Discrimination between Cr(VI) and Cr(III) load by sequential leaching methods

M. Sager

Sequentielle Löseverfahren zur Unterscheidung einer Beladung mit Cr(VI) oder Cr(III)

1. Introduction

In recent years the load of heavy metals discharged from industry to soils and water has become of increasing interest. Besides the determination of total metal contents, selective dissolution procedures have gained importance, because they yield more information about the environmental mobility and biological availability of metals although the results depend upon the method applied.

In the case of chromium, there can be a large residual fraction, which can only be dissolved with acid mixtures containing hydrofluoric acid, and probably derives from chromite or micas; hence total chromium values does not necessarily indicate a high anthropogenic load (SAGER et al., 1989). For an estimation of the ecological impact of chromium containing effluents, it would be useful to know whether the ecosystem has been charged with the relatively harmless Cr(III), which behaves like Fe(III), or with the toxic Cr(VI) (FRIBERG et al., 1979). There are several me-thods for discrimination between Cr(III) and Cr(VI) in solution, but their use in field work is limited to in situ measurements because of the high reactivity of Cr(VI).

In natural waters, dissolved Cr(VI) reacts with suspended matter and sediment and is at least partly reduced to Cr(III) (HARZDORF, 1987). Therefore, at least in rivers and reservoirs of the Ukraine, no dissolved Cr(VI) could be detected, even at a redox potential of 300–400 mV and 140–160 % oxygen saturation. At 100 µg/l, Cr(VI) is reduced by Fe(II), sulfide and sulfite quantitatively within less than one hour. Aminoacids and fulvic acids need two hours, and carboxylic acids need 2–5 days for quantitative reduction of chromate (LESHCHINSKAYA and LINNIK, 1990). Similarly, in the activated sludge process, Cr(VI) is reduced at pH 8–9 within 2–4 days, and at pH 5 within one week (IMAI and GLOYNA, 1990). Enterobacter cloacae in activated sludge has been found to be capable of reducing Cr(VI) at pH 6.0–8.5, if conditions turn anaerobic. This bacterium can live in the presence of high concentrations of Cr(VI)

Zusammenfassung

Sedimente aus österreichischen Flüssen wie auch technische Tone und Böden wurden über Nacht mit Cr(III) oder Cr(VI) hältigem Leitungswasser geschüttelt und dadurch beladen. Während Cr(III) quantitativ aufgenommen wurde, hing die Aufnahme von Cr(VI) von der Zusammensetzung der Probe ab, besonders vom Gehalt an organischem Kohlenstoff.

Die Desorption des Chroms wurde von beladenen und unbeladenen Proben mit zwei unabhängigen sequentiellen Löseverfahren untersucht. Die erhaltenen Lösemuster hingen von der ursprünglichen Art der Chromspezies sowie auch von den Hauptkomponenten der Festkörper ab. Während die Cr(VI) Beladung teilweise von Ammonchlorid desorbiert wurde, war die Freisetzung von Cr(III) vernachlässigbar. Im Gegensatz dazu waren die Unterschiede in einer Löse-folge, die mit Ammonacetat pH 7 begann und mit Ammonacetat pH 5 fortsetzte, gering.

In den durchgeführten Lösefolgen wurden die Hauptmengen der Beladung in 0.5M HCl bzw. in Hydroxylamin/25 % Essigsäure wiedergefunden. Hingegen löste heiße Salpetersäure gleich große Gehalte von den beladenen oder den unbeladenen Proben. Einiges von der Chrombeladung ging auch an Anteile, die nicht ohne Flußsäure löslich waren.

Schlagworte: Chromadsorption und Freisetzung, Bindungsformen des Chroms, sequentielle Löseverfahren.

Summary

Freshwater sediments from Austrian rivers as well as clays and soils were spiked with Cr(III) or Cr(VI) by shaking them overnight with non-acidified tap water. Whereas the adsorption of Cr(III) was quantitative, chromium(VI) adsorption depended on the sample composition, especially on the organic carbon contents.

The desorption of chromium from spiked and non-spiked samples was investigated by two independent sequential leaching methods. The resulting leaching patterns depended on the original form of the chromium species as well as on the main components of the solids. Whereas the Cr(VI) spike was partially desorbed by ammonium chloride, the displacement of Cr(III) was negligible. Contrary to this, in a leaching sequence starting with ammonium acetate pH 7 and followed by ammonium acetate pH 5, the differences in the release patterns of both spikes were small.

In the leaching sequences applied, major parts of the spikes were found in 0.5M HCl, or in hydroxylamine/25 % acetic acid. From the original sample, hot HNO_3 mobilized the same amounts than from the spiked ones. Some of the Cr-spikes moved to fractions not leachable without HF.

Key words: chromium adsorption and release, chromium speciation, sequential leaching.

under both aerobic and anaerobic conditions (WANG PI CHAO et al., 1989). Therefore, input of Cr(VI) cannot be detected just by determination of Cr(VI) in the water phase.

As it cannot be expected a priori that the chromium found in the environment will be in its original oxidation state, it would be informative to monitor the history of a given substratum. This could be done if the Cr(III) and Cr(VI) arriving via the water phase, each move to a different type of adsorption site. It should then be possible to discriminate between the Cr(III) and Cr(VI) load by suitable sequential leaching methods.

In this work, two independent sequential leaching techniques, already used for the characterization of river sediments (SAGER et al., 1989; SAGER and VOGEL, 1993), are applied to sediments, clays and soils, either in their original state or spiked with Cr(III) or Cr(VI), to look for significant patterns of release in relation to the main composition of the sample.

Some slight changes have been introduced into the leaching procedures. The sequence originally developed for phosphate speciation (PSENNER et al., 1984) was started with NH_4Cl/NH_3-buffer at pH 7 instead of distilled water; this was introduced 1980 (HIELTJES and LIJKLEMA, 1980) as an extractant for adsorbed and weakly bound sediment phosphate. It may act as a model extractant for ion-exchangeable anions, such as arsenate or chromate. The use of a buffer implies that the ionic strength and pH will be constant for all samples. In the sequence primarily designed for speciation studies of cationic elements (TESSIER et al., 1979), hydroxylamine was preferred to be used in 25 % acetic acid medium instead of in 0.01M nitric acid; if dolomite is present in the samples, it is mainly not dissolved in the preceding dissolution step for carbonates (pH 5). Carbo-

nates consume the 0.01M nitric acid, and hydroxylamine is not effective any more (LUOMA and BRYAN, 1981). The oxalate buffer leach was introduced to yield an additional fraction of iron/aluminium/manganese hydroxides which are very important for trace element adsorption (SAGER et al., 1989; HONG and FÖRSTNER, 1983).

2. Literature data on chromium speciation in freshwater systems

Together with Al, Mn, Fe and Co, Cr is mainly transported with the suspended matter because of adsorption and coprecipitation reactions; its geochemical mobility is regarded as low (BRONDI et al., 1984). In the suspended matter of the River Po, good correlations of Cr with Mn and Ni have been found (BRONDI et al., 1984).

Whereas Cr(III) is strongly adsorbed on various clay minerals, such as montmorillonite, kaolinite, or illite, as well as on iron and manganese oxides at pH 7, this is not the case for chromate and molybdate. Cr(III) is quantitatively coprecipitated with iron and aluminium hydroxides at pH > 5, whereas coprecipitation of chromate begins at about pH 4, but decreases at pH > 6 (YAMAZAKI et al., 1980). In dilute aqueous solutions, the stability of chromate increases with increasing pH (PAVEL et al., 1985).

In suspended particles in the Shonai and Kiso Rivers in Japan, major amounts of chromium have been found as dissolved chromate, and minor amounts as Cr(III) associated with negatively charged colloids, such as humic acids or clays (HIRAIDE and MIZUIKE, 1989). Cr(III) seems to be precipitated or adsorbed rather rapidly.

In Lake Orta (Northern Italy), which is heavily pollut-

ed with effluents from electro-plating, the Cr and Zn contents of the sediment were strongly correlated with the organic carbon, even more than Cu is (PROVINI and GAGGINO, 1984). Similarly, in sediments in Lake Geneva, both Cr and Cu are correlated with organic carbon (WANG et al., 1986).

In sequential leaching procedures applied to freshwater sediments, Cr is very immobile, contrary to As, Co, Cu, Ni, Pb or Zn. The proportion which can be mobilized with neutral salts or weak acid buffers (up to pH 5) has been largely only about 1 % of the total content (SAGER et al., 1989; SAGER and VOGEL, 1993; PROVINI and GAGGINO, 1984; HONG and FÖRSTNER, 1983; SAGER et al., 1990). Only in the Karst region, higher mobility has been found (PROHIC and KNIEWALD, 1987). Approximately half of the total chromium in these sediments, depending on the grain size, cannot be dissolved without the aid of hydrofluoric acid.

In the modified Tessier leaching sequence (SAGER et al., 1989; SAGER and VOGEL, 1993; HONG and FÖRSTNER, 1983), the largest releasable fraction is obtained with oxalate buffer. It is surface-related and has Fe, Mn, and Al as its main components (SAGER et al., 1989). The net load of chromium from municipal effluents added to a non-calcareous sediment of a small river was released by oxalate and hydroxylamine/acetic acid (SAGER et al., 1990).

Citrate/dithionite does not dissolve much less chromium than dilute hydrochloric acid does (MALO, 1977), but without citrate, the amount leached with bicarbonate/dithionite at pH 7 is generally negligible (SAGER et al., 1989; this work).

3. Literature data about adsorption and desorption of trace metal cations

Concerning clay minerals, Ag, Cu and Cr were quantitatively adsorbed from kaolinite, smectite, and bacterial cell walls. As exceptions, Ag on kaolinite (48 %), Ag on smectite (70 %) and Cu on kaolinite (52 %) were found (FLEMMING et al., 1990).

At pH 3, major amounts of previously adsorbed Cu and Ag are remobilized from clay minerals and bacterial cell walls, but the release of Cr needs stronger conditions. On the other hand, complexants like EDTA or fulvic acid, preferably desorb Cu, but nearly no Cr (FLEMMING et al., 1990).

4. Material and methods

Wet sediment, corresponding to 1–2 g dry weight, was weighed into centrifuge tubes, and 50 ml tap water (water hardness equivalent to about 80 mg CaO/l) containing a known amount of chromium were added. The buffer capacity of the tap water was probably low enough to establish the original sediment pH. As Cr(III), 1000 ppm Merck Titrisol standard solution ($CrCl_3$ in diluted HCl) was added. Other trace elements, like Cu, Zn or Pb, were added as Merck Titrisol standards as well. As Cr(VI), a solution equivalent to 1000 ppm Cr was prepared by dissolution of $K_2Cr_2O_7$ in water.

After shaking overnight, the tubes were centrifuged and the supernatant liquid was decanted and analyzed for chromium to determine the amount of chromium transferred as a spike of the solid. The spiked sediments were submitted to two independent sequential leaching procedures (PSENNER et al., 1984; HIELTJES and LIJKLEMA, 1980) (see Table 1) and (TESSIER et al., 1979) (see Table 2).

Table 1: Fractionation procedure developed for phosphate speciation (PSENNER et al., 1984)

Tabelle 1: Fraktionierungsverfahren entwickelt zur Ermittlung der Bindungsformen von Phosphat (PSENNER et al., 1984)

The reagent solutions were applied sequentially. After shaking, the samples were centrifuged and decanted. 1 g sample (dry weight) was extracted with 50 ml of reagent each.
A) 1 M ammonium chloride/sodium hydroxide pH = 7, overnight
B) 0.1 M sodium dithionite/0.1 M sodium hydrogencarbonate, pH = 7, 2 hours
C) 1 M sodium hydroxide, overnight
D) 0.5 M hydrochloric acid, overnight
E) 1 M sodium hydroxide, 3 hours, boiling
(1 M NH_4Cl/NaOH buffer pH = 7 for exchangeable amounts after HIELTJES and LIJKLEMA, 1980).

Table 2: Fractionation procedure developed for trace metal speciation (TESSIER et al., 1979; HONG and FÖRSTNER, 1983)

Tabelle 2: Fraktionierungsvefahren entwickelt zur Ermittlung der Bindungsformen kationischer Spurenelemente (TESSIER et al., 1979; HONG and FÖRSTNER, 1983)

The reagent solutions were applied sequentially. After shaking, the samples were centrifuged and decanted. 1 g sample (dry weight) was extracted with 50 ml of reagent each.
A) 1 M ammonium acetate pH = 7, overnight
B) 1 M ammonium acetate buffer pH = 5, overnight
C) 0.1 M hydroxylamine hydrochloride/25 % acetic acid, overnight
D) 0.2 M oxalate buffer pH = 3, overnight
E) Oxidation with boiling 20 ml 30 % hydrogen peroxide, then leaching with 1 M ammonium acetate pH = 7, overnight
F) boiling conc. 20 ml HNO_3, washing with water

Determinations were mainly done by simultaneous ICP-spectrometry. The standards were prepared with the same reagent solutions which were used for the leaching, to cope with matrix effects. For the calibration curves, both the slopes and the counts for the zero-solutions were matrix dependent (FLEMMING et al., 1990). The signal had to be corrected for non-specific background caused by Ca. Low Cr levels in the presence of high Na were determined by atomic absorption in the graphite furnace, employing dilution 1 + 4 and standard addition (SAGER et al., 1989).

The solid samples were characterized by total decomposition with $HClO_4/HNO_3/HF$, as well as by sequential leaching. The soils were treated with aqua regia, as it is usual in soil analysis.

When the µg/g Cr released in each fraction from the unspiked samples are subtracted from the spiked ones, the net leaching patterns are obtained. The percentage of release of the adsorbed amounts did not depend on the concentration of spike within the range investigated.

As technical bentonite, a commercial product PACT-s (International GmbH) was used. It contains a mixture of clay minerals of octaedric type, mainly montmorillonite.

The halloysite sample was kindly submitted by the institute of geology of Vienna university. It is a two layered clay mineral, precipitates from acid watersheds, and closely resembles kaolinite.

5. Results and discussion

5.1 Chromium adsorption

Cr(III) was nearly quantitatively retained by all sediment samples and soils investigated, within the range of 100–2300 µg/g (Table 3), at the proper pH of the sample. Among the pure clays treated, the effect of changing pH during adsorption was monitored in three cases; this effected the amount of adsorption, whereas it did not influence the subsequent pattern of sequential leaching. The montmorillonite/Fe-hydroxide was a deep red clay, which adsorbed more Cr after addition of some HCl; whereas the halloysite and the technical bentonite were faintly grey, and increased adsorption after addition of some NaOH (Table 4).

Table 3: Adsorption of Cr and other trace elements on various substrates from tap water, shaking overnight
Tabelle 3: Adsorbierte Mengen an Cr und anderen Spurenelementen an verschiedenen Proben aus Leitungswasser beim sich mit der Probe selbst einstellenden pH

Type	Location	Cr^{3+}	CrO_4^{2-}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	pH	% org.	% $CaCO_3$
Sediment	Danube AW-S18	100	12.6	-	-	-	-	7.2	2.2	15
	Danube AW-S23	99.2	8.1	100	-	98	100	7.0	2.3	19
	Danube Greif	100	-	100	-	98.1	100	6.8	2.0	14
	Schwechat	99.8	27.9	100	87.8	97.5	100	-	-	24
	Stempflbach 156	99.7	24.8	100	97.5	99.7	100	-	-	35
	Stempflbach 158	99.7	-	99.9	61.0	82.1	99.7	-	-	12
	Stempflbach 160	99.9	23.0	99.9	74.8	99.0	100	-	-	3
	Gurk GK1	99.4	25.2	-	-	-	-	8.5	11	5
	Gurk GK7	99.5	21.7	-	-	-	-	8.4	4	4
	Piesting 123 G	98.6	19.6	-	-	-	-	-	5.5	46
	Piesting 124G	99.7	67.6	-	-	-	-	-	8.8	46
	Piesting 127G	97.4	37.2	-	-	-	-	-	8.6	46
	Triesting 106T	99.3	53.5	-	-	-	-	-	10.0	23
Clay	Kaolin	99.6	-	99.7	-	97.9	100	-	<	0.2
	Bentonite	99.4	21.7	99.3	-	99.4	98.0	7.3	<	4
	Fe-Montmorillonite	99.8	11.2	96.7	-	91.7	99.6	8.7	<	2.7
	Illite	89.4	-	77.7	-	50.6	100	-	<	0.3
	Halloysit	94.1	20.4	97.5	-	69.5	99.8	5.2	<	0.3
	from Friedlandt/Mecklenburg	99.1	-	98.9	-	95.5	93.2	-	0.5	<
Soil	Salzburg 98405	96.4	10.0	96.6	23.9	49.7	-	7.1	0.6	0.3
	Salzburg 98446	97.3	11.5	97.3	13.6	38.2	-	4.7	1.8	<
	Salzburg 98514	99.9	10.0	97.6	46.8	74.7	-	7.0	2.6	0.4

Table 4: Effect of pH on adsorption
Tabelle 4: Einfluß des pH auf die Adsorption von Cr

Substrate	pH	Cr^{3+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
Bentonite	6.8	99.5 %	99.0 %	98.2 %	94.7 %
	7.2	99.4 %	99.4 %	98.0 %	99.7 %
	11.4	93.1 %	92.4 %	98.8 %	93.3 %
Halloysite	2.6	53.4 %	0 %	99.8 %	4.0 %
	5.2	86.4 %	97.0 %	99.8 %	52.2 %
	5.9	98.8 %	99.4 %	99.9 %	79.6 %
	11.6	99.2 %	98.7 %	99.9 %	98.6 %
Fe₂O₃Mont- morillonite	7.4	92.4 %			
	8.7	65.1 %			
	10.1	68.2 %			

For Cr(III), no trend of adsorbed amount versus concentration in the adsorbed solution was noticed for the first two sediment samples treated for this investigation. The adsorption of Cr (VI), however, varied within a broad range (2–68 %), depending on the composition of the sample (see Table 3). The concentration in the adsorbent solution was varied for three sediment samples; one of them showed more adsorption for small amounts in relative terms.

Concerning Cr containing effluents, this means that the input of Cr(III) is immediately fixed in the sediments just below the source, whereas Cr(VI) can be transported some distance in the water phase depending on the composition of the sediment as well as on the composition and the amount of suspended matter (cf. HARZDORF, 1987).

The retention of Cr(VI) clearly increased with the organic carbon content (r = 0.79 for % retention/ignition loss), but it did not significantly depend on the amount of Fe obtained by selective leaching (hydroxylamine in 25 % acetic acid; 0.2M oxalate buffer pH 3; dithionite pH 7; 0.5M HCl).

Among the samples treated, the sediment components organic carbon, total Ca, and amorphous hydroxides were independent from one another. The load of Cr(III) or Cr(VI) to the sediment samples did not change the patterns of release of other constituents in the procedures applied (e. g. Al, Ca, Cu, Fe, Mg, Mn, Ni, P), which were measured simultaneously by ICP.

5.2 Comparison of Cr-adsorption with other metal ions

The extent of adsorption is dependent on the metal ion, the pH, and the solid substratum, like contents of carbonates, clay minerals, hydroxides, or organics.

Cr^{3+} is rather immobile on solid surfaces, in comparison with other cations investigated (Cu, Ni, Pb, Zn). The chromate anion, however, is always less adsorbed than the most mobile cation, which was nickel (see table 3).

Whereas Pb was adsorbed more than 98 %, the adsorbable amount of Ni and Zn may differ widely. Within table 4, the effects of pH on the adsorption of 2 mg of various metal ions, shaken with 1 g solid within 50 ml solution, is shown.

Generally, the previously adsorbed amounts were more mobile than those originally present, being preferably released in exchangeable and weak-acid-desorbable fractions. The release of additional trace elements in the last fractions, i. e. hot HNO_3 or hot NaOH was negligible. The differences were greater in the leaching sequence developed for cationic trace elements.

Differences among metal ions

Adsorbed Cr(III) is more tightly bound than adsorbed Pb and Zn. Thus, nearly all of adsorbed Pb and Zn is released in 25 % acetic acid, whereas adsorbed Cr(III) is not exchangeable at neutral pH, and largely needs oxalate as complexing releasing agent, or dilute hydrochloric acid. The release by reduction with dithionite can be substantial in the case of Cu, but it is low for Zn, Cr, Tl, Ni, and Pb; it is usually less than the release from the solid at pH 5.5. Surprisingly, the release in 1M NaOH can vary widely, from 0 to 50 % relative.

Differences between sediments, soils, and clays

No significant differences of the desorption pattern of the cations from sediments, soils and pure clays have been observed. Generally, Ni is the most mobile, and Pb the least one. This coincides with the relative mobility in column experiments (SAGER, 1991), where a cocktail of Pb/Cd/Cu/Ni has been applied to clays and soils. Differences might be expectable for chromate, because of reduction capabilities of many sediment samples.

Chromium (III)

An increase of oxalate-soluble Al shifts the remobilization of adsorbed Cr from exchangeable fractions (pH 7 + pH 5.5) towards amorphous hydroxides, which means tighter bonding to the solid. The effect is due to Al only, Fe or the molar sum of Fe + Al do not contribute. No relations of the release of adsorbed Cr(III) to any Fe, Ca, and K fraction could be found.

Chromium (VI)

The remobilization of chromium into neutral ammonium chloride (see table 5), which has been previously adsorbed from chromate solution, is lowered much by carbonate in the sample, if more than 1 % of Ca (referring to the solid) is released in ammonium acetate at pH 5.5 or in 25 % acetic acid. At low carbonate contents, however, remobilization is inversely related to the organic carbon-content of the solid, possibly because of immediate reduc-

tion to immobile Cr(III) on the solid surface. No relations to the release of Fe and Al were found.

Copper

Like for Cr(III), an increase of oxalate-soluble Al leads to a stronger bonding to the solid matrix. The remobilization of adsorbed Cu is shifted from exchangeable to acid-soluble fractions. In the clay samples, where organic carbon is very low, an increase in hydroxylamine-leachable Fe shifts

Table 5: % Desorption of Cr^{3+} and CrO_4^{2-} from various previously loaded substrates/sequence for phosphate
Tabelle 5: % Desorption von Cr^{3+} und CrO_4^{2-} von verschiedenen vorher beladenen Substanzen/Lösefolge für Phosphat

Type	Location	NH_4Cl pH 7	$Na_2S_2O_4$ pH 7	1M NaOH	0.5M HCl	hot 1M NaOH	pH	% org.	% $CaCO_3$
Sediment	Danube AW-S18	0 *17*	15.1 *4.7*	2.4 *0*	61.4 *14.2*	0.2 *2.4*	7.2	2.2	15
	Danube AW-S23	09.2 *21*	1.3 *2.8*	3.7 *0*	37.2 *3.4*	0.2 *0.2*	7.0	2.3	19
	Danube Greif	0.2	5.1	3.6	44.8	2.3	6.8	2.0	14
	Schwechat	0.5 *3.3*	1.6 *0.9*	9.3 *18.8*	88.5 *77*	0 *0*	-	-	24
	Rußbach 156	- *54.6*	- *0*	- *0*	- *45.4*	-	-	-	35
	Rußbach 160	0 *19.7*	0.4 *3.2*	14.1 *27.5*	83.7 *49.6*	1.8 *0*	-	-	3
	Gurk GK1	0 *12.2*	7.6 *3.2*	14.9 *7*	52.9 *25.1*	0.4 *0*	8.5	11	5
	Gurk GK7	0 *5.6*	3 *4.4*	10.5 *5.8*	69.3 *49.3*	0.1 *0.3*	8.4	4	4
	Piesting 123 G	0.4 *9.3*	9.7 *7.9*	18.2 *0*	40.7 *21.9*	0.9 *2.2*	-	5.5	46
	Piesting 124G	0.4 *0.3*	9.7 *8.5*	18.2 *10.2*	40.7 *49.8*	0.9 *0.8*	-	8.8	46
	Piesting 127G	0.6 *0.9*	7.9 *18.6*	14.9 *17.3*	38.6 *37.9*	0.8 *1.4*	-	8.6	46
	Triesting 106T	0.2 *0.2*	4.7 *3.5*	6.2 *4.5*	64.8 *55.2*	1.1 *0.8*	-	10.0	23
Clay	Bentonite	3.8 *42.4*	4.1 *0*	8.3 *0*	78.5 *57.6*	5.3	7.3	<	4
	Halloysit	0 *90.7*	4.6 *0*	3.6 *2.9*	65.5 *6.4*	3.1 *0*	5.2	<	0.3
Soil	Salzburg 98405	1.2 *68*	17.7 *0*	7.1 *0*	74 *32*	0 *0*	7.1	0.6	0.3
	Salzburg 98446	1.9 *70*	3.3 *0*	11.4 *14*	86.1 *45*	0 *0*	4.7	1.8	<
	Salzburg 98514	1.6 *80*	4.7 *0*	14.6 *0*	77.8 *20*	1.3	7.0	2.6	0.4

Note: the values for Cr^{3+} are given in standard letters, and the values for chromate in fat italics

the dithionite-releasable Cu towards the fraction releasable in HCl; this effect has not been observed in the soil and sediment samples investigated.

No relations of the release of previously adsorbed Cu to the release of Ca and K in any fraction was found.

Lead

The retain of Pb generally increases with increasing carbonate contents.

An increase in ammonium-chloride soluble Ca decreases exchangeable Pb. More total carbonates, found as the HCl-soluble Ca-fraction, shift the release of adsorbed Pb from exchangeables to acetic acid; but more total carbonate results in an increase of alkali-soluble Pb also. If the release of Ca at pH 5.5 is low, the release of previously adsorbed Pb into the same reagent solution is below 40 % and variable. But if it is more than 1 % (referring to the entire sample), the release of Pb increases simultaneously with Ca. Similar to Ca, also the HCl-soluble Al lowers the remobilization of Pb (sum pH 7 + pH 5,5).

No relations to the release of K and Fe have been found.

Zink

Like for Pb, Cr(III) and Cu, Al-hydroxides tend to retain also Zink. Thus, HCl-soluble Al lowers the remobilization of Zn (sum pH7 + pH5.5), but less than for Pb.

Similarly, if there is an increase of alkali-soluble Fe, which is probably an organically complexed form, the remobilization of zink is shifted from the exchangeable to the oxalate soluble fraction.

An increase in the number of adsorption sites at the amorphous hydroxides, expressed as the oxalate-releasable K, results in a shift from exchangeable to dithionite-releasable Zn.

No relations of the release of Zn to any Ca-fraction have been found.

5.3 Leaching sequence developed for trace metals (Tessier et al., 1979)

In a first experiment, one of the samples had been loaded 8 times (double det. at 4 levels) with Cr(III) or Cr(VI), and subsequently submitted to the leaching sequence after Tessier, to get an idea of the precision of the method (see Table 6). Only minute differences occurred between the adsorption/desorption behaviour of Cr(III) and Cr(VI).

The main amount of both types of spike had been

Table 6:   % Desorption of Cr^{3+} and CrO_4^{2-} from various previously loaded substrates/sequence for cationic trace metals
Tabelle 6: % Desorption von Cr^{3+} und CrO_4^{2-} von verschiedenen vorher beladenen Substanzen/Lösefolge für kationische Spurenelemente

Type	Location	NH$_4$Ac pH 7	NH$_4$Ac pH 5	NH$_2$OH- 25% HAc	Ox pH 3	H$_2$O$_2$	HNO$_3$	pH	% org.	%CaCO$_3$
Sediment	Danube Greif	0	43.3	51.6	4.0	0	1.0	6.8	2.0	14
	Schwechat	1.3	36.3	10.1	32.8	15.4	4.1	-	-	24
	Rußbach 156	0	33.9	28.9	34.2	0.7	2.3	-	-	35
	Rußbach 158	0.8	28.8	50.5	16.2	2.1	1.7	-	-	12
	Rußbach 160	2.1	31.3	37.4	22.8	2.9	3.5	-	-	3
	Gurk GK1	1.3	11.3	53.3	11.4	5.7	0	8.5	11	5
		5.6	*5.7*	*50.6*	*19.1*	*9.6*	*0*			
Clay	Kaolin	x	48.5	29.7	17	0	4.9	-	<	0.2
	Bentonite	1.6	54.6	31.6	5.9	5.0	1.3	7.3	<	4
	Fe-Montmorillonite	x	45.9	40.7	10.6	2.8	0	8.7	<	2.7
	Halloysite	0.4	59.7	27.5	7.4	4.1	0.9	5.2	<	0.3
	from Friedlandt/ Mecklenburg	39.3	24.8	23.6	5.3	1.8	4.9	-	0.5	<
Soil	Salzburg 98405	38.8	50.5	9.2	0.8	0	0.7	7.1	0.6	0.3
		58	*0*	*42*	*0*	*0*	*0*			
	Salzburg 98446	10.3	64.9	23	1.8	0	0	4.7	1.8	<
		67	*16*	*18*	*0*	*0*	*0*			
	Salzburg 98514	15.9	59.3	17.5	2	5.2	0	7.0	2.6	0.4
		76	*12*	*12*	*0*	*0*	*0*			

released in acetic acid, followed by oxalate. Cr(VI) loaded samples gave slightly higher yields in neutral ammonium acetate and after oxidation with H_2O_2, whereas Cr(III) loaded samples were on the whole higher in ammonium acetate pH 5. The yields obtained with final hot HNO_3 were the same from the spiked and the unspiked samples, which shows, that this fraction of the sediment does not derive from absorption from the water phase, but is bulky geogenic.

To obtain additional information about possible reaction sites, fractions of hydroxylamine/acetic acid leachable Fe and Mn, as well as oxalate extractable Fe and Al were taken as indicative of amorphous hydroxides.

5.4 Mobilization of Cr(III) spike using the sequence developed for phosphate speciation (Psenner et al., 1984)

Major proportions of the adsorbed load were released in 0.5M HCl whereas the fractions exchangeable with NH_4Cl or kdissolved with hot NaOH were negligible (Table 5). The low amounts mobilized with dithionite did not show significant correlations. They sould yield the release from iron oxides upon reduction, but readsorption could decrease the dissolved amounts, which was not properly investigated. The NaOH-extract decreased with amorphous hydroxides. The acid leachable Cr decreased with acid-leachable Ca, and also carbonate according to Scheibler's method (r = 0.71/N = 12). Some of the spike remained irreversibly bound, which did not correlated with total C, Ca, Fe or Al contents. Contrary to this, the irreversibly bound part was much lower in the other sequence when hot HNO_3 was used in the last step. Organic carbon obviously did not influence the leaching pattern.

Starting with NH_4Cl/NaOH pH = 7 extract (PSENNER et al., 1984; HIELTJES and LIJKLEMA, 1980) or with NH4Ac pH = 7 extract, yielded approximately the same fraction for previously adsorbed Cr(III).

Ca leached with dilute Hl in this sequence, was taken indicative for carbonates.

The amount of matrix of clay minerals cannot be estimated by chemical leaching techniques (Prohic and Kniewald, 1987), because they act via their exchangeable sites, but hardly dissolve themselves.

5.5 Mobilization of Cr(VI) spike in the sequence developed for phosphate speciation (Psenner et al., 1984)

The fraction exchangeable with ammonium chloride was markedly high in some cases, but varied widely, as well as the HCl leachable amount. Like above, hot NaOH exerted only negligible action upon adsorbed Cr, although much Al is dissolved.

The NH_4Cl, HCl and hot NaOH fractions did not correlate significantly with the contents of C, Ca, Fe or Al in the samples. Factor analysis of the relative amounts of desorbed chromium originally introduced as chromated showed a clear increase of NH_4Cl exchangeable amounts with increasing amorphous hydroxides, and with decreasing organic carbon. Contrary to the desorption of Cr(III) lead, alkaline leachable Cr increased with carbonate contents, whereas amorphous hydroxides were rather negative to HCl-leachable Cr.

5.6 Comparison of leaching patterns resulting from load with Cr(VI) versus load with Cr(III)

When Cr(VI) is added to the sediment, it can be either adsorbed as chromate as such, or reduced to Cr(III). The main differences between the desorption of the Cr(III) load and the Cr(VI) load clearly lies in the ammonium chloride exchangeable fraction. Factor analyses of the desorption patterns further show some differences in the role of amorphous hydroxides and carbonates.

The amount of Cr(VI) being reduced upon contact with the sediment seems to behave like the proper spike of Cr(III) during the sequential dissolution procedure. The proportion of chromium given as chromate, but not regained exchangeable with neutral ammonium chloride, shows a leaching pattern like the Cr(III) spike. The addition

Table 7: Accuracy of the sequential leaching procedures applied
Tabelle 7: Genauigkeit der angewendeten sequentiellen Lösefolgen

	Average percentage of net desorption after Cr adsorption on River Gurk sediment (N=8):	
	Cr(III) regain	Cr(VI) regain
1M NH4Ac pH 7	1.3 ± 0.7 %	5.6 ± 2.3 %
1M NH4Ac pH 5.5	11.2 ± 4.6	5.7 ± 3.0
25 % HAc/0.1M NH2OH	53.5 ± 7.4	50.6 ± 9.2
0.2M Ox pH 3	11.4 ± 1.4	19.1 ± 4.5
H_2O_2	5.7 ± 1.1	9.6 ± 1.7
1M NH4Cl pH 7	< 0.1 %	5.6 ± 1.6 %
dithionite/HCO3	3.0 ± 2.0	4.4 ± 1.7
1M NaOH	10.5 ± 2.8	5.8 ± 1.4
0.5M HCl	69.3 ± 1.5	59.0 ± 1.7

of chromate to the sediment leads to an exclusive increase of the ammonium chloride extract, if C/Fe is low, or if Ca/Fe is high. It can be assumed that this is due to the chromate bound exchangeably to clay minerals. High organic contents (more than 8 %), or an increase in C/Fe, resp., leads to a marked decrease in the exchangeable fraction, with similar increase in dithionite and sodium hydroxide leaches, relative to Cr(III). High Ca/Fe favours the release in NaOH over that in dithionite, but no linear relationship could be established, however. NaOH causes stabilization of Cr(VI), which is difficult to reduce under these conditions. The dithionite reduces Cr(VI) quantitatively to Cr(III), which will then readsorb.

A decline of the exchangeable fraction simultaneously leads to an increase of the amount of chromate not leachable with the cited reagents. On the other hand, the proportion of added chromate acting like Cr(III) strongly correlates with organic carbon.

Thus, reduction of chromate by the organic substance occurs which partly leads to an additional fraction of organic complexes, soluble in alkali, or soluble because of reduction of the ligands.

Concerning the explanation for the fraction not recovered, it is known that chromate can enter the crystals of Ca aluminate from neutral solutions unchanged, where it is only partially extractable with sulfate, selenate or molybdate (FREGERT and GRUVBERGER, 1982). Thus, irreversible incorporation into a matrix component is possible.

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Table 8: Results of sequential leaching without any chromium spike, together with total Ca, total Fe and organic carbon contents

Tabelle 8: Ergebnisse der sequentiellen Löseverfahren ohne Chrombeladung, zusammen mit dem Gesamtgehalt an Calcium, Eisen und organischem Kohlenstoff

	Sample composition			µg/g chromium leached					total contents
	% org. subst.	% Ca	% Fe	NH$_4$Cl	Na$_2$S$_2$O$_4$	NaOH	HCl	NaOH	Σµg/g Cr
GK1	-	2.0	5.4	0.1	0.2	4	7.8	< 0.1	127
GK7	4	1.5	4.9	< 0.1	< 0.1	0.1	5.0	5.1	112
S18	2.2	6.2	3.0	< 0.1	2.2	1.6	8.0	0.3	66
124G	8.8	26.2	1.1	< 0.1	< 0.1	< 0.1	2.8	0.3	36
Soil A	8.6	23.6	1.1	< 0.1	< 0.1	< 0.1	2.0	0.2	26
Soil B	5.5	22.3	0.8	< 0.1	< 0.1	< 0.1	2.0	< 0.1	15
Soil C	10.0	14.7	2.3	< 0.1	0.9	< 0.1	10.4	0.9	102

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Anschrift des Verfassers

Manfred Sager, Bundesamt und Forschungszentrum für Landwirtschaft, Institut für Agrarökologie, Spargelfeldstraße 191, A-1226 Wien.