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The use of leaching tests to study the potential mobilization of heavy metals from soils and sediments: a comparison

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Abstract

In the present study, different leaching tests were applied on well-characterised samples in order to obtain information on the potential mobility of heavy metals and arsenic. The information deduced from the different methods was compared and evaluated. Besides the comparison of heavy metal release in cascade-, column- and pH_{stat} leaching tests, attention was also paid to the assessment of release kinetics during leaching tests and to the mathematical modelling of leaching behaviour. The aim of this study was to understand the origin of possible discrepancies between the results of different leaching tests. The compatibility of the results of different leaching tests is, besides the inherent differences between methods (single batch tests versus dynamic leaching tests, the duration of the tests, liquid/solid (L/S) ratio,...) to a major extent determined by key-factors such as pH and redox potential. Depending on soil and sediment properties (e.g. acid neutralizing capacity (ANC)) these 'key-factors' varied during and at the end of extractions and leaching test, even when the initial test conditions (e.g. the pH of the reagent) were equal for all test cases. During cascade- and column leaching tests, pH (which is initially 4) will mostly increase, but the extent of this pH-increase mainly depends on the acid neutralizing capacity of the sample. Therefore, measuring the pH of all leachates that are collected during these tests is mandatory for the interpretation of the results. Moreover, the monitoring of other variables such as DOC, anions and major elements can give indications on the reactions that are responsible for the release of elements (e.g. the dissolution of organic matter) and greatly improve the interpretation of the results.

1. Introduction

The contamination of river sediments is widespread and is a potential threat for the environment on the short and long term. The impact of heavy metals on the environment depends on their speciation, mobility and bio-availability in soils and sediments.

'Heavy metal mobility' is an operationally defined term, which is determined by the method applied. Different approaches can be used to determine the mobile, labile or available metal species in soils and sediments. Although spectroscopic tools such as X-ray adsorption fine structure (XAFS) spectroscopy can give information on the coordination chemistry of metals (e.g. Scheinost et al., 2002), the quantification of the most mobile species is still difficult.

The composition of soil porewater is important from an environmental point of view because it gives an indication of the 'actual mobility' of heavy metals and because the uptake of trace elements by plants occurs via the porewater. Moreover, porewater is also the carrier for elements to the groundwater. Leaching is the process by which inorganic or organic contaminants in the porewater are moved to deeper soil layers or to the groundwater by infiltrating water. However, the porewater composition only gives a momentary picture of trace element mobility, since porewater composition can change over time. To assess heavy metal mobility on the long term ('potential mobility') and under changing environmental conditions a variety of leaching and extractions tests are used, which can be grouped in 5 categories, namely (1) Single batch extractions (2) Sequential batch extractions (3) Column leaching tests (4) Isotope exchange methods and (5) diffuse gradients in thin films.

In laboratory leaching tests, one or more samples of the study material are brought in contact with a liquid to determine which constituents will be leached by or dissolved into the liquid and potentially released to the environment in a liquid phase (e.g. to ground water or surface water).

Two types of laboratory leaching tests are distinguished in the present study: single batch tests and multiple extraction/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 (Washington State Department of Ecology, 2003). The mixing is

performed over a relatively short time period (hours to days) with the aim of reaching equilibrium conditions. pH_{stat} leaching tests are an example of batch extraction tests. In dynamic tests, in which time is also an important variable, a specific amount of leaching solution and test material are mixed and the leaching solution is periodically or continuously renewed. The mixing is performed over a relatively long time period (days to months) compared to extraction tests (Washington State Department of Ecology, 2003). In the present study, two types of dynamic leaching tests were performed: a cascade leaching test (in which the leaching solution is periodically renewed) and a column leaching test (in which the leaching solution is continuously renewed)

The 3 different leaching tests (Table 1) were applied on well-characterised samples in order to obtain information on the chemical speciation and potential mobility of heavy metals. The information deduced from the different methods was compared and evaluated. The aim of this study was to clarify the use and interpretation of conventional leaching tests and to understand the origin of possible discrepancies between the results of different leaching tests. Besides the comparison of heavy metal release in cascade-, column- and pH_{stat} leaching tests, attention is also paid to the assessment of reaction kinetics during leaching tests and to the mathematical modelling of leaching behaviour.

1.1 Column leaching test and cascade leaching test

The column test used in this study (NEN 7343, 1995a) aims at simulating the leaching of inorganic components from granular materials (waste material, soil, ...) in aerobic conditions. Column test results in conjunction with L/S ratios can be used to estimate "the time-dependence of the leaching of a material under practical conditions (NEN 7343, 1995a)."

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. The investigation of leaching as a function of the L/S (liquid/solid) ratio can also be performed with the NEN 7349 test (NEN 7349, 1995b) or cascade leaching test. This is a serial batch test in which the material is successively extracted 5 times, resulting in L/S ranges from 20 to 100.

As such, the cascade leaching test can be considered as an extension of the column leaching test, in which leaching is investigated in the L/S range 0.1-10. In both types of tests, local equilibrium is assumed (LEA: Local Equilibrium Assessment) (Van der Sloot, 1997). This implies that the flow rate must be sufficiently slow so that at any point within the column thermodynamical equilibrium must exist between material and percolating liquid. Because of the continuous outflow during column tests, material is leached with new leachate. Consequently, leaching is less influenced by substances that are already in the leachate, especially at high contaminant levels. This is in contrast with a single batch test in which all leached substances stay in the leachate until the test is finished. In the serial batch test the leachate is renewed several times and this test represents as such an intermediate between batch and column tests.

Despite the inherent differences between serial batch and column tests, a serial batch test is a useful extension of the column tests, since it is rather unpractical to perform column test at high L/S ratio. In order to obtain porewater velocities that are not too high and to obtain the necessary information in a reasonable time, high L/S ratio's are usually required. The comparison between the results of column and batch test should allow establishing a relationship between both tests. For example, Zevenbergen et al. (1997) found a statistical relationship between the amount of metals released in the NEN 7343 column leaching test and a two-step batch test (L/S = 5 and 10).

1.2 pH_{stat} leaching tests

The 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 characterisation leaching tests provide a better means of assessing environmental impact than analysis of total composition. 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 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. Tackett et al., 1986), buffer components can induce heavy metal complexation, resulting in unusually high leaching (Gäbler, 1997). Manual titrations are rather unpractical and require some knowledge of the acid neutralizing capacity of the sample. Cremer and Obermann (1992) introduced a computer-based titration system allowing continuous registration and fine-tuning of pH during leaching experiments. This system was used by Gäbler et al. (1997) and Paschke et al. (1999), 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 test 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^{-1}) and the duration is 24 hours (Hamer and Karius, 2002). The standardized availability test NEN 7341 (1995c) 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 liquid/solid ratio (L/S) of 50 (L kg^{-1}) is used. The total extraction time amounts to only 3 hours. 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), 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 $\text{L/S}=10$ (L kg^{-1}) 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 Van Herreweghe et al., 2002), is the longer duration of the test (96 h) and the monitoring of metal release during the test.

2. Materials and methods

2.1 samples

3 sediment samples with different physico-chemical characteristics were selected for analysis.

All the samples were taken along the Grote Beek river, situated in the south-eastern part of the Flemish Community (North-Belgium) (see Cappuyns and Swennen (2004) for more information). Alluvial soils are contaminated with heavy metals due to the activities of a phosphate ore processing plant.

Sample GB(dr) is a dredged sediment, disposed on land more than 12 years ago. It was sampled on the left riverbank that was slightly more elevated because of the storage of dredged sediments. Samples GB(fo) and GB(cl) were sampled on the right riverbank, in a regularly inundated floodplain. Sample GB(cl) is a green clay-rich sediment, sampled in the upper part (0-20 cm) of a overbank profile at a distance of 20 m from the 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. All the samples were oxidised at the moment of sampling.

On overview of the different leaching tests and samples is provided in Table 1.

Table 1 here

2.1 General sample characterization

Sediment samples were dried in oven at 30 °C during 5 days. For the physico-chemical analysis, part of the soil sample was disaggregated in a porcelain mortar and sieved (<2 mm). $\text{pH}(\text{H}_2\text{O})$ was measured in a soil/water suspension (1/2.5). Organic carbon was determined according to the Walkey and Black method (Nelson and Somers, 1982). Grain size was determined by laser diffraction analysis (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK) and effective cation exchange capacities (ECEC) were analyzed applying the 'silver thiourea method' (Chhabra et al., 1975; Van Reeuwijk, 1992). Total element

concentrations (Al, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn, Fe, Mn, K, P and Ca) 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 $\text{HNO}_{3\text{conc}}$ 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. These solutions were analyzed by AAS (Varian® Techtron AA6) for Ca, Fe, K and Al. For As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn a multi-element analysis by ICP-MS (HP 4500 series, Hewlett Packard, Palo Alto, CA). The samples were diluted just before analysis with 5% HNO_3 (ultrapure). Standard series were made up starting from the '10ppm 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. Each ICP-MS measurement was carried out with three repetitions holding relative standard deviations below five percent. A certified reference material (GBW07411 Soil) and sample triplicates were used for quality control. Values (in mg kg^{-1}) 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) and As: 193 (certified value 205 ± 11). All reagents used for analysis were of analytical grade. All glassware was acid rinsed with HNO_3 0.2 M before usage.

2.2 Column test

The NEN 7343 column test (NEN 7343, 1995a) was performed by means of the Titrocol7343® apparatus. The samples were air-dried, homogenized and sieved retaining the < 1 mm fraction. Distilled water, acidified to pH 4 with HNO_3 , (ultrapure) was used as leachate. Before filling, the bottom of the column (5 cm diameter) was fitted with a screw cap with a perforated plastic plate connected to a plastic tube. In the screw cap a 0.45 μm membrane filter was mounted. The column was carefully packed with soil material to obtain a minimum height of 20 cm of soil. The exact mass (m in mg kg^{-1}) of the soil was calculated from the weight of the column before and after filling. The flow rate of the pump was adjusted according to $q \leq a * m$,

with q the flow rate of the leachate through the column in $L\ h^{-1}$, $a = 0.025\ l\ kg^{-1}\ h^{-1}$. After filling, the top of the column was also sealed with a $0.45\ \mu m$ membrane filter in a perforated plastic cap to which a plastic tube was attached. The soil was first saturated upflow with leachate and then the column test was started. Samples of the leachate were collected at L/S 0.1, 0.2, 0.5, 1, 2, 5 and 10 ($L\ kg^{-1}$). A part of each leachate fraction was acidified with concentrated HNO_3 (ultrapure), while another part was kept untreated for the determination of pH, DOC and electrical conductivity. Before usage, the equipment was rinsed with HNO_3 (1 M) and then with acidified water.

According to Van der Sloot et al. (1997), the cumulative release of an element as a function of L/S ratio can be described with the Continuous Stirred Tank Reactor Model (CSTR) whereby the column is modelled as a plug flow reactor with continuous dispersion.

Equation 1 **$R = AVB(1 - e^{-(L/S)/K}) + C_0$**

With:

R = release in $mg\ kg^{-1}$

AVB = availability in $mg\ kg^{-1}$

K = matrix retention factor in $L\ kg^{-1}$

L/S = liquid over solid ratio in $L\ kg^{-1}$

C_0 = constant

The continuous stirred-tank reactor (CSTR) model is used to estimate the key variables when using a continuous agitated-tank reactor to reach a specified output. It assumes perfect mixing, a constant temperature and a constant density (Reinhardt et al., 2005).

Equation 1 can be used to deduce the matrix retention parameter (K) and the availability (AVB) for the different elements in different contaminated materials. The experimental output curves were fitted with the software package MATLAB to estimate the values of the parameters of Equation 1.

2.3 Cascade leaching test

A Cascade Leaching Test (NEN 7349, 1995b) was performed to study the mobile fraction of heavy metals. The extractions were carried out in triplicate in acid rinsed 50 mL polyethylene centrifuge tubes with screw caps. 30 mL of distilled water, acidified to pH 4 with ultrapure HNO₃ was added to 1.5 g of dry sediment sample. The suspension was shaken during 22 h on a reciprocal shaker, centrifuged (3000 rpm, 10 min), decanted off and filtered (0.45 µm). This extraction was repeated to obtain five fractions, with a liquid/solid (L/S) ratios ranging from 20 to 100.

The cumulative release curves of metals as a function of L/S ratio were modelled with:

Equation 2
$$C_x = C_{20}k^* \ln x + cte$$

Wherein $x = L/S$ ratio (L kg⁻¹, dimensionless in Equation 2), C_x = the amount of an element (mg kg⁻¹) released at $L/S = x$, C_{20} = the amount of an element (mg kg⁻¹) released at $L/S = 20$, k^* = retention factor (dimensionless), cte = constant. The retention factor k^* is a quantification of heavy metal retention. A higher retention parameter points to a stronger binding of the metal to the soil or sediment.

2.4 pH_{stat} test

The pH_{stat} experiments were carried out with an automatic multtitration system (Titro-Wico Multititrator®). Sediment 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 (resulting in an L/S ratio of 10) 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 (Van Herreweghe et al., 2002) 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). 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. Cremer and Obermann (1992) proposed a pH_{stat} procedure in which the pH was adjusted to pH 4 and 11 during a time period of 24 h. However, Paschke et al. (1999) and Van Herreweghe et al. (2002) demonstrated that a 24 h experiment is not sufficient for a thorough assessment of metal leaching. Additionally, liquid/solid ratio, shaking intensity and grain size are important factors that determine the metal release during pH_{stat} leaching tests (Paschke et al., 1999). In the present study, pH_{stat} leaching tests were performed for 96 h. 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 (Acrodisc® 0.45 µm) by means of a syringe attached to a flexible tube (for more details see also Van Herreweghe et al., 2002). This allows to sample the suspension without interruption of the experiment and to monitor the metal release during the experiment in a quasi continuous mode. Moreover, the *in situ* filtration of the material diminishes the risk of contamination.

Immediately after sampling, the sample was acidified with a drop of concentrated HNO₃ (ultrapure) to bring the pH < 2. Subsequently the sample was kept in a refrigerator until analysis. In the final leachates (not acidified), dissolved organic carbon (DOC), sulfate, electrical conductivity (EC) and redox potential were also determined. Geochemical modelling was performed with the thermodynamical speciation model MINTEQA2 (Allison et al., 1999). ANC and leaching of metals as a function of time was described mathematically for both types of titration experiments by the use of MATLAB and EXCEL software.

ANC curves obtained in the pH_{stat} tests with continuous setpoint titration were modeled according to Schwarz et al. (1999). The proton buffering capacity of soils during pH_{stat} experiments can be formulated as the sum of two independent first-order reactions, i.e.:

Equation 3 $H_b(t) = BC_1 (1 - \exp(-k_1 t)) + BC_2 (1 - \exp(-k_2 t))$

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

The cumulative release of an element m at time t is expressed as:

Equation 4 $RL_m = RC_1(1 - \exp(-r_1t)) + RC_2(1 - \exp(-r_2t))$

With RC_i = the release capacity of buffer system i (in mg kg^{-1} or %), r_i is the rate coefficient of the buffersystem i (in h^{-1}) and t (in h) 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 soil properties.

Theoretically, it is possible to consider more than two buffer systems, since the soil consists of a variety of components such as clay minerals, Fe-and Al-oxides, organic matter. Moreover, minor and trace elements can be adsorbed to soil constituents by inner or outer sphere complexes or retained by precipitation or coprecipitation. It can be questioned whether the definition of more compartments would lead to a more comprehensive interpretation of the results of the leaching test.

2.5 Analysis of the leachates

Concentrations of Mg, Al, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba and Pb were measured by ICP-MS (HP 4500 series). Standard series for ICP-MS were made up starting from the "10 ppm Multi-Element Calibration Standard 2A in 5% HNO_3 " 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, Brockhoff et al., 1999). Dissolved organic carbon (DOC) and Dissolved inorganic carbon (DIC) were measured with a TOC analyser (Skalar Formacs^{HT} TOC analyser). Sulfate (Vogel, 1961) and phosphate (Peachy et al., 1973) were measured by turbidimetry and chloride by colorimetry (Jeffery, 1981). Electrical conductivity (Eijkelkamp® 18.34 EC-meter) and redox potential (Mettler Toledo Pt 4805-S7/165 Combination redox electrode) were also determined.

3. Results

3.1 Physico-chemical and mineralogical sample characteristics

The 3 sediments have a circum neutral pH and an elevated Fe- and organic matter content (Table 2). Elevated Cd-, As- and Zn- concentrations were detected in all the sediments (compare to Table 3). 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 consisted with the occurrence of glauconite. A mixed layer illite-smectite clay mineral was also identified in this sample.

Table 2 here

Table 3 here

Glauconite and quartz were found in the 3 samples. Sample GB(fo) contained hematite and pyrrhotite. Pyrrhotite is a non-stoichiometric Fe-compound with an excess of sulphur over iron. Pyrrhotite is a species considered stable at low temperatures (Kissin and Scott, 1982). It is noteworthy here to mention that the presence of sulphate reducing bacteria at a hematite surface results in mineral dissolution and the formation of the stable iron sulphide pyrrhotite and reactive polysulphides (Neal et al., 2001). The sulphide/polysulphide formation by sulphate reducing bacteria has the potential to greatly affect Fe, S and other trace metal concentrations in anoxic soils and sediments. In the dredged sediments, Ca-phosphate particles $((Ca,Mg)_2(PO_4)_2 \cdot H_2O)$ and particles consisting of amorphous Fe(hydr)oxides were identified and separated manually (subsamples GB(ca) and GB(fe) respectively).

The 3 sediments are characterised by a different grainsize distribution : while sediment GB(cl) can be classified as a clayey sediment, samples GB(dr) and GB(fo) are respectively characterised by a loamy sand and sandy texture (Table 2).

3.2 Column leaching test

The column leaching tests was performed for samples GB(dr) and GB(fo). The bulk density of the material packed in the soil column was 1.26 g cm^{-3} for sample GB(dr) and 1.31 g cm^{-3} for sample GB(fo), resulting in an estimated total porosity of 48% and 49% respectively. Sample GB(cl) exhibited a too low permeability to perform a column test. The flow rate of the water was 10 mL h^{-1} , yielding a porewater velocity of approximately 24 mL h^{-1} . During the column tests, pH increased in the successive fractions and redox potential decreased (Fig. 1). A decrease in electrical conductivity was observed with increasing L/S ratio, while DOC-concentrations increased (Fig. 1).

Generally, As, Cu and Ni concentrations increased in the successive fractions, while Cd-concentrations decreased (Fig. 1), except in GB(dr). Zn displayed a similar concentration in the different fractions.

Figure 1 here

The cumulative leaching of heavy metals as a function of L/S is given in Fig. 2. In both samples (note that Cu and As were below detection limit in sample GB(fo)), the cumulative release of As, Cu and Ni exhibits a stronger increase with L/S ratio than Cd and Zn.

Figure 2 here

Since Ca was principally released at the beginning of the column leaching experiment, its release reaches a plateau phase at $L/S = 1$. Fe displayed the highest concentrations in the last fractions, so that the release of Fe still increases at $L/S = 1$.

The cumulative release of As, Cd, Cu, Ni, and Zn in the column leaching test was mathematically fitted according to Equation 1. The parameters (matrix retention parameter K and availability AVB) obtained from the fitting are given in Fig. 3. In sample GB(fo), the retention increased in the order $\text{As} < \text{Ni} < \text{Cu} < \text{Zn} < \text{Cd}$, i.e. Cd displayed the strongest binding to the sediment GB(fo) and As was the most mobile element. In the dredged sediment (GB(dr)), a lower matrix retention parameter was obtained for all elements compared to the sample GB(fo) and Zn displayed the strongest retention. The availability of As, Cd, Cu, Ni and

Zn was higher in sample GB(dr) and decreased in the order As > Ni > Cu > Cd > Zn. The availability sequence of sample GB(fo) was Ni > Zn > Cd > As > Cu.

Figure 3 here

3.3 Cascade leaching test

Relatively low total metal concentrations were released during the cascade leaching test (Fig. 4). The dredged sediment displayed a more important heavy metal and As release than sediments GB(fo) and GB(cl). The comparison with pH_{stat} leaching tests at pH 6 is made because pH 6 is close to the pH of the cascade leaching test (which is in the range 6-7). As-, Cd-, Zn-, Ni-, Cu- and DOC-concentrations released after 96 h of pH_{stat} leaching at pH 6 (Fig. 4) were in the same range as the amounts released by cascade leaching.

Figure 4 here

For the cascade leaching test, the cumulative release of As, Cd, Cu, Ni, and Zn was mathematically fitted according to Equation 2. Zn, Ni and Cu were characterized by a higher retention factor in sample GB(dr) compared to sample GB(cl), indicating that they are released more slowly from sample GB(dr) (Fig. 5). In sample GB(fo), Ni was retained more strongly than in the two other samples (GB(dr) and GB (cl)). For Cd and As in samples GB(fo) and GB(cl), no fit was obtained because their release was below detection limit or because they were only released in the first fraction of the cascade leaching test. Arsenic has a higher retention factor than Cd, Zn, Cu and Ni in sample GB(dr) (Fig. 5), indicating that As is more strongly bound to the sediment than Cd, Zn, Cu and Ni.

Figure 5 here

3.4 pH_{stat}

3.4.1 pH-dependent leaching behaviour

Different patterns of leaching as a function of pH were observed during the pH_{stat} test (Fig. 6). 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 characterized by a lower solubility in the pH-range 2-6 in sample GB(fo).

Figure 6 here

Arsenic and P have a somewhat different behaviour since the maximal release of these elements occurs after 6 hours, after which their concentrations in the solution start to decrease. The solubility of heavy metals and As as a function of pH can be explained by the variation in surface charge as a function of pH. At pH values above the point of zero charge (PZC), the sediment surface is negatively charged; pH values below the PZC result in a positively charged surface. This partly explains why cationic metals (e.g. Cd, Zn, Ni, Cu) are generally more soluble at low pH-values. However, complex formation with DOC can keep metals in solution at alkaline pH-values. Since, As occurs as arsenate in oxidized soils and sediments, a higher solubility is generally observed as pH increases. Nevertheless, the considerable solubility of As in the acid pH-range in sample GB(dr) (and GB(cl) to a lesser extent) (Fig. 6) can not be explained by a variable surface charge as a function of pH. The increased solubility of As in sample GB(cl) at pH 2 might be due to the dissolution of clay minerals at low pH. Goldberg (2002) also observed a decreased sorption of arsenate on clay minerals (illite, montmorillonite and kaolinite) at pH-values below 4. However, the leaching of As in the study of Goldberg (2002) was much smaller than in the present study. Phosphate can also play a role in the desorption of As.

The pH at the PZC for some minerals found in samples GB(dr), GB(fo) and GB(cl) is given in Table 4. Fe-(hydr)oxides have a pH_{PZC} in the range 6.3 – 9.1 (Table 4). The pH_{PZC} of quartz is 2, but in sample GB(fo), quartz grains are coated with Fe-(hydr)oxides. Moreover, all the samples are characterised by an elevated organic carbon content, which tends to decrease the pH_{PZC} .

Table 4 here

The solubility of dissolved organic carbon (DOC) and anions (Fig. 6) generally increased with increasing pH, although 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 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 pollutants, whereas DOC can mobilise metals and organic contaminants.

3.4.2 *Release rate of heavy metals during pH_{stat} leaching at pH 4.*

As mentioned before, the mathematical description of heavy metal release allows a kinetic fractionation of metals into a labile (RC_1) and a slowly labile (RC_2) pool. At pH 4 (only pH 4 is given, for comparison with column and cascade leaching tests), the release of Zn, Cd and Ni could be described as a sum of two exponential equations, but the release from the slowly labile pool (RC_2 , with release constant r_2) was by far dominant (Table 5). The slow release constant (r_2) of Zn, Cd, Ni, Cu and As is very similar for the 3 samples ($r_2 = 0.02\text{--}0.03 \text{ h}^{-1}$) and is an order of magnitude lower than the release rate of the labile pool ($r_1 = 0.4\text{--}0.3 \text{ h}^{-1}$). (Table 5). 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 5).

The leaching curve of Zn, Cd, Ni and Cu at pH 4 follows the same pattern as the ANC curve, as is also expressed by the very similar release rate (k_1 in Table 6 and r_1 in Table 5). The amount of cations released is however higher than the amount of protons introduced into the system (ANC). This was also observed by Schwartz et al. (1999).

Table 5 here
Table 6 here

4. Discussion

Although many different elements were measured, the discussion will principally be focussed on Cd, Zn, Ni, Cu and As. Major elements (Fe, Ca, P, Al) will be discussed for the interpretation of release mechanisms of trace metals.

4.1 pHstat leaching

4.1.1 *Leaching as a function of pH during pH_{stat} leaching*

Generally, heavy metals display the highest mobility at low pH values and heavy metal mobility decreases with increasing pH. For example Zn and Cd are only released at a pH below 6 from sample GB(cl) (Fig. 6). Ni, Cu, Zn and Cd are also released to some extent at alkaline pH values. This is due to complexation of these metals with DOC or inorganic ligands (e.g. OH⁻). For Cu a higher leachability was even observed at pH 10 than at pH 2 in sample GB(fo). The release at pH 10 was faster than at pH 2. A comparable observation was made for Fe, that was released in similar amount at pH 2 and 10, but for which a different leaching behaviour was observed at both pH's. At pH 2, the dissolution of poorly stable Fe-oxides can be responsible for the leaching of Fe, while at pH 10, Fe is released in complexed form, probably with DOC based on the general observation that Fe has a high affinity for DOC.

Arsenic occurs as an anion (arsenate in this case) in soil; consequently higher pH values promote the leaching of As. The samples GB(dr), GB(fo) and GB(cl) displayed a rather different leaching behaviour of As. The Fe-rich overbank sediment (GB(fo)) only released As at pH 8 and 10, presumably by desorption of arsenate from a negatively charged sediment surface. A similar amount of As was released from the dredged sediment (GB(dr)) at pH 2 and pH 10 (Fig. 6), but different patterns of As-release as a function of pH suggest that different mechanisms are involved in the release of As. At acid pH values, As can be released by the dissolution of mineral phases (e.g. the partial dissolution of Ca-phosphate), while desorption reactions are more likely at alkaline pH. PO₄³⁻ displayed a similar behaviour as As in the different samples. Finally, a small amount of As was released from the clayey overbank sediment (GB(cl)) in the acid pH range, the majority of As being released at pH 10.

4.1.2 *Assessment of equilibrium conditions*

During leaching, the driving force is the concentration gradient between the porewater and the free water volume (Fälmann and Aurell, 1996). Chemical equilibrium is reached when there is no concentration gradient between the porewater and the free water volume. Batch tests are based on the assumption that chemical equilibrium is reached during the test. Reaching equilibrium in single batch leaching tests is critical to predicting leaching behaviour over long

periods of time. If tests are conducted at non-equilibrium conditions, leaching behaviour does not reach capacity, and predictions of long-term leaching behaviour will be based on leachate concentrations that are too low or too high (EQM, 1998).

The mathematical description of leaching behaviour in pH_{stat} leaching tests allows an estimation of equilibrium conditions. 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 Equation 4). For example, the release of Cd from the clayey sediment (GB(cl)) has reached 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 (last column in Table 5: $\text{RC}_{\text{depleted}} = 95\%$). 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.

4.2 Influence of 'key-factors' in the column leaching test

In the column leaching test, a clear pH-dependent leaching behaviour of heavy metals was noticed. In the course of the test, the pH of the leachate increased (Fig. 1). The pH-increase is accompanied by a decrease in redox potential and also resulted in an increase in DOC- and Ni-concentrations in the successive leachates, while As and Cu showed a different behaviour in both samples. Modelling with MINTEQA2 suggested that complexation with DOC was important for Cu and Ni, but less important for Zn. This is consistent with the results of Ashword and Alloway (2004), who showed that the mobility of Cu and Ni in soil columns was greatly enhanced in the presence of dissolved organic carbon (DOC), but that DOC did not prevent the adsorption of Zn. The concomitant increase in DOC and Ni-concentrations may indeed indicate that DOC is a crucial factor in determining heavy metal release from samples GB(dr) and GB(fo). For Cu, however, a concentration decrease was observed with increasing L/S ratio in sample GB(fo), whereas leached Cu-concentrations in sample GB(dr) were not correlated with the release of DOC. pH can also be evoked to explain the release of heavy metals in the successive fractions. The release of Zn seems not influenced by the formation of organic complexes, since leaching behaviour of Zn and DOC are opposite in both samples. In sample

GB(fo), Cd also displayed a lower mobility with increasing pH. In sample GB(dr), however, a considerable amount of Cd was release in the last fraction of the column leaching test (at L/S = 10), most probably as complex with DOC. Both samples show the same evolution of pH whereas leached As was quite different in GB(dr) and GB(fo) (Fig. 1). The fact that As occurs in anionic form in soils and sediments explains the increased leaching of As with increasing pH in sample GB(dr). In sample GB(fo), the concentration of As was relatively constant in the different fractions.

Towards the end of the column test, an increase in the release of Fe was also noticed. It can be questioned whether the release of Fe is related to the release of Fe-DOC complexes or the reduction of Fe-oxides. However, the redox potential measured in the leachate is too high to cause the reductive dissolution of Fe-oxides. Nevertheless, it can not completely be ruled out that the redox potential inside the column was lower than the value measured in the leachate. The release followed the same pattern as the release of DOC, suggesting that the leaching of Fe is due to the release of Fe complexed with DOC.

The results of the column leaching test show that “key-factors” such as pH, E_h and DOC can in some cases be evoked to explain the release of heavy metals, but the results of different samples sometimes seem contradictory because other (not measured and/or not known) factors prevail.

4.3 Compatibility of cascade- and column leaching

When the results of a column leaching test (pH of the leaching solution is 4) and a cascade leaching tests (pH of the leaching solution is also 4) are presented together (Fig. 2), it is clear that the results of column and cascade leaching test are not entirely compatible. The release of elements at L/S = 10 (highest L/S ratio obtained in the column leaching test) is in some cases higher than the release at L/S = 20 (lowest L/S ratio in the cascade leaching test).

The cascade leaching test uses relatively high L/S ratios that correspond to a relatively long timeframe of leaching. Column tests can be run at much lower L/S ratios (<1) thus providing a means to evaluate leaching under conditions approaching field conditions. For sample GB(dr) the leachate at L/S = 10 had a pH of 7.5, while the pH at L/S = 20 was 7.0. Although a lower heavy metal release is usually expected at higher pH values, heavy metal complexation by

DOC may explain the more important release of heavy metals in the column test. The pH difference between the leachates of the column test and the cascade test seems an important reason for the discrepancy between the cascade- and column-leaching test. The pH increase of the leachate during column leaching is most likely due to the occurrence of reducing conditions in the column.

4.4 Compatibility of cascade- and column leaching with pH_{stat} leaching

The results of the cascade leaching test can be compared with the results of the pH_{stat} leaching test at pH 6, since this is more or less the pH obtained in the cascade leaching test. The amount of Cu and As leached in the pH_{stat} test at pH 6 ($L/S = 10$) was in line with the amount of Cu and As released in the cascade leaching test (Fig. 4). However, more Zn, Cd and Ni were released in the pH_{stat} test than in the cascade leaching test at $L/S = 20$. Latter elements are more sensitive to changes in pH.

It is also interesting to compare the results of the column test with the results of the pH_{stat} leaching test (pH 4). When the results of the column test (Fig. 2) are compared to the results of the pH_{stat} leaching test, (96 h) (Fig. 6), the cumulative leaching of Cu and As at $L/S = 10$ exceeds the amount of Cu and As released after 96 h in a pH_{stat} test at pH 4, 6 and 8. Ni also exhibits a considerable higher leachability. Different release mechanisms in the column and pH_{stat} leaching test explain the heavy metal and As leaching behaviour in both leaching tests. Comparing results obtained from different tests and making extrapolations to other samples is hardly feasible, because test conditions can not (completely) be controlled.

Although column, cascade- and pH_{stat} leaching tests are not completely compatible, batch tests (such as a pH_{stat} test) can be useful to estimate the release of elements from samples that are not suited to be analysed with a more complicated test such as a column leaching test. For example, column experiments were not performed for the clay-rich sediment (GB(cl)) because of the low permeability of this sediment. However, the very low leaching during the cascade leaching test and during the pH_{stat} test at pH 6 indicate a very small labile pool of heavy metals in this sediment.

4.5 Conclusion

During the investigation of leachability of contaminants in materials it is important to focus on key parameters (Van der Sloot et al., 1996). pH, redox potential and complexing ligands are important parameters towards heavy metal mobility in soils and sediments.

Column tests represent the time-dependent leaching behaviour and allow for quantification of retention in the soil or sediment matrix. The pH_{stat} test gives an indication of chemical speciation of components in the leachate and the influence of controlling factors such as pH on metal leaching behaviour. Moreover, additional information on heavy metal leachability and retention by the solid matrix in relation with variable surface charge is obtained from the kinetics of metal release during a pH_{stat} test.

The mathematical description of leaching behaviour during pH_{stat} tests allows a kinetic fractionation of metals in 'pools' with different reactivity. Contrary to single and sequential extractions, where attention is focussed on the reactivity towards a *reagent* (which is often difficult to link with a natural process), the reactivity and mobility of metals as a consequence of a *process* (acidification in the case of pH_{stat} leaching) is assessed. Column leaching tests investigate the 'actual' heavy metal mobility as a consequence of the infiltration of rainwater in soil. Analogously, the 'available' pool of metals can be deduced from the (mathematical) description of leaching behaviour in column tests.

The compatibility of the results of different leaching tests is, besides the inherent differences between methods (single batch tests versus dynamic leaching tests, the duration of the tests, L/S ratio,...) to a major extent determined by key-factors such as pH and redox potential. Depending on soil and sediments properties (e.g. acid neutralizing capacity (ANC)) these 'key-factors' will vary during and at the end of extractions and leaching test, even when the initial test conditions (e.g. the pH of the reagent) are equal for all test cases. During cascade- and column leaching tests, pH (which is initially 4) will mostly increase, but the extent of this pH-increase mainly depends on the acid neutralizing capacity of the sample. Therefore, measuring the pH of all leachates that are collected during these tests is mandatory for the interpretation of the results. Moreover, the monitoring of other variables such as DOC, anions and major

elements can give indications on the reactions that are responsible for the release of elements (e.g. the dissolution of organic matter) and greatly improve the interpretation of the results.

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Table captions

Table 1 Overview of leaching test and samples of this study

Table 2 Physico-chemical characteristics of samples GB(dr), GB(fo), GB(cl) (mean $\pm$ standard deviation of 3 replicates).

Table 3 Background concentrations of heavy metals (agricultural and natural areas) corrected for organic matter and clay content according to VLAREBO (OVAM, 1995)

Table 4 pH_{PZC} for some minerals

Table 5 Parameters from the fitting of heavy metal release according to Equation 3. (number of data points=1730, R is significant at $\alpha= 0.05$)

Table 6 Parameters from the fitting of ANC-BNC curves according to Equation 4. $t_{1,90\%}$ and $t_{2,90\%}$ give the time (h) to neutralize 90% of buffer component BC_1 and BC_2 respectively.

Tables

Table 1

Leaching test	duration	L/S	Use	Samples
Column leaching test (NEN7343)	3 weeks	0.1 to 10	Simulation of leaching of inorganic components from granular materials in aerobic conditions in a soil column	GB(dr) and GB(fo)
Cascade leaching Test (NEN 7349)	5 days	20 to 100	Simulation of leaching of inorganic components from granular materials in aerobic conditions in a serial batch test	GB(dr), GB(fo) and GB(cl) Subsamples GB(ca) and GB(fe)
pH_{stat} leaching test	96 h	10	Assessment of changes in leaching behaviour when <i>in situ</i> pH changes occur. Information is also obtained on the potential buffering capacity of the sample and its sensitivity to pH changes as a result of external stresses	GB(dr), GB(fo) and GB(cl)

Table 2

	Zn mg kg ⁻¹	Ni mg kg ⁻¹	Cd mg kg ⁻¹	Cu mg kg ⁻¹	As mg kg ⁻¹	
GB(dr)	4083 ± 345	84 ± 6	213 ± 16	182 ± 11	254 ± 25	
GB(fo)	320 ± 13	36 ± 2	40 ± 2	11 ± 1	196 ± 4	
GB(cl)	545 ± 12	20 ± 0,5	11 ± 0,4	26 ± 1	103 ± 2	
	Pb mg kg ⁻¹	Cr mg kg ⁻¹	Ba mg kg ⁻¹	Mn mg kg ⁻¹	Fe %	
GB(dr)	54 ± 2	84 ± 4	709 ± 28	527 ± 17	8,2 ± 1,0	
GB(fo)	67 ± 1	60 ± 1	199 ± 4	122 ± 6	14,7 ± 0,5	
GB(cl)	30 ± 1	282 ± 8	69 ± 3	64 ± 2	11,9 ± 0,6	
	Ca %	P %	Al %	K %	S %	
GB(dr)	1.67 ± 0.17	1.97 ± 0.19	1.21 ± 0.01	0.80 ± 0.02	0,35 ± 0,02	
GB(fo)	0.51 ± 0.03	0.46 ± 0.02	1.33 ± 0.10	0.66 ± 0.03	0,57 ± 0,03	
GB(cl)	0.26 ± 0.04	0.34 ± 0.01	3.38 ± 1.06	3.26 ± 1.20	0,16 ± 0,01	
	Org C %	CEC cmol kg ⁻¹	pH (H₂O)	clay %	silt %	sand %
GB(dr)	8.8 ± 1.0	19 ± 0.5	6.8 ± 0.2	45	42	13
GB(fo)	9.0 ± 1.0	31 ± 0.6	6.3 ± 0.2	21	29	50
GB(cl)	5.3 ± 0.4	33 ± 0.6	6.4 ± 0.2	81	15	4

Table 3

	Zn mg kg ⁻¹	Ni mg kg ⁻¹	Cd mg kg ⁻¹	Cu mg kg ⁻¹	As mg kg ⁻¹	Pb mg kg ⁻¹	Cr mg kg ⁻¹
GB(dr)	131	20	2,5	28	37	80	58
GB(fo)	105	15	1,8	20	25	74	44
GB(cl)	157	25	3,3	38	55	77	80

Table 4

Mineral	pH _{PZC}	References
hematite	6.3-8.5	Kosmulski (2004)
goethite	7-9.1	Kosmulski (2004)
ferryhydrite	6.8	O'Reilly and Hochella (2003)
quartz	2-4.2	Kosmulski (2004)
illite	2.5	Hussain et al. (1999)
	2.8	Hu et al. (2003)
kaolinite	2.8-3.8	Kosmulski (2004)

Table 5

			RC ₁	RC ₂	r ₁	r ₂	R	¹ RC _{depleted}
			%	%	h ⁻¹	h ⁻¹		%
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

$$^1\text{RC}_{\text{depleted}} = \text{RC}/(\text{RC}_1 + \text{RC}_2) \times 100$$

Table 6

Sample	pH	BC ₁	BC ₂	k ₁	k ₂	R	t _{1,90%}	t _{2,90%}
		%	%	h ⁻¹	h ⁻¹		h	h
GB(dr)	4	19	81	1.19	0.06	0.994	1.9	39.7
GB(fo)	4	18	82	0.45	0.02	0.998	5.2	129.2
GB(cl)	4	74	26	1.76	0.03	0.993	1.3	71.2

Figure captions

Figure 1: pH, redox potential and electrical conductivity (EC), DOC, Cd, Ni, Cu, Zn and As in the successive fractions of the column leaching test of samples GB(dr) and GB(fo).

Figure 2: Cumulative release of Zn, Cd, As, Ni, Cu in a column leaching test ($L/S = 0.1$ to 10) and cascade leaching test ($L/S = 20$ to 100). Cd, Cu and As were below detection limit in the cascade leaching test of sample GB(fo).

Figure 3: Availability (AVB, mg kg^{-1}) and retention parameters (K , L kg^{-1}) of As, Cd, Zn, Ni and Cu calculated according to Equation 1 for samples GB(dr) and GB(fo).

Figure 4: Cumulative leaching of As, Cd, Zn, Ni, Cu and DOC from samples GB(dr), GB(ob) and GB(cl) during the cascade leaching test. The overall concentration released during the 96 h pH_{stat} leaching test at pH 6 is also given by the grey symbol.

Figure 5: Retention factor (k^*) of Cd, Zn, Ni, Cu and As in sample GB(dr, GB(fo) and GB(cl) (according to Equation 2) as obtained from the cascade leaching test NF = No fit.

Figure 6: Leached amount (mg kg^{-1}) of Cd, Zn, Ni, Cu, As, DOC, SO_4^{2-} , PO_4^{3-} and ANC-BNC (mmol kg^{-1}) as a function of pH during the pH_{stat} test after 96 h in samples GB(dr), GB(fo) and GB(cl).

Figures

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6