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RISK ASSESSMENT OF HEAVY METAL POLLUTION IN ALLUVIAL SOILS AND SEDIMENTS OF THE GROTE BEEK RIVER (BELGIUM)

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1. Introduction

Wastewater discharge from the processing of phosphate ores has contributed to pollution by heavy metals and As in soils adjoining the Grote Beek river (15km long) (Central Belgium). Moreover, elevated chloride concentrations comparable to concentrations in seawater are discharged into the river. The study area is characterized by sandy soils and underlain by the Diestian Formation, containing between 30-40% glauconite. Organic- and iron-rich wetland soils have developed along this stream. The river follows a very meandering path and is characterised by several flooding zones that are inundated a few times a year. The analysis of soil and porewater samples from the area indicated a severe contamination of the floodplain soils and sediments with Cd, Cu, Ni, Zn, Ba and As (up to 276, 531, 172, 7507, 523 and 496 mg/kg respectively) (Cappuyns et al, 2002). The porewater contained elevated concentrations of Cd, Cu, Ni, Zn and Ba (up to 43, 187, 138, 1034 and 4432 µg/l respectively), while As did not seem of immediate environmental concern.

However, porewater composition only gives an indication on the availability and mobility of heavy metals in soils on one specific moment, yet fluctuations in porewater compositions often occur. To perform a risk assessment, predictions about the long-term behaviour of pollutants are necessary, which cannot only rely on porewater analysis. Also the capacity controlling parameters (CCP's) have to be taken into account since they control geochemical and microbiological processes that determine the fate of pollutants in soils and sediments (Stigliani et al., 1991). CEC, pH, redox potential, soil organic matter, salinity and microbiological activity are the CCP's of soils and sediments for heavy metals. In this study, different extractions and leaching tests were used to assess the influence of CCP's on heavy metal behaviour and to estimate the potential (long-term) mobility of heavy metals. Present discussion focuses on the results obtained for two samples (an overbank sediment rich in Fe and organic matter and a dredged sediment that was disposed on the riverbank) representative for the studied area.

2. Material and methods

Physico-chemical analysis, extractions and leaching tests were performed on two oven-dry samples, one representative for overbank sediments (O) and the second for dredged sediments (D). pH(H_2O) 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); effective cation exchange capacities (ECEC) were analyzed applying the 'silver thiourea method' (Van Reeuwijk, 1992). Total element concentrations (Al, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn, Fe, Mn, K, P and Ca) were determined after dissolution of the samples with a mixture of 3 concentrated acids (4 ml HCl_{conc}, 2 ml HNO_{3conc} and 2 ml HF_{conc}). These solutions were analyzed by AAS (Varian® Techtron AA6) for Ca, Fe, K and Al. For As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn, Mn and P a multi element analysis by ICP-MS (HP 4500 series) was carried out. A certified reference material (Montana Soil 2710) and sample duplicates were used for quality assurance of the analytical data. A mineralogical sample characterization was conducted by X-ray diffraction.

The influence of reducing conditions on heavy metal mobility was assessed by making use of a reducing agent ($NH_2OH.HCl$ in 25% CH_3COOH) at different concentrations (Davranche and Bollinger, 2002). 30 ml of $NH_2OH.HCl$ in 25% CH_3COOH (0.01, 0.05, 0.1, 0.2 and 0.5 M) was added to 0.2 g of oven dry soil in a 50 ml centrifuge tube. The experiment was conducted at 96 °C with a 5 h equilibration time as determined by Tessier et al. (1979). After reaction, the suspension was centrifuged (2500 r.p.m., 10 min.), decanted off and filtered (Millipore 0.45 µm).

To investigate the impact of elevated Cl^- concentrations in the floodwater on heavy metal mobility, extractions with Cl^- solutions at different concentrations (0, 250, 500, 1000, 2000, 4000 and 6000 mg/l) were performed. 20 ml of a NaCl solution was added to 1 g of sample in a polyethylene centrifuge tube, shaken on a reciprocal shaker during 10 h, centrifuged (3500 r.p.m, 10 min.), decanted off and filtered (Millipore 0.45µm). The samples were acidified and stored at 4°C until their analysis (ICP-MS)

A modified BCR-extraction scheme was applied (Table 1). Because of the elevated Fe-content of the samples, a reducing extraction with $NH_2OH.HCl$ 0.5 M was added to the original sequence. pH_{stat} leaching tests with continuous setpoint titration (pH 2, 4, 6, 8 en 10) were used to assess long-term effects of pH on heavy metal mobility and predict possible chemical time bombs (cfr. Van Herreweghe et al., 2002*).* The pH_{stat} tests were conducted during 96 h. However the pH_{stat} test for sample O was prolonged to 176 h because a sudden increase in the BNC curve at pH 10 after 71 h. Reaction kinetics was also considered by mathematical fitting of leaching curves as a function of time (Schwarz et al., 1999).

A Cascade Leaching Test (NEN 7341) was used to estimate the actual leachability of heavy metals in the samples. 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 HNO_3 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 until five fractions, with a solid/liquid ratios ranging from 20 to 100 were obtained. The cascade leaching test was also performed on $Ca_3(PO_4)_2$ (sample C) en Fe-oxide (sample F) subsamples that were separated from the dredged sediment (sample D). Element concentrations in the leachates of the pH_{stat} and cascade leaching tests were measured with ICP-MS. SO_4^{2-} was determined by turbidimetry (Vogel, 1961).

Table 1: Modified BCR extraction scheme

	Fraction	Chemical agents	Duration
Step 1	Acid-extractable	CH_3COOH 0.11M	16 h
Step 2a	Reducible	$NH_2OH.HCl$ 0.1M, pH 2	16 h
Step 2b	Reducible	$NH_2OH.HCl$ 0.5M in CH_3COOH 25%, 90°C	5 h
Step 3	Oxidisable	H_2O_2 15%, pH 2, 80°C; CH_3COONH_4	2x evaporate; 16 h
Step 4	Residual	$HNO_3/HCl/HF_{conc}$	

3. *Results*

Total concentrations of heavy metals are shown in Table 2. Intervention Values for Soil Contamination (Anonymous, 1995) were exceeded for Cd, As (both samples) and Zn (sample D). Quartz, hematite, amorphous Fe-oxides, pyrrhothite and glauconite were identified in the overbank sediment (O) by XRD-analysis. The dredged sediment (D) contained amorphous Fe-oxides, quartz, glauconite and $Ca_3(PO_4)_2$. $Ca_3(PO_4)_2$ and Fe-oxide grains were separated manually from the dredged sediment sample (D), characterised by XRD and analysed for major and trace elements. Amorphous Fe-oxides (F) were enriched in As and Ni. Small white particles which consisted of $Ca_3(PO_4)_2$ (C) contained elevated concentrations of Cd, Zn, Cu and As .

Table 2: Concentrations of heavy metals, As, Fe, organic carbon (org. C), CEC, pH (H_2O) in the 2 samples (D= dredged sediment, O= overbank sediment, C= $Ca_3(PO_4)_2$, F=Fe-oxide). NA = Not Analysed

	Cr	Ni	Cu	Zn	As	Cd	Ba	Pb	P	Ca	Fe	Org. C	CEC	pH
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	%	%	cmol/kg	
D	84	108	182	4083	254	213	753	84	20521	1.67	8,2	8,8	19.2	6,8
O	44	30	10	265	176	40	292	67	3920	0.53	14.7	9,0	31.2	6,3
C	119	78	462	8025	305	374	516	23	122659	3.43	0.47	NA	NA	NA
F	41	183	67	1773	446	210	350	27	12336	0.93	23.5	NA	NA	NA

3.1 Single Extractions

EDTA was capable of extracting between 50 to 100 % of the total concentrations of Cd, Ni, Zn, Cu an Pb. Only negligible amounts of Ba, As and Cr were released (Fig. 1). Cl$^-$ had the most significant effect on the leaching of Cu, Cd (Fig. 2a), Zn and Ni. In absolute concentrations the metal leachability decreased in the order Cu > Zn > Cd > Ni. Relative to their total concentrations in soil the order was: Cu > Ni, Cd > Zn. Stronger reducing conditions induced a significant increase of the release As (Fig. 2b), Pb, Ba and Cr.

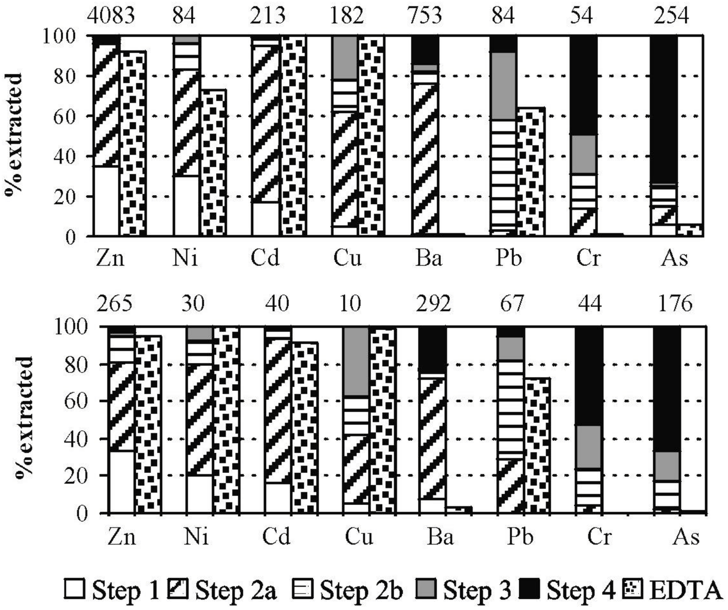


Figure 1: Heavy metal and As fractionation according to the BCR extraction (Table 1) in sample D (a) and O (b)

3.2 Sequential extractions

The fractionation of trace elements was very similar for both samples. Zn, Ni and Cd were principally released during the CH_3COOH (Step 1) and the $NH_2OH.HCl$ 0.1M (Step 2) extractions. For Cr an As, the residual fraction prevailed, while Pb was mostly recovered in Step 2b and 3. In the dredged sediment, a low but significant As-concentration (6 mg/kg) was extracted with CH_3COOH (Step 1) and EDTA. Cu and Ba are generally characterized by a considerable reducible fraction (Step 2a) and a significant amount of Cu was also released during the oxidising extraction (Step 3).

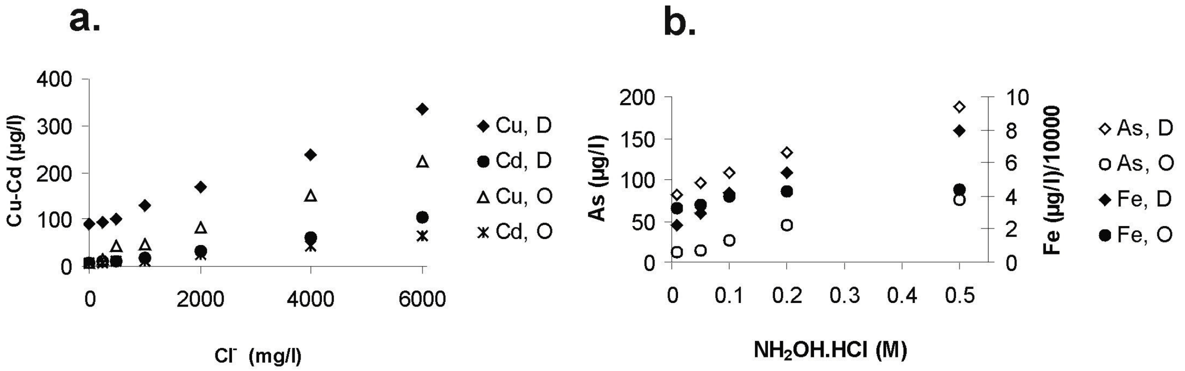


Figure 2: (a) Leaching of Cd and Cu as a function of Cl$^-$ concentration (b) Leaching of As and Fe as a function of $NH_2OH.HCl$ concentrations.

3.3 Leaching tests

Heavy metal concentrations in the leachates of the cascade test performed on the dredged sediment (D) were significantly higher than for the overbank sediment (O) (Table 3). Although Cu, Ni, Zn, As, Cd and Ba-concentrations were in the µg/l range for sample D, only Zn, Ni and Ba were leached from sample O in significant amount. The pH remained more or less constant during the leaching experiment. Nevertheless, sample O had a lower acid neutralizing capacity than sample D, as the pH of the extracts was on the average 0.5 units lower in the overbank sediment than for the dredged sediment.

Element concentrations in the leachates of the pH_{stat} tests after 96 h (D) and 167 h (O) at different pH values are given in Table 4. The dredged sediment is characterised by an elevated acid neutralising capacity (ANC). In general, the highest pollutant concentrations are released at the lowest pH values, except As in sample O, which is only leached at pH 10. In this sample also a considerable SO_4^{2-} and DOC release was observed at pH 10.

Table 3: Concentrations of selected trace elements (µg/l) and pH of the leachates of the cascade leaching test (mean ± standard deviation of three replicates). DL = below detection limit

	L/S	20	40	60	80	100
D	pH	7 ± 0,08	6,97 ± 0,04	7,06 ± 0,11	7,05 ± 0,01	6,95 ± 0,13
	Ca	18837 ± 1107	6158 ± 456	5215 ± 505	4658 ± 57	3859 ± 122
	Fe	107 ± 58	447 ± 95	151 ± 43	351 ± 126	320 ± 15
	P	1290 ± 5	2271 ± 130	1692 ± 153	1805 ± 47	1654 ± 46
	Ni	51 ± 6,0	35,2 ± 2,5	18,8 ± 1,2	16,1 ± 0,5	11,9 ± 0,3
	Cu	59 ± 3,1	43,6 ± 4,1	20,9 ± 6,2	15,9 ± 1,6	17,3 ± 3,4
	Zn	60 ± 11	53 ± 14	76 ± 32	25 ± 5	28 ± 9
	As	22 ± 0,5	37,9 ± 1,8	28,2 ± 2,5	29,4 ± 0,9	26,8 ± 1,0
	Cd	2 ± 0,49	1,65 ± 0,93	0,18 ± 0,16	0,60 ± 0,67	DL
	Ba	10 ± 1,46	6,82 ± 0,69	3,75 ± 0,55	3,89 ± 0,87	3,61 ± 0,24
O	pH	6,07 ± 0,04	6,43 ± 0,07	6,62 ± 0,14	6,57 ± 0,22	6,51 ± 0,21
	Ca	35060 ± 465	5908 ± 153	3328 ± 141	3222 ± 191	2368 ± 98
	Fe	113 ± 7	743 ± 189	505 ± 216	765 ± 114	721 ± 80
	P	DL	DL	DL	DL	DL
	Ni	18 ± 1,7	15,7 ± 1,0	8,0 ± 1,2	8,0 ± 1,1	5,7 ± 3,4
	Cu	0,1 ± 0,1	DL	DL	DL	1,0 ± 1,8
	Zn	27 ± 1	18 ± 13	20 ± 4	4 ± 1	13 ± 11
	As	DL	0,2 ± 0,2	DL	0,1 ± 0,2	0,1 ± 0,1
	Cd	0,86 ± 0,03	DL	DL	DL	DL
	Ba	29,04 ± 0,80	8,00 ± 0,82	3,52 ± 0,80	4,63 ± 1,36	3,31 ± 0,66

Table 4: pH_{stat} leaching of sample D and O. 'Time' gives the time to reach a certain ANC assuming a worst case scenario. DL = below detection limit

		D						O					
		pH2	pH4	pH6	pH_{soil}	pH8	pH10	pH2	pH4	pH6	pH_{soil}	pH8	pH10
Ca	mg/kg	22841	8537	1827	401	113	92	6712	4256	1401	779	299	250
Fe	mg/kg	206	25	4	3	7	160	876	10	<1	<1	12	325
P	mg/kg	7813	1155	48	22	66	504	2	3	2	1	8	128
Ni	mg/kg	99	25	1	1	2	4	38	3	0,39	0,34	1	6
Cu	mg/kg	67	2	DL	1	2	15	1	DL	DL	DL	0,28	2
Zn	mg/kg	4066	347	5	0,19	0,08	3	276	148	4	2	3	8
As	mg/kg	14	6	1	1	1	11	DL	DL	DL	DL	DL	2
Cd	mg/kg	140	10	0,42	0,06	0,08	0,41	40	3	0,1	DL	DL	0,3
Ba	mg/kg	43	7	1	DL	DL	1	205	8	1	1	DL	1
SO_4^{2-}	mg/kg	61	22	20	24	45	192	24	27	43	147	58	489
DOC	mg/kg	174	57	32	32	95	339	46	45	76	90	174	828
ANC/BNC	meq/kg	2331	680	64	-	276	788	994	409	46	-	208	590
Time	year	1485	433	41	-	-	-	633	261	29	-	-	-

4. Discussion

4.1 Sequential extractions and EDTA

The pool of potentially available metals consists of those fractions, which can deliver metals from the solid phase of the soil to the soil solution in a relatively short time period. EDTA extractions are often used to estimate this potentially available pool. Sequential extractions divide the total content of heavy metals in a soil sample in different pools according to their reactivity. Assuming that stronger chemical reagents can be related to lower potential mobility and availability, metals released at the beginning of the sequence have a higher potential availability then the fractions obtained at the end.

When comparing the information on heavy metal mobility obtained from EDTA-extraction and sequential extraction, (Fig. 1) some apparent incompatibilities can be deduced. Cd, Zn and Ni were mostly extracted in the first two steps of the sequential extraction, pointing to a considerable potential availability. This is confirmed by the almost complete extraction of these elements by EDTA. Cu and Pb displayed a rather low potential availability according to the sequential extraction, still Cu is completely extracted by EDTA and also a significant amount of Pb (50-70% of its total concentration) was released by EDTA, suggesting an important potential availability of these elements. This may indicate that organic matter, which is also dissolved by EDTA, is an important sink for Cu. Another possibility is the readsorption of Pb on Cu on non-dissolved compounds during the sequential extraction, while EDTA forms stable complexes with the extracted elements, keeping them in solution.

4.2 Reducing conditions

Fe-oxides have a high capacity to adsorb heavy metal cations and oxyanions. In poorly drained soils with a high water table, a rise of the piezometric level or flooding of the soil will cause a redistribution or depletion of Fe-oxides and a release of contaminants. Although the reducing conditions brought about by $NH_2OH.HCl$ are not representative for a flooding period of a few days up to a few weeks, they give an indication on the reactivity of Fe-oxides and the potential mobilisation of metals.

Cd, Zn, Ni and Cu leachability do not significantly increase with increasing $NH_2OH.HCl$ concentrations, indicating that they are not incorporated in stable Fe-oxides. Increasing reducing conditions have the most significant effect for As, Pb, Ba and Cr. This suggests that stable (crystalline) Fe-oxides are an important sink for As, Ba, Pb and Cr. These results also show that the modification of the BCR extraction scheme, which consisted on the addition of a strongly reducing extraction step, was most important for As, Ba, Pb and Cr. Although a considerable readsorption of As is possible at the low pH value of the extract, CH_3COOH seems to significantly diminish this readsorption. A different reactivity of Fe-oxides in sample D and O, related to a different crystallinity, was apparent from the amount of Fe extracted by increasing $NH_2OH.HCl$ concentrations.

4.3 Actual availability: Cascade leaching test and influence of chlorides

Although the EDTA extraction indicates a considerable potential availability of Zn, Ni and Cd, the actual leachability of Zn, Cd and Cu (cascade leaching test) is relatively low with respectively less than 1%, 1% and 4% of the potentially extractable pool of the dredged sediment that was released. The amount of Ni and As released in the cascade leaching test represent about 25% of the potentially available pool. A completely different heavy metal mobility is obtained for the overbank sediment, in which only Zn, Ni and Ba have significant but low actually available pool (less than 2% of the potentially available pool for Zn and Ni. 30% for Ba). No As and Cd were released from this sample during the cascade leaching test.

However, when the elevated Cl^- concentrations in the riverwater and the porewater are taken into account, a much higher actual availability of Cd, Cu and to a lesser extend Zn and Ni is observed, pointing to the importance of chlorides towards the mobility of these elements. Increasing the Cl^-- concentration from 0 mg/l to 6000 mg/l resulted in a 9-fold increase in the mobility of Cd and the release of Cu was multiplied by a factor 3 (D) to 10 (O). Doner (1978) studied the mobility of chlorocomplexes through soil and found that Cl^- had a marked effect on the mobility of Cd, and to a lesser extend on Ni and Cu. The mixing of humic bound metals with seawater can release these metals and make them more available for uptake (Lores and Pennock, 1998).

Additional information on the processes that are responsible for heavy metal release in the dredged sediment is obtained from the cascade leaching test on $Ca_3(PO_4)_2$ (C) and Fe-oxides (F). Desorption of Ni from Fe-oxides is more important than from the bulk sample and from $Ca_3(PO_4)_2$. Arsenic on the other hand is principally released from $Ca_3(PO_4)_2$, which thus represents a major sink of As in the dredged sediment.

Notice that very little As is released from the Fe-oxides. More Cd, Zn and Cu are released from the bulk sample than from the Fe-oxides and $Ca_3(PO_4)_2$, indicating that other components of the dredged material (e.g. clays and organic matter) are also responsible for the release of Cd, Zn and Cu.

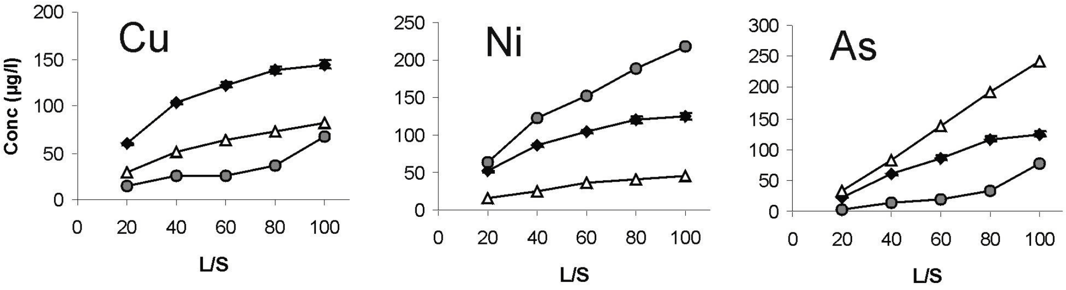


Fig. 3: Cumulative leaching of Cu, Ni and As from sample D (◆),F (Fe-oxide) (●) and C ($Ca_3(PO_4)_2$ (△)

4.4 pH_{stat} leaching tests

The amount of acid added to a soil-water suspension to keep the pH at a predefined constant value gives an estimation of the acid neutralizing capacity (ANC) of this sample. ANC depends on the reference pH chosen and on the duration of the pH_{stat} experiment. Acid buffering capacities of sample D display a different pattern as for sample O. While ANC has an asymptotical behaviour as a function of time in samples D, a steeper curve is obtained for sample O. ANC curves obtained in the pH_{stat} tests with continuous setpoint titration were described according to Schwartz et al. (1999). The proton buffering capacity of soils during pH_{stat} experiments can be described as the sum of two independent first-order reactions:

$$\mathbf{H_b(t) = BC_1\,(1- \exp(-k_1t)) + BC_2\,(1-\exp(-k_2t))} \qquad \mathbf{(1)}$$

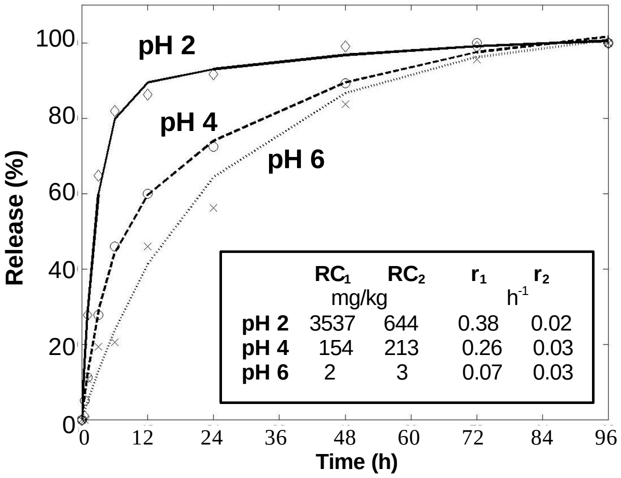
With: $H_b(t)$ = buffered protons at time t (meq/kg), BC_i = buffering capacity of system i (meq/kg), k_i is the rate coefficient of the buffer system i and t is the time after starting the titration (h). Analogously, heavy metal release as a function of time was described in a similar way as the ANC. The cumulative release of an element m at time t is given by:

$$\mathbf{RL_m = RC_1(1- \exp(-r_1t)) + RC_2(1- \exp(-r_2t))} \qquad \mathbf{(2)}$$

With RC_i = the release capacity of buffer system I, r_i is the rate coefficient of the buffersystem i [h^{-1}] and t is the time after starting the titration.

As pH increases from 2→ 4 → 6 in the respective pH_{stat} experiments, the release rate (r_1) of most elements decreases (Fig. 4). In the dredged sediment, 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 equation 2, is characterised by a release rate that is an order of magnitude lower (r_2 = 0.02-0.03 h^{-1}). The leaching curve of these elements also follows the same pattern as the ANC curve. 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). As, P and Ba 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. Readsorption of negatively charged arsenate and phosphate ions on the positively charged soil surface can explain the behaviour of As and P (Fig. 6a). The decrease in Ba concentrations with time, which is less pronounced than for As and P, seems to be caused by the precipitation of $BaSO_4$. While competition between As (AsO_4^{3-} and $HAsO_4^{2-}$) or P (PO_4^{3-} and HPO_4^{2-}) and OH^- ions, that were added to the system, explains for the release of As and P at pH 10 in the dredged sediment, complexation with DOC is an important release mechanism for Cu.

Desorption of heavy metals in sample O 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 D. The release of Fe, Cu and Pb at pH 2 is even linear as a function of time, indicating a slow dissolution of Fe-oxides and the concomitant release of associated (coprecipitated) elements. The release rate of Cd displayed a constant decrease, as the sink for Cd is progressively depleted (Fig. 5). At pH 4, only 50 % of the total amount of Cd present in sample O was leached and almost no Fe was released. Both desorption and dissolution processes account for the leaching of Cd in the acid pH range (pH 2). Geochemical modelling (MINTEQA2) suggests that the Cd leached at pH 4 was desorbed from the surface of Fe-oxides. The extra amount of Cd leached at pH 2 was probably released as a result of the dissolution of poorly stable Fe-oxides. Leaching of most elements at pH 10 in sample O started after 48 h (Fig. 6b). 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 at that time. After 71 h, a break appeared in the BNC curve, suggesting the start of new base neutralizing reactions. The elevated DOC concentrations indicate a considerable dissolution of organic matter. MINTEQA2 modelling however indicates that the speciation of Ni and Zn is dominated by hydroxy-complexes ($Zn(OH)_{2aq}$ en $Ni(OH)_{2aq}$), while Cd mainly occurs as chlorohydroxy-complex (Cd(OH)(Cl)).



	RC_1	RC_2	r_1	r_2
	mg/kg		h^{-1}	
pH 2	3537	644	0.38	0.02
pH 4	154	213	0.26	0.03
pH 6	2	3	0.07	0.03

Figure 4: Release (% of concentration after 96 h) of Zn in sample D as a function of time during the pH_{stat} test at pH 2, 4 and 6. (Symbols: experimental results, lines: fitted results according to equation 2)

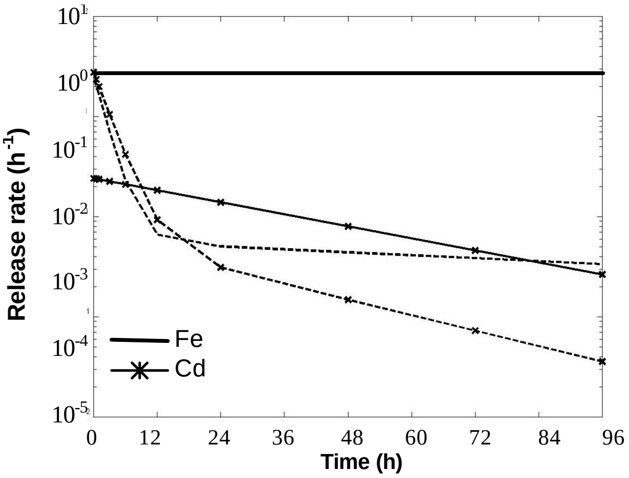


Figure 5: Release rate of Cd, Fe and Ca as a function of time during the pH_{stat} test at pH 2 (full lines: sample O, dotted lines: sample D)

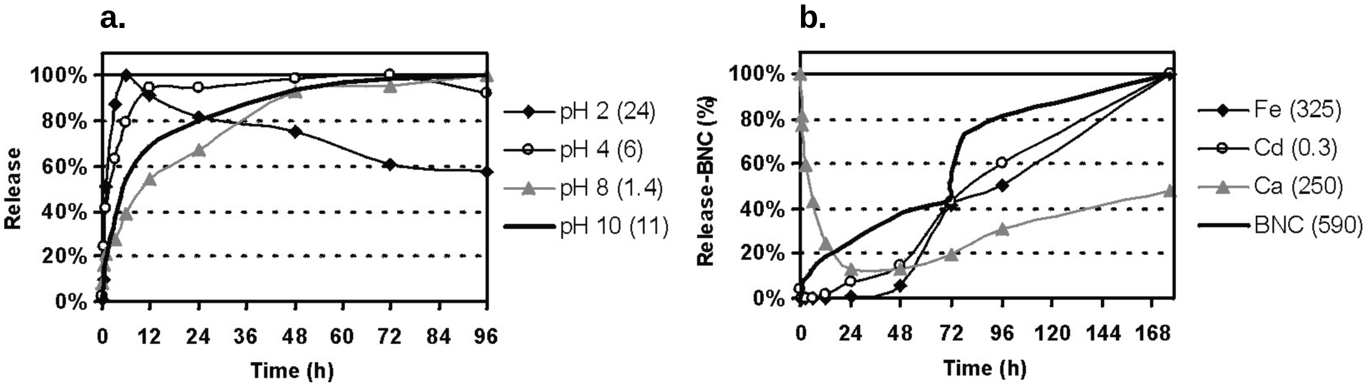


Fig. 6: (a) Leaching behaviour of As in sample D at pH 2, 4, 8 and 10 (b) Leaching behaviour of Fe, Cd and Ca and BNC in sample O at pH 10 (% of maximal concentration, which is given between brackets (in mg/kg)).

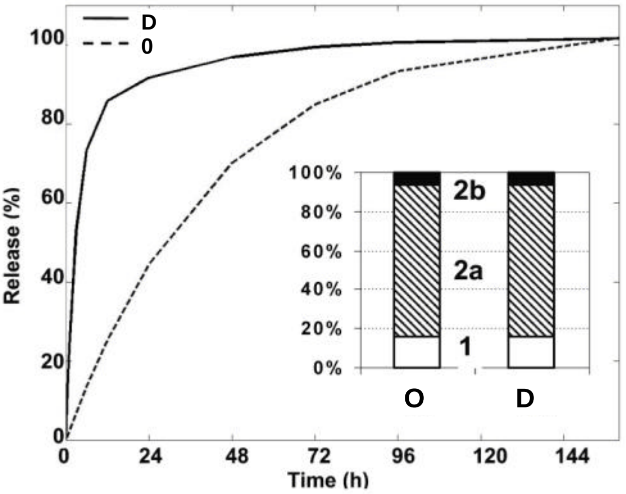


Figure 7: Release (% of concentration at the end of the experiment) of Cd as a function of time during the pH_{stat} test at pH 2 and Cd fractionation according to the BCR sequential extraction

Sequential extractions give a similar fractionation for Cd in samples O and D (Fig. 7) and the EDTA-extract suggests a comparable potential availability of Cd in both samples. At pH 2 (Fig. 7) and 4, a much slower release of Cd was nevertheless observed in the overbank sediment (O) compared to the dredged sediment (D). This different leaching behaviour, related to differences in reaction kinetics, indicates a different speciation of Cd in both samples.

The total acid deposition by rain in Flanders in 1998 amounted to 4082 equivalents of acid per hectare and per year (Mensink et al., 2000). Assuming quasi constant emissions of SO_x, NO_x and NH_x compounds in the coming years and accepting that ANC is correctly estimated by the pH_{stat} leaching tests, future contaminant leaching can to some extent be predicted. The time needed to reach a certain ANC is given in table 3. Assuming a worst case scenario, 2.4 mg/kg Cd will be leached from the dredged sediment and 1.06 mg/kg from the overbank sediment in a timespan of 100 years. The considerable acid neutralizing capacity of the dredged sediment and the elevated Fe-concentrations in sediments of the study area contribute significantly to the immobilization of heavy metals and As.

5. Conclusion

Heavy metal mobility in alluvial sediments of the Grote Beek river was evaluated by using different extractions and leaching techniques. The actual availability of heavy metals (Zn, Cd, Cu, Ni and As) was higher in the dredged sediment than in the overbank sediment. Flooding of the riverbank with Cl^- rich water mainly has an influence on the mobility of Cu and Cd. While Cd was already of concern because its concentrations exceed by far Intervention Values for Soil Contamination, the information on mobility of Cu is very important since this metal doesn't display excessive total concentrations in the sediments.

pH_{stat} leaching tests were applied to study the long-term heavy metal behaviour. They also allowed to assess reaction mechanisms involved in the release of heavy metals and to consider reaction kinetics. pH_{stat} tests indicated a strong binding of As with the soil matrix in the overbank sediment since almost no As was released in the pH range 2-10. Strongly reducing conditions brought about by $NH_2OH.HCl$ caused a substantial release of As, pointing to the incorporation of As in Fe-oxides. A higher As-mobility was found in the dredged sediments, because of the association of As with $Ca_3(PO_4)_2$ particles. Despite some artifacts in sequential and EDTA extractions, additional information on the reactivity of heavy metals was obtained. Although EDTA extractions suggest a considerable potential availability of Cd, Zn, Ni and Cu, pH_{stat} leaching tests indicate that this potentially available pool will only be released very progressively.

6. References

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