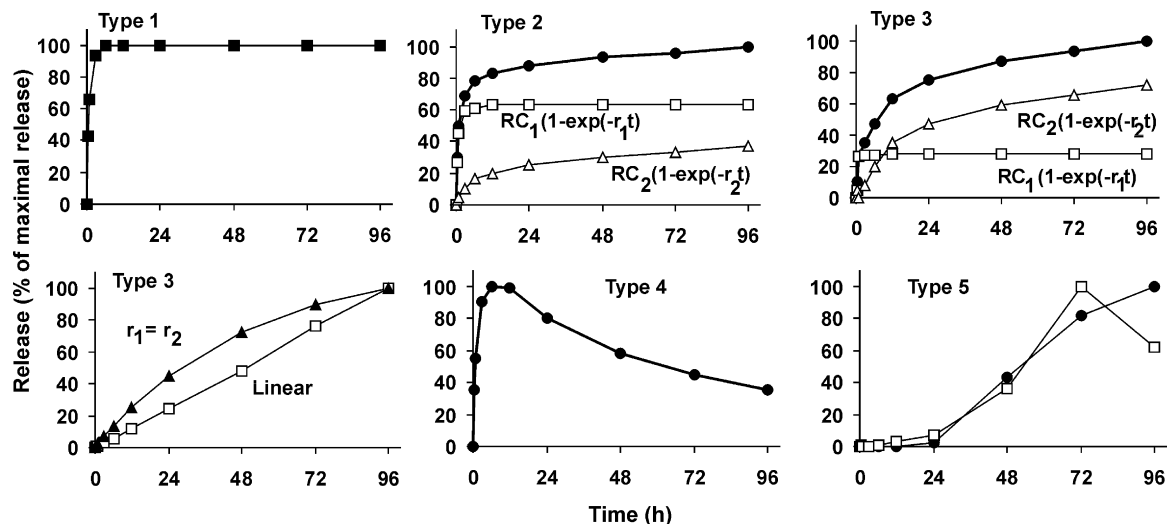


Fig. 1. Illustration of the different patterns of metal release observed during pH_{stat} leaching tests and the fitting of metal release from 2 buffer systems or sinks (RC_i).

link with classical sediment or waste components (e.g. elements bound by inner and outer sphere complexes, minerals that can dissolve upon titration) is missing, the definition of more than two buffer systems would not lead to a more comprehensive interpretation of the results of the leaching test. Therefore, in the present work, two compartments, namely a ‘labile’ and a ‘slowly labile’ pool are considered. Besides the quantification of a ‘labile’ and ‘slowly labile’ pool of metals, each ‘pool’ is characterised by a release constant (k_1). Additionally, it should be mentioned that, in some cases, the release patterns are not consistent with the two exponentials models.

The mathematical modelling will only be discussed for the samples from the Grote Beek river (GB(cl), GB(fo), GB(dr)).

Geochemical modelling was performed with the thermodynamical speciation model MINTEQA2 4.02 [43]. The datasets included in MINTEQA2 were used for the calculations.

3.2. Patterns of metal release as a function of time

In general, 5 different types of heavy metal leaching behaviour as a function of time can be observed during pH_{stat} leaching tests (Fig. 1).

- Type 1: elements are rapidly released at the beginning of the experiment (e.g. Mg, Na, K); the ‘labile’ pool is by far dominant and likely related to cation exchange reactions.
- Type 2: some elements display an initially rapid release, followed by a slow but substantial release in the final stage of the experiment. The ‘labile’ pool is more important than the ‘slowly labile’ pool ($\text{RC}_1 > \text{RC}_2$ in Eq. (2)). This pattern is typical for the more mobile metals in the soils (Cd, Zn, Ni) that are easily desorbed upon acidification or indicates the dissolution of poorly stable solid phases (e.g. carbonates).

- Type 3: elements are released more slowly. In this case, the ‘slowly labile’ pool is more significant than the labile pool ($\text{RC}_1 < \text{RC}_2$ in Eq. (2)). This release pattern points to the desorption of elements that are more strongly bound to soil constituents (e.g. Pb, Cr, Cu and Co) or to the slow dissolution of solid phases such as Fe-oxides. Sometimes, the release was linear as a function of time or could be described with only one exponential equation ($r_1 = r_2$ in Eq. (2)).
- Type 4: some elements exhibit readsorption (As, P, which occur as anions in soil) or precipitation behaviour (e.g. Ba precipitates as BaSO_4).
- Type 5: during combined oxidation and pH_{stat} leaching of anoxic sediments, the release of metals often only starts after a certain period of time (between 6 and 48 h) ([14]). This is due to the slow oxidation kinetics of heavy metal sulphides.

4. Results and discussion

4.1. General sample characteristics

The 3 soils and sediments have an average neutral pH and an elevated Fe- and organic matter content (Table 2). Elevated Cd-, As- and Zn-concentrations were detected in all the sediments. The dredged sediment (GB(dr)) has the highest heavy metal concentrations and is also contaminated with Cu and Ni. The high amount of clay in sample GB(cl) is both reflected in the elevated Al-content and in the grain size distribution (Table 2), while the K-content is consistent with the occurrence of glauconite. A mixed layer illite–smectite clay mineral was also identified in this sample. Glauconite and quartz were found in the 3 samples. Sample GB(fo) contained hematite and pyrrhotite.

The waste material from the mine tailing pond of La Calamine (sample LC) contained elevated concentrations of Pb, Zn, As and Cd. XRD analysis of this sample revealed the occurrence of quartz, kaolinite, illite, calcite, cerrusite, pyrite, marcassite and anglesite.

Table 2

Physico-chemical and mineralogical characteristics of samples GB(dr), GB(fo), GB(cl) (mean \pm standard deviation of 3 replicates) and LC

	Zn (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	As (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
GB(dr)	4083 \pm 345	84 \pm 54	213 \pm 16	182 \pm 11	254 \pm 25	54 \pm 2	527 \pm 17
GB(fo)	320 \pm 13	36 \pm 67	40 \pm 2	11 \pm 1	196 \pm 4	67 \pm 1	122 \pm 6
GB(cl)	545 \pm 12	20 \pm 30	11 \pm 0.4	26 \pm 1	103 \pm 2	30 \pm 1	64 \pm 2
LC	108,100	ND	297	60	1491	20,600	4843
	Ba (mg/kg)	Fe (%)	Ca (%)	Al (%)	S (%)	K (%)	Org C (%)
GB(dr)	709 \pm 28	8.2 \pm 1.0	1.67 \pm 0.17	1.21 \pm 0.01	0.35 \pm 0.02	0.80 \pm 0.02	8.8 \pm 1.0
GB(fo)	199 \pm 4	14.7 \pm 0.5	0.51 \pm 0.03	1.33 \pm 0.10	0.57 \pm 0.03	0.66 \pm 0.03	9.0 \pm 1.0
GB(cl)	69 \pm 3	11.9 \pm 0.6	0.26 \pm 0.04	3.38 \pm 1.06	0.16 \pm 0.01	3.26 \pm 1.20	5.3 \pm 0.4
LC	ND	11.77	4.72	3.08	13	1.06	ND
	CEC (cmol/kg)	pH (H ₂ O)	clay (%)	silt (%)	sand (%)	Mineralogy	
GB(dr)	19 \pm 0.5	6.8 \pm 0.2	45	42	13	Quartz, glauconite, amorphous Fe-hydroxides	
GB(fo)	31 \pm 0.6	6.3 \pm 0.2	21	29	50	Quartz, glauconite, hematite, pyrrhotite	
GB(cl)	33 \pm 0.6	6.4 \pm 0.2	81	15	4	Quartz, glauconite, illite, smectite	
LC	ND	6.4 \pm 0.2	59	37	4	Quartz, kaolinite, illite, calcite, cerrusite, pyrite, marcassite, anglesite	

ND, not determined.

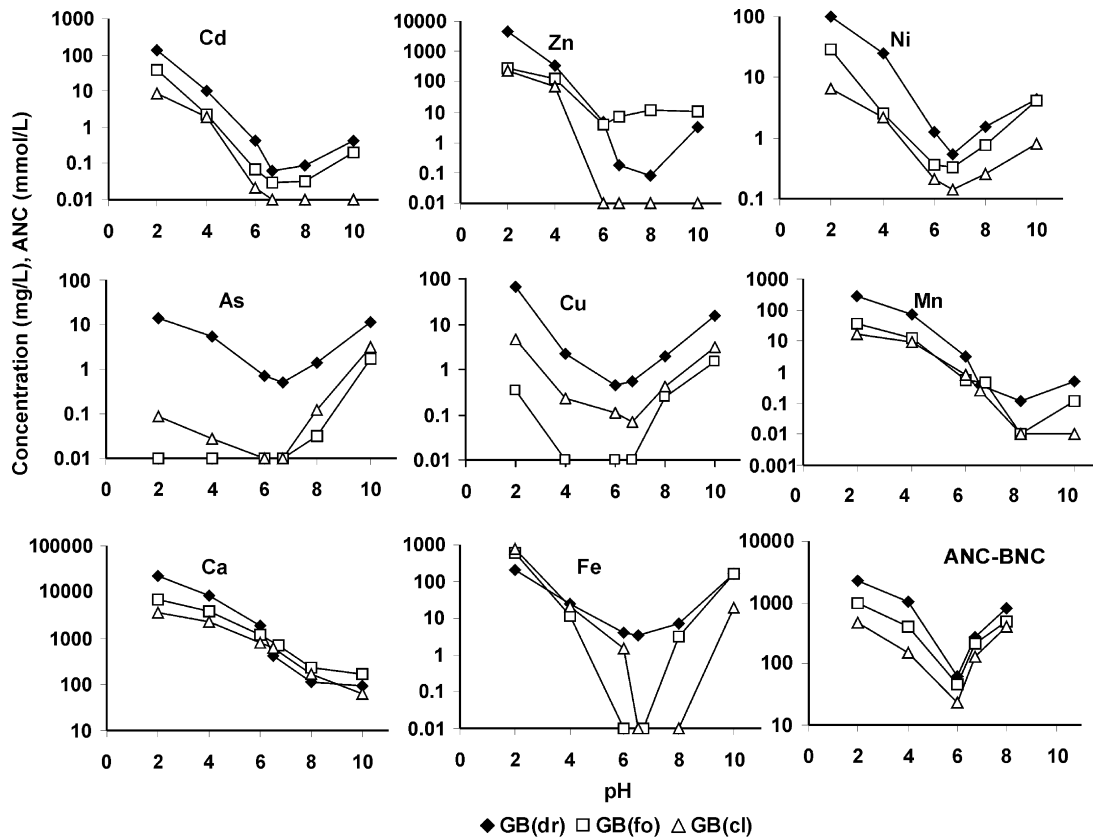


Fig. 2. Leached amount (mg/L) of Cd, Zn, Ni, As, Cu, Mn, Ca, Fe and ANC-BNC as a function of pH during the pH_{stat} test after 96 h in samples GB(dr), GB(fo) and GB(cl).

4.2. Leaching as a function of pH

Different patterns of leaching as a function of pH were observed during the pH_{stat} test (Fig. 2). The leaching of Cd, Zn, Cu, Ni, Mn, Ca and Fe increased with decreasing pH, although a non negligible amount of these elements was also leached in the alkaline pH-range, especially Cu, Ni and Fe. The solubility of Cd and Ni (relative to total concentration) as a function of pH is very similar for the different samples. In sample GB(fo), Zn is more soluble at high pH-values than in samples GB(dr) and GB(cl); Cu is characterised by a lower solubility in the pH-range 2–6 in sample GB(fo).

In soils, the sorption of metals is directly and indirectly affected by pH. The pH-dependent sorption reactions of cationic metals are partly due to the preferential sorption of hydrolyzed metal species in comparison with the free metal ion [44–46]. The proportion of hydrolyzed metal species increases with pH. Additionally, adsorption sites in soils and sediments are pH-dependent, the number of negative sites for cation sorption decreasing with decreasing pH. Moreover, under alkaline conditions, trace metals can precipitate as oxides, hydroxides, carbonates and phosphates [47].

The solubilisation of organic complexes can compete with the soil surface for the metal cation and influence metal sorption and release. The stability of the metal complex on its turn is also pH-dependent [48].

Since As occurs as arsenate in oxidized soils and sediments, a higher solubility is expected as pH increases. Nevertheless, arsenic displayed a considerable solubility in the acid pH-range in samples GB(dr) and GB(cl) (Fig. 2). The increased solubility of As in sample GB(cl) at pH 2 is most likely due to the dissolution of clay minerals at low pH. Goldberg [49] also observed a decreased sorption of arsenate on clay minerals (illite, montmorillonite and kaolinite) at pH-values below 4. It should be noticed that only a relatively small amount of As is released at pH 10 from the 3 samples (less than 6% of its total concentration, confirming the relatively low mobility of As). Nevertheless, from a practical point of view, investigation of heavy metal release at alkaline pH-values, can be used to estimate the consequences of liming, a measure that is often recommended to immobilise heavy metals in contaminated soils. The mobilisation of Cu from GB(cl) and GB(fo) at pH 10 is relatively important (resp. 18 and 13% of the total concentration). Consequently, an increase in soil pH will cause an immobilisation of Cd and Zn, but the mobility of Cu, whose total concentration is not especially of concern in samples GB(cl) and GB(fo) (26 and 11 mg/kg resp.), will significantly increase upon alkalisation.

The solubility of DOC and anions (Fig. 3) increased with increasing pH, although the release of Cl^- was hardly influenced by pH. The behaviour of PO_4^{3-} and DOC was different in sample GB(dr), since a considerable leaching of PO_4^{3-} and DOC

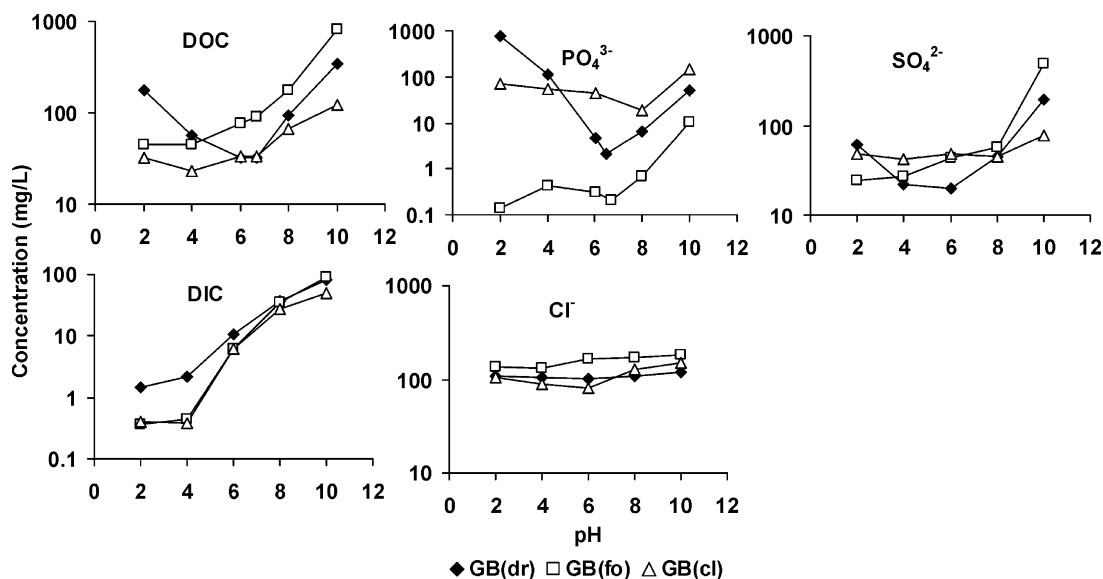


Fig. 3. Leached amount of DOC, DIC (dissolved inorganic carbon), PO_4^{3-} , SO_4^{2-} and Cl^- as a function of pH in samples GB(dr), GB(fo) and GB(cl).

was observed at low pH. The release of heavy metals from soils and sediments is to a large extent determined by the release of DOC. Organic carbon can bind metals and organic contaminants, whereas DOC can mobilise metals and organic contaminants. DOC is a sum of parameters for all organic species in solution, such as sugars, organic acids, amino acids, lignin and humic and fulvic acids, but in natural soil systems, humic and fulvic acids control heavy metal binding. Fulvic acids are soluble under acid and alkaline conditions, while humic acids are only soluble under alkaline conditions. Generally, the solubility of DOC increases with increasing pH. However, aquatic sediments contain a higher proportion of fulvic acids than terrestrial soils and sediments, which is reflected in the important solubility of organic matter at low pH-values [46]. A possible explanation of the release of Cu, Ni, Zn (Fig. 2) at alkaline pH-values is the dissolution of organic matter and the complexation of dissolved Cu, Ni and Zn by DOC.

4.3. Assessment of equilibrium conditions

Two types of laboratory leaching tests can be distinguished: single batch tests and flow-through (“dynamic”) leaching tests.

Batch extraction tests typically involve mixing a sample with a specific amount of leaching solution without renewal of the leaching solution [50]. The mixing is performed over a relatively short time period (hours to days) with the aim of reaching equilibrium conditions. Chemical equilibrium is reached when there is no concentration gradient at all between the porewater and the free water volume [48]. The mathematical fitting of leaching behaviour in pH_{stat} leaching tests allows an estimation of equilibrium conditions, assuming that metal release during pH_{stat} leaching will be at equilibrium at $t = \infty$. As a consequence, the reactive pool of an element released at a certain pH-value is given by $\text{RC} = \text{RC}_1 + \text{RC}_2$ ($t = \infty$ in Eq. (2)). In Fig. 4, the release of Cd from the clayey soil (GB(cl)) has reached more or less a plateau phase, suggesting equilibrium conditions.

Consequently, the depletion of the reactive pool (=sum of ‘labile’ and ‘slowly labile’ pool) for Cd in sample GB(cl) is almost completed during the test. In sample GB(fo), however, leaching of Cd proceeds more slowly and equilibrium is not reached within the duration of the pH_{stat} test, since only 85% of the ‘labile’ and ‘slowly labile’ Cd is released after 96 h (Fig. 4).

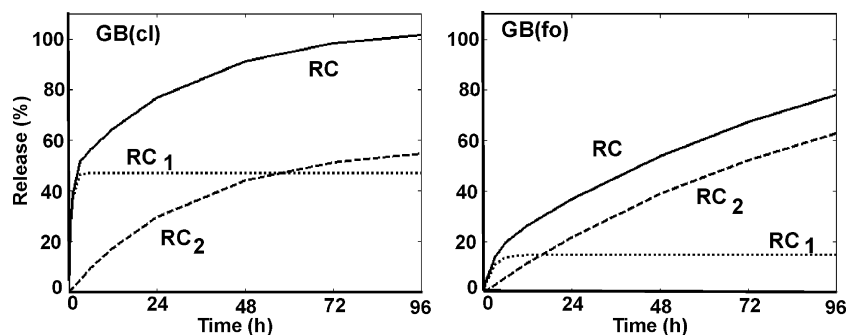


Fig. 4. Illustration of the kinetic fractionation of Cd at pH 4 into a ‘labile’ (RC_1) and ‘slowly labile’ (RC_2) pool according to Eq. (2) in samples GB(cl) and GB(fo). The release of Cd is represented as % of the calculated maximal release.

Table 3
Parameters from the fitting of heavy metal release according to Eq. (2)

		RC ₁ (%)	RC ₂ (%)	r ₁ (h ⁻¹)	r ₂ (h ⁻¹)	R	RC _{depleted} (%) ^a
pH 2							
Zn	GB(dr)	87	16	0.38	0.02	0.993	97
	GB(fo)		102		0.03	0.987	98
	GB(cl)	67	31	4.06	0.08	0.999	102
Cd	GB(dr)	81	21	0.33	0.03	0.995	98
	GB(fo)		105		0.02	0.992	95
	GB(cl)	62	37	3.49	0.12	0.999	102
Ni	GB(dr)	69	57	0.43	0.01	0.993	80
	GB(fo)	75	48	0.02	0.00	0.993	81
	GB(cl)	67	31	4.05	0.05	0.995	102
Cu	GB(dr)	71	39	0.47	0.01	0.991	90
	GB(fo)	RC = 0.60t + 3.7629				0.976	
	GB(cl)	35	61	3.86	0.08	0.998	103
pH 4							
Zn	GB(dr)	44	62	0.26	0.03	0.999	94
	GB(fo)	19	96	0.15	0.01	0.991	87
	GB(cl)	69	31	1.64	0.04	0.998	100
Cd	GB(dr)	53	50	0.32	0.03	1.000	97
	GB(fo)	15	102	0.43	0.01	0.994	85
	GB(cl)	47	58	1.60	0.03	0.997	95
Ni	GB(dr)	29	75	0.28	0.03	1.000	96
	GB(fo)	19	101	0.58	0.01	0.998	83
	GB(cl)	44	53	1.57	0.04	0.989	103
pH 10							
As	GB(dr)	48	53	0.37	0.04	0.997	99
	GB(cl)	44	59	1.15	0.02	0.997	97
Cu	GB(dr)	42	58	0.34	0.04	0.998	100
	GB(cl)	50	46	1.39	0.03	0.993	104

Number of data points = 1730, significance level $p < 0.05$.

^a $RC_{depleted} = RC / (RC_1 + RC_2) \times 100$.

4.4. Release rate of heavy metals during pH_{stat} leaching

As pH increases from 2 → 4 → 6 in the respective pH_{stat} experiments, the release rate of most elements decreases, which is quantified by mathematical fitting according to Eq. (2).

In the dredged sediment GB(dr), Zn, Cd, Ni and Cu show a rapid initial release at pH 2 and 4, ($r_1 = 0.4–0.3 h^{-1}$) while the second buffer system, according to Eq. (1), is characterised by a release rate that is an order of magnitude lower

($r_2 = 0.02–0.03 h^{-1}$) (Table 3). Desorption of heavy metals at pH 2 in sample GB(fo) could be described by only 1 exponential equation (1 buffer system), with a rather slow release rate ($r = 0.02–0.08 h^{-1}$) compared to sample GB(dr) (Table 3). In sample GB(cl), the initial heavy metal release was always faster than in samples GB(dr) and GB(fo), which is expressed by the higher release constant (r_1 , Table 3). The slow release constant (r_2) of Zn, Cd, Ni, Cu and As at different pH-values is very similar for the 3 samples (Table 3). $RC_{depleted}$ (Table 3) gives

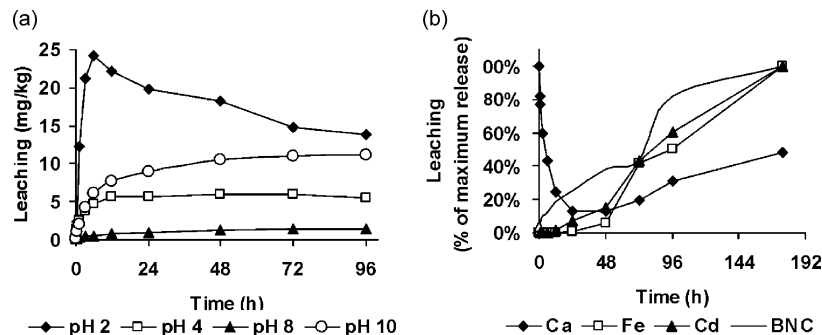


Fig. 5. (a) Leaching behaviour of As in sample GB(dr), at pH 2, 4, 8 and 10, and (b) leaching behaviour of Fe, Cd and Ca and BNC in sample GB(fo) at pH 10 (% of maximal release).

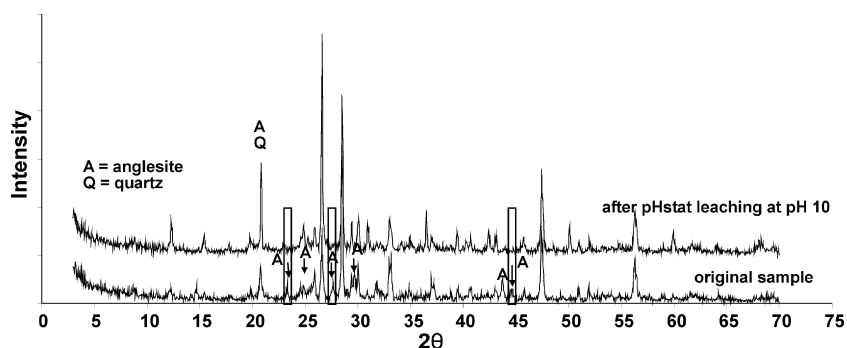


Fig. 6. XRD-pattern of sample LC before (original sample) and after pH_{stat} leaching at pH 10.

the proportion (in %) of an element that has been released after 96 h, relative to its concentration that would be released at $t = \infty$ (as determined by fitting). More than 80% of the ‘reactive pool’ of the elements in Table 3 has been released after 96 h.

At pH 2, arsenic (Fig. 5a) has a somewhat different behaviour since the maximal release of this element at pH 2 occurs after 6 h, after which its concentration in the solution starts to decrease. Readsorption of negatively charged arsenate ions on the positively charged soil surface can explain the behaviour of As.

Leaching of most elements at pH 10 in sample GB(fo) started after 48 h (Fig. 5b). While a decrease in Ca-concentrations (because of precipitation reactions and/or sorption to the negatively charged soil surface) was observed in the initial stage of the experiment, an increase in Ca-concentrations also occurred from $t = 48$ h onwards. After 71 h, a break appeared in the BNC curve (Fig. 5b), suggesting the start of new base neutralizing reactions. The elevated DOC-concentrations indicate a considerable dissolution of organic matter, so that a complexation of heavy metals with DOC can be expected. MINTEQA2 modelling, however, indicates that the speciation of Ni and Zn at pH 10 is dominated by hydroxy-complexes ($\text{Zn}(\text{OH})_{2\text{aq}}$ en $\text{Ni}(\text{OH})_{2\text{aq}}$), while Cd mainly occurs as chlorohydroxy-complex ($\text{Cd}(\text{OH})(\text{Cl})$).

4.5. Combination with mineralogical analysis and thermodynamical modelling

After pH_{stat} leaching of sample LC, the residual sample was dried and analysed with XRD. At low pH-values (pH 2 and 4), no heavy metal containing minerals disappeared from the sample. At alkaline pH, however, anglesite was removed from the sample (Fig. 6). However, almost no Pb was measured in the pH_{stat} leachate at pH 10. Geochemical modelling of heavy metal release as a function of pH was carried out with the speciation code MINTEQA2 (Fig. 7). Therefore, it was assumed that all the sulphate released at pH 10 came from the dissolution of anglesite and the sulphate concentrations were used to calculate the amount of anglesite in the sample. Hereafter, the solubility of anglesite as a function of pH was modelled. The results showed that anglesite is indeed completely dissolved at pH 10, but Pb precipitates again as Pb-(hydr)oxides, explaining for the very low Pb-concentration found in the leachate at pH 10. According to the MINTEQA2-calculations, a partial dissolution of anglesite occurs at pH 2 and 4, but XRD-analysis

indicates that the dissolution of anglesite is not significant at acid pH-values.

4.6. Prediction of soil acidification

The total acid deposition by rain amounted in Flanders in 2005 to 3810 equivalents of acid per hectare and per year [51]. Assuming quasi-constant emissions of SO_x , NO_x and NH_x compounds in the coming years and accepting that ANC is correctly estimated after 96 h leaching, future contaminant leaching can to some extent be predicted. If 1 ha is considered and a soil layer of 20 cm is taken into account, the mass of this volume can be calculated. Bulk density values for the sandy loam samples of 1.30 (tonnes/m^3) were used. The time to reach a certain acid neutralization can be calculated by applying the following equation:

$$\text{Time (years)} = \frac{\text{ANC}_{96\text{h}}(\text{mmol}/\text{kg})}{[3810 \times 1000 (\text{mmol}/\text{ha y})/\text{mass} (\text{kg}/\text{ha})]} \quad (3)$$

It must however be kept in mind that these results should be considered as a worst-case scenario since the considered experimental conditions do not occur in nature. The experimental results suggest that sample GB(cl) is most sensitive to acidification (Table 4). In less than 100 years, soil pH can decrease to a value of 4, resulting in a considerable release of Cd and Zn. Sample GB(fo) is less sensitive to acidification. Moreover, this sample was collected in an overbank profile below the clay-rich

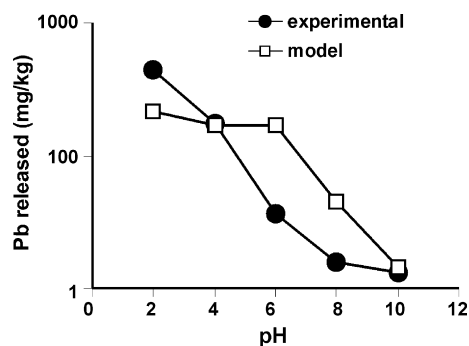


Fig. 7. Experimental and modelled solubility of Pb as a function of pH in sample LC (in mg/kg dry matter). The model is based on the assumption that anglesite determines the solubility of Pb. See text for explanations.

Table 4
Release of Ni, Cu, Zn, As and Cd (in mg/kg dry matter) and ANC at pH 2, 4 and 6 and at natural soil pH ('soil') after 96 h of pH_{stat} leaching

pH	Cd (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	As (mg/kg)	ANC (mmol/kg)	Time (y)
GB(dr)							
2	140	99	4466	67	14	2331	1591
4	10	25	347	2	6	680	464
6	0.42	1.3	5	<0.05	0.7	64	44
Soil	0.06	0.6	0.19	0.5	0.5	–	–
GB(fo)							
2	40	38	276	0.5	<0.05	994	678
4	3	3	148	<0.05	<0.05	409	280
6	0.1	0.39	4	<0.05	<0.05	46	31
Soil	<0.05	0.34	2	<0.05	<0.05	–	–
GB(cl)							
2	8.89	6.6	240	4.8	0.08	477	326
4	2.7	1.44	70	0.1	0.27	150	103
6	<0.05	0.21	<0.05	0.11	<0.05	24	16
Soil	<0.05	0.14	<0.05	0.07	<0.05	–	–

'pH' is the pH at which the pH_{stat} leaching test was performed. 'Time' gives the time necessary to reach a certain ANC according to Eq. (3).

soil sample and we can expect that acidification will first affect the upper part of the soil. The dredged sediment (GB(dr)), which displays the highest total metal concentrations, is also characterised by a considerable acid neutralizing capacity. According to the calculations (Eq. (3)), acidification to pH 6 as a consequence of acid deposition can occur in less than 50 years, but will not release important heavy metal concentrations. Further acidification will lead to a more important heavy metal release, but this will only occur after a long period of time (e.g. 433 years to reach pH 4) because of the favourable ANC of the sediment.

Based on the acid neutralizing capacity of the sample from the waste material LC, heavy metal release upon acidification of the tailing material can be predicted. On medium long term (± 100 years) a rather limited release of Pb (± 4 mg/kg) has to be expected upon acidification. For Zn, however, more than 900 mg/kg could be released in a time span of 100 years as a consequence of acid deposition.

5. Conclusions

- Based on pH_{stat} leaching tests, an insight in heavy metal mobility in soils, sediments and waste materials as a function of pH is obtained and reactions occurring during acidification and alkanilisation are derived. Mathematical fitting of leaching behaviour as a function of time enables to distinguish between groups of elements with a different leaching behaviour, which can also be interpreted in terms of 'pools' of different reactivity. Additionally, pH_{stat} titrations allow a determination of acid neutralizing capacity, making it possible to predict heavy metal release upon acidification, assuming a worst-case scenario.
- A multidisciplinary approach combining solid-phase characterization (e.g. by X-ray diffraction, SEM-EDX, ...) and geochemical modelling with chemical analysis and pH_{stat} leaching tests can provide information on the composition of soils, sediments and waste materials and the reactivity of heavy metals in these matrices. Besides the solid phase char-

acterization of a material, the results of pH_{stat} leaching tests can be supported by modelling predictions with thermodynamical codes (e.g. MINTQA2).

- The European pH_{stat} test, which is currently being standardized within the CEN framework (CEN-TC292/WG6), consists of a 48 h pH_{stat} test at 8 different pH-values in the range 4–12 [10]. Whereas, based on practical considerations, only the final leachate (after 48 h) is analysed, the analysis of the leachate at different time intervals is interesting because it allows to assess the kinetics of metal release. Additionally, the analysis of 'matrix elements', such as Fe and Ca, can provide information concerning the processes responsible for the release of contaminants.

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