FRACTIONATION OF CHROMIUM IN SOILS TREATED WITH AQUEOUS SOLUTIONS OF Cr(VI) AND Cr(III)

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Abstract

Fractionation of chromium was studied in various soils (clay, peat, sand and luvi-chromic cambisols) incubated thirty days with an aqueous solution of Cr(VI) or Cr(III) employing a sequential extraction procedure. The total concentration of chromium in easily and sparingly soluble fractions of soil (organic, Fe and Mn oxides and hydroxides, carbonate, sulfide and silicate mineral) was investigated and compared with the same soils of the natural origin. The concentration of Cr(VI) in the easily exchangeable fraction of soil was also determined.

The results of fractionation studies in soils treated with an aqueous solution of Cr(VI) thirty days after application indicated that chromium remained mostly as exchangeable chromium in luvi-chromic cambisols, clay and sand soil. The exchangeable chromium was below the detection limit in peat soil. Chromium was mostly found in the organic fraction. In all four soils, the concentration of chromium in Fe and Mn oxides and hydroxides fraction was also higher in comparison to other sparingly soluble fractions of soil.

On the other hand, thirty days after the application of an aqueous solution of Cr(III), chromium was found mostly in organic fraction, bound to Fe and Mn oxides and hydroxides and in carbonate fraction. The concentration of exchangeable chromium was also very high in clay and luvi-chromic cambisols with respect to peat and sand soil.

Introduction

Fractionation studies in soils treated with various industrial waste materials containing chromium in various forms are very important from an ecological point of view. Soluble chromium in soils can be taken up by plants or leached through the soil horizons into drinking water. If it is present in a form of Cr(VI), it may have hazardous effects on living organisms. On the other hand, chromium bound to sparingly soluble soil fractions is environmentally less hazardous. Therefore, for the evaluation of the real risk of chromium contaminated soil, it is important to identify chromium content in easily and sparingly soluble soil fractions as well as to identify and to understand the reactions of chromium species with main soil components. Understanding the reactions between the soils components are also important.[1]

In fractionation studies, samples are sequentially treated with more vigorous selective extractants in order to dissolve a particular soil phase and to liberate associated analytes. Numerous sequential extraction procedures have been developed or modified for determination of metal species in sediments,[2-6] soils,[7-9,13,14] waste materials[10] and various waste treated soils.[11,12] Tessier and Campbell[2] and Reddy et al.[8] suggested a sequential extraction procedure for the partitioning of Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn in river sediments and Cr, Ni and Cd in soils between exchangeable, carbonate, Fe-Mn oxides, organic and residual fractions. Magnesium chloride (1 M $MgCl_2$, pH 7.0) or sodium acetate solution (1 M NaOAc, pH 8.2) were used to determine exchangeable fractions, sodium acetate solution (1 M NaOAc, pH 5.0) for metals in carbonate fraction and a mixture of 0.3 M $Na_2S_2O_4$ + 0.175 M Na-citrate + 0.025 M H-citrate or 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc for metals in Fe-Mn oxides fraction. A mixture of 0.02 M HNO_3 + 30% H_2O_2 at 85 $^{\circ}$C was used for metals in organic fraction. Digestion with a $HF\text{-}HClO_4$ mixture was employed to determine chromium in residual fraction. Calmano and Forstner[3] studied the distribution of heavy metals among major sedimentary phases in polluted rivers by a five-step sequential extraction procedure. Rauret et al.[4] reported the optimization of the Tessier procedure[2] for solid metal speciation in river sediments. They paid a special attention to optimization of the volume-to-weight (v/w) ratio.

Shuman[7] reported a fractionation scheme for the determination of Zn, Mn and Cu distributed among exchangeable, organic matter and Fe oxides fractions in various soil samples.

McGrath[13] described the use of single and sequential extraction procedures for polluted and unpolluted soils. Single extractions were performed using various chelating agents. $MgCl_2$, NaOAC, $NH_2OH\text{-}HCl$, $HNO_3\text{-}H_2O_2\text{-}NH_4OAc$ and $HF\text{-}HClO_4$ were used for solubilisation of trace metals associated with exchangeable, carbonate, sesquioxide, organic mater and residual fractions, respectively. Ure[14] presented different kinds of elemental soil analysis for the determination of total, pseudo-total and extractable soil contents. The author has critically evaluated differences between various extraction schemes used and pointed out that the harmonisation of the methodology is needed. Quevauviller et al.[15] reported some conclusions of the workshop on harmonization of

leaching/extraction tests for environmental risk assessment later. They concluded that the lack of uniformity of the sequential extraction schemes did not allow the results be comparable worldwide so far nor the procedures to be validated. They also reported that the significance of the analytical results is highly dependent on the extraction scheme used.

The European Commission proposed a standardized three-step sequential extraction procedure through the BCR programme. It was based on acetic acid extraction to liberate exchangeable/acid-extractable metals (step 1), hydroxylammonium chloride extraction for metals associated with the reducible phases (step 2) and on the end metals released by oxidation with hydrogen peroxide that are isolated with ammonium acetate extraction (step 3). This scheme was tested in a first inter-laboratory trial on Cd, Cr, Cu, Ni, Pb, and Zn in soils and sediments and reported by Quevauviller et al.[16] A three-step sequential extraction procedure was than employed for certification of the trace metal extractable contents in a sediment reference material (CRM 601)[17] and improved prior to the certification of new sediment, soil[18,19] and sewage sludge amended soil reference materials.[20] The extractant pH, extractant concentration, time of extraction, extraction temperature and some other parameters were critically evaluated. The use of alternative reagents was also considered.

All investigations and improvements of single and sequential extraction procedures are published in the book edited by Quevauviller.[21]

In addition, the determination and monitoring of more toxic and mobile hexavalent form of chromium in easily exchangeable fraction of soils is of a prime concern because chromium frequently appears as a pollutant in the environment. The behavior of chromium especially in tannery waste- and tannery sludge-amended soils has been investigated.[12,22-25] Milačič et al.[25] reported the fractionation studies of chromium in sewage sludge and tannery waste amended soils. The data indicated only a slight increase of chromium in the water-soluble and exchangeable fractions during first months after the start of the experiment. In the continuation of the experiment, chromium in these two fractions decreased to its natural content in the soils. Several months after the sewage sludge application, chromium in sand and clay soils was found mainly in mineral and hydroxylamine hydrochloride extractable fraction. They also

reported that oxidation of Cr(III) was not observed in the sewage sludge-amended soils due to the reducing characteristics of sewage sludge and very low concentrations of chromium in the water-soluble fraction. However, in the tannery waste amended soils oxidation of chromium was observed in clay and sandy soils.

In our previous work reduction and oxidation processes of chromium in various soils treated with aqueous solutions of Cr(VI) and Cr(III) were investigated. In addition, the fractionation of chromium was also studied. The aim of our present work was to investigate the distribution of chromium among various sparingly soluble fractions of soils (clay, peat, sand and luvi-chromic cambisols) thirty days after chromium application. The sequential extraction procedure was employed for the determination of chromium in a particular soil fraction. The results of fractionation studies in treated soils were compared to fractionation in the same soils of the natural origin.

In addition, the concentration of Cr(VI) in the easily exchangeable fraction of soils was also determined.

On the basis of these data, the potential hazardous effects of chromium in soils contaminated with an aqueous solution of Cr(VI) or Cr(III) were critically evaluated.

Results and discussion

In addition to the knowledge on the reduction and oxidation processes of chromium in various soils[26] it is also important to know the partitioning of chromium between easily and sparingly soluble soil fractions. Our previous experiments[26] confirmed that the reduction and oxidation of soluble chromium may occur in natural soils.

Fractionation of chromium in soils of the natural origin. Soils of the natural origin (clay, peat, sand and cambisols) were fractionated to determine the distribution of chromium between various sparingly soluble soil fractions. The results are presented in Table 1. Concentrations of total easily exchangeable chromium were found to be very low, < 5.0 ng g^{-1} in clay, cambisols and peat soil, and < 2.5 ng g^{-1} in sand soil.

It is evident from Table 1 that chromium in all four soils predominates in the mineral fraction (from 60.6% in cambisols to 77.4% of total chromium in clay soil). From 9.8% in clay to 34.2% of total chromium in cambisols was also found in Fe and

Mn oxides and hydroxides fraction. In peat soil (high in organic matter) the mineral fraction prevailed (about 66%), but a substantial amount of chromium (about 15%) was found in Fe and Mn oxides and hydroxides fraction and about 11% in organic fraction. It is therefore reasonable to expect very low concentration of exchangeable chromium in all four soils of the natural origin (about 0.03 – 0.08% of total chromium).

Table 1. Fractionation of chromium in soils of the natural origin.

soil fraction	clay soil Cr (%)	peat soil Cr (%)	sand soil Cr (%)	cambisols Cr (%)
exchangeable	0.03	0.08	0.07	0.05
organic	2.9	11.0	2.9	0.52
carbonate	1.4	3.3	3.8	0.38
Fe and Mn oxides and hydroxides	9.8	15.4	17.5	34.2
sulfide	8.3	3.3	9.5	4.33
silicate minerals	77.4	66.4	64.7	60.6

Fractionation of chromium in soils treated with an aqueous solution of Cr(VI). Fractionation of chromium in soils treated with the aqueous solution of Cr(VI) (clay, peat, sand and cambisols) was investigated thirty days after Cr(VI) application. The results are presented in Table 2.

The data presented in Table 2 respond only to fractionation of the added aqueous soluble Cr(VI) in soils. In peat soil with a high reductive capacity for soluble Cr(VI),[26] the added aqueous soluble Cr(VI) was probably first reduced and then adsorbed/ion exchanged[1] as trivalent chromium to organic molecules (49.7% of total added Cr(VI)). It could also precipitated as Cr(III)-hydroxide or adsorbed[1] to Fe and Mn oxides and hydroxides (30.9% of total added Cr(VI)). The concentration of exchangeable chromium was very low (only 0.5% of total added Cr(VI)). On the other hand, in cambisols with a very low reductive capacity for soluble Cr(VI),[26] the added aqueous soluble Cr(VI) remained as an exchangeable chromium (84.2% of total added Cr(VI)) and only 15.8% of chromium was found in Fe and Mn oxides and hydroxides fraction.

In clay and sand soils, the concentration of exchangeable chromium was also very high (from 55.1% to 56.4% of total added Cr(VI)). The rest of the added chromium in clay soil was mainly found in Fe and Mn oxides and hydroxides as well as in sulfide fraction. In sand soil, the rest of the added chromium was found in Fe and Mn oxides and hydroxides, and in carbonate fraction. Although some studies have already been performed in order to explain possible reactions of Cr(III) and Cr(VI) with particular soil components,[1] further systematic investigations should be carried out to demonstrate whether the added aqueous soluble chromium in these phases is in hexavalent or in trivalent form.
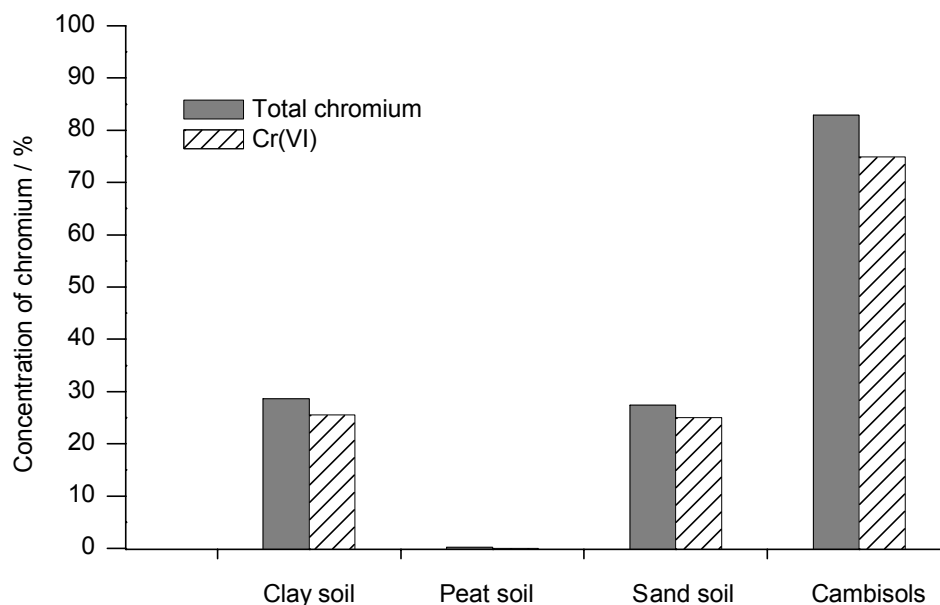
Table 2. Fractionation of chromium in soils treated with an aqueous solution of Cr(VI) thirty days after application.

soil fraction	clay soil Cr (%)	peat soil Cr (%)	sand soil Cr (%)	cambisols Cr (%)
exchangeable	55.1	0.5	56.4	84.2
organic	7.0	49.7	8.2	0.4
carbonate	7.2	12.8	13.7	2.2
Fe and Mn oxides and hydroxides	19.5	30.9	13.1	7.8
sulfide	12.3	3.7	4.1	< 0.05
silicate minerals	0.7	1.42	4.9	0.03

In addition to the total easily exchangeable chromium, the concentration of Cr(VI) was also determined (Figure 1).

It is shown in Figure 1 that approximately 90% of the total easily exchangeable chromium remained as Cr(VI) in cambisols, clay and sand soils because of their low reductive capacity for soluble Cr(VI). The concentration of the total easily exchangeable chromium and Cr(VI) was below the detection limit in peat soil (< 0.03%). This is an additional prove of our previous results on possible reduction and oxidation of the aqueous soluble chromium added to these soils[26] (1-10 days after the application), because high concentrations of Cr(VI) were found even thirty days after the addition of an aqueous soluble Cr(VI) in cambisols, clay and sand soils.

Figure 1. The concentrations of total easily exchangeable chromium and Cr(VI) in soils treated with an aqueous soluble Cr(VI) thirty days after application.

Fractionation of chromium in soils treated with an aqueous solution of Cr(III). Fractionation of chromium in soils treated with the aqueous solution of Cr(III) was investigated thirty days after Cr(III) application. The results of this investigation are presented in Table 3. The data respond only to fractionation of the added aqueous soluble Cr(III) in soils.
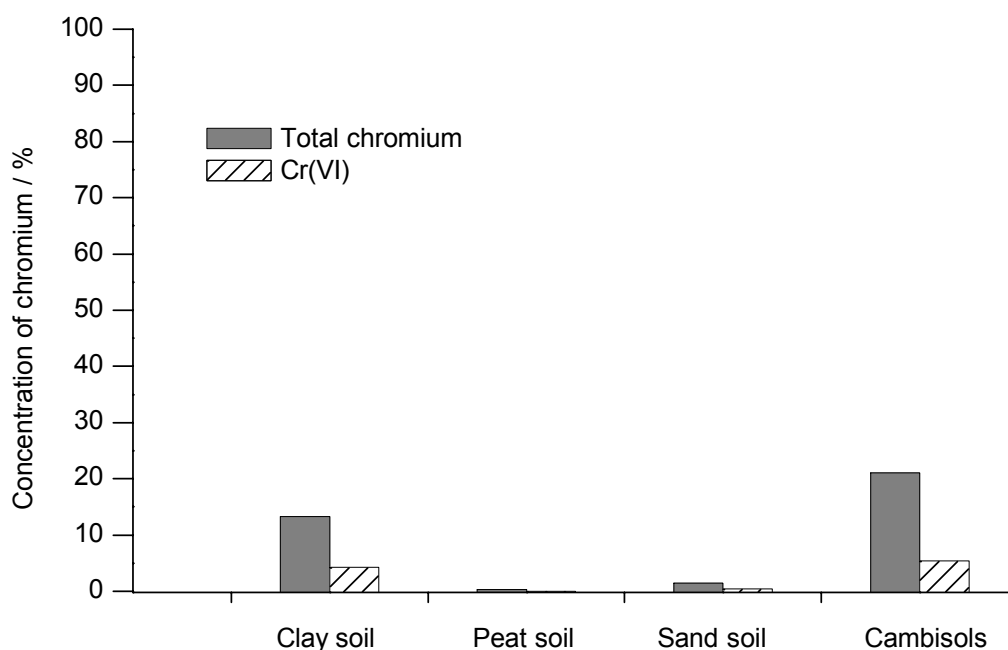
From the data in Table 3 it can be seen that added chromium was found predominantly in Fe and Mn oxides and hydroxides fraction (from 26.5% to 31.9% of total added Cr(III)) but also in organic fraction (from 17.8% to 27.4% of total added Cr(III)) in clay, sand and cambisols. The concentration of chromium in carbonate fraction was also high (from 18.8% to 20.5% of total added Cr(III)). It is also shown (Table 3 and Table 2) that in peat soil the distribution of added chromium among sparingly soluble fractions of soil was the same in spite of the fact that chromium was added as an aqueous soluble Cr(VI) or as aqueous soluble Cr(III). Chromium was found predominantly in organic fraction (approximately 50% fof total added chromium), Fe and Mn oxides and hydroxides fraction (approx. 30% of total added chromium) and in carbonate fraction (from 12.8% of total added soluble Cr(VI) to 19.5% of total added soluble Cr(III)). These features could confirm that the added Cr(VI) (Table 2) was first

reduced and then adsorbed/ion exchanged[1] to various fractions of peat soil as trivalent chromium or precipitated as Cr(III)-hydroxide.[1] In addition, the concentration of chromium in sulfide and silicate minerals fraction was negligible for all four soils. In addition to the total easily exchangeable chromium, the concentration of Cr(VI) was also determined (Figure 2).

Table 3. Fractionation of chromium in soils treated with an aqueous soluble Cr(III) thirty days after application.

soil fraction	clay soil Cr (%)	peat soil Cr (%)	sand soil Cr (%)	cambisols Cr (%)
exchangeable	30.0	0.06	4.0	25.4
organic	26.1	50.5	27.4	17.8
carbonate	20.5	19.5	18.8	6.9
Fe and Mn oxides and hydroxides	26.5	29.9	28.7	31.9
sulfide	1.2	3.9	6.6	5.3
silicate minerals	< 0.05	< 0.05	14.6	11.1

Figure 2. The concentrations of total easily exchangeable chromium and Cr(VI) in soils treated with an aqueous soluble Cr(III) thirty days after application.

It is shown in Figure 2 that the concentration of total easily exchangeable chromium was the highest in cambisols and clay soil, about 13% and 22% respectively, while in peat soil Cr(VI) was below the detection limit (< 0.03%). The concentrations of Cr(VI) in this fraction in cambisols and clay soil were approximately 30% of the total chromium. High concentration of Cr(VI) in these two type of soils could be expected due to low reductive and relatively high oxidative capacity of both soils for soluble chromium.[26]

Conclusions

Our experiments confirmed that thirty days after chromium application chromium prevailed in the exchangeable fraction while the concentration of chromium in the mineral fraction was negligible in all four soils, compared to soils of the natural origin. The exception was peat soil in which chromium was predominantly found in organic fraction and in Fe and Mn oxides and hydroxides fraction of soil, in spite of the fact that it was added as Cr(VI) or Cr(III). The concentration of exchangeable chromium in peat soil was negligible. The concentration of exchangeable chromium in cambisols, sand, and clay was approximately from 55% to 84% of total added soluble Cr(VI) and approximately 25% to 30% of total added soluble Cr(III). In soils of the natural origin, chromium predominates in mineral fraction while the concentration of the exchangeable chromium is negligible.

In the case of possible contamination of soils with an aqueous soluble Cr(VI) or Cr(III) special attention should be paid to cambisols, clay, and sand soil. In these soils, Cr(VI) could remain in the hexavalent form due to the low reductive capacity of these soils and relatively high content of Mn(IV) oxides (high oxidative capacity).[26] High concentration of Cr(VI) in the easily exchangeable fraction of soil could be expected even if the soil is contaminated with aqueous soluble Cr(III), because the later could be oxidized to Cr(VI). This could cause serious hazardous effect in the environment. Chromium distribution among soil fractions and reactions of chromium with soil components should be systematically investigated and explained in order to evaluate the extent of chromium contamination. Further systematic investigations should be carried

out to demonstrate chromium species in particular soil fraction employing mineralogical analysis.

Experimental

Instrumentation. An atomic absorption spectrometer (Varian AA 575 with an HGA 76B Perkin- Elmer graphite furnace) and Varian AA5 flame atomic absorption spectrometer, N_2O-acetylene flame were employed for the determination of total chromium and Cr(VI) in soil extracts. A Varian Cary Model 1650 spectrophotometer adjusted to a wavelength of 540 nm was used for the determination of Cr(VI) by 1,5-diphenylcarbazide spectrophotometric method.[11,27,28]

A Dohrmann TOC analyzer (high temperature, combustion oxidation method) was used for the determination of soluble TOC in soil extracts.[29,30]

Soil extractions were performed in 38-cm³ polyurethane tubes, with phase separation obtained by centrifugation using a Heraeus Sepatech Biofuge 17S.

Reagents. Merck suprapure acids and doubly distilled water were used for the preparation of samples and standard solutions. All other chemicals used for the sequential extraction procedure (Table 5) were of analytical-reagent grade.

Standard Cr(VI) (potassium dichromate; $K_2Cr_2O_7$) and Cr(III) (chromium(III) chloride; $CrCl_3$) stock solutions (Cr: 1000 µg cm⁻³) were used.

Physicochemical characteristics of soils. In order to study the fractionation of chromium in soils treated with an aqueous solution of Cr(VI) or Cr(III) four typical soils (clay, peat, sand and luvi-chromic cambisols (cambisols)) were collected from A horizon at different locations and were classified according to pedological parameters, i.e. texture, organic matter content and total soluble carbon content.

Samples were stored in 30 dm³ plastic vessels under atmospheric conditions. Several physical and chemical parameters were measured in parallel with the experiments. The results are summarized in Table 4. The parameters shown provide a wide variation of values between soils.

The concentration of total chromium in soils was found to be 57.7 µg g⁻¹ in clay, 57.3 µg g⁻¹ in peat, 48.8 µg g⁻¹ in sand and 144 µg g⁻¹ in cambisols. It was mostly bound

in sparingly soluble fractions of soils (Table 1); therefore, it could not affect the analysis of the added soluble chromium.

Table 4. The characteristics of the investigated soils.

soil type	moisture (%)	pH of soil	TOC* (%)	SOM** (%)	soil particle diameter (μm)	exch. Cr ($\mu g\ g^{-1}$)	total Cr ($\mu g\ g^{-1}$)	exch. Mn(IV) -oxides ($\mu g\ g^{-1}$)
clay	22.0	7.3	1.52	$6.8\ 10^{-5}$	50-2, 53% < 2, 17%	< 5.0	57.7	399
peat	50.2	7.0	41.1	$4.3\ 10^{-4}$	most of particles < 2	< 5.0	57.3	60
sand	13.0	7.4	3.0	$1.7\ 10^{-4}$	most of particles 20-50 and < 2	< 2.5	48.8	150
cambisols	24.4	5.4	0.22	$4.6\ 10^{-5}$	2-20, 32% < 2, 61%	< 5.0	144	234

* Total organic carbon (TOC) determined by Walkley-Black method[31]
** SOM – soluble organic matter

Determination of physicochemical characteristics of soils. 25-30 g samples of soil were dried at 60 $^{\circ}$C for 12 hours and the moisture content (at the sampling time) calculated from the weight loss. The pH was determined in a suspension of 10 g of soil in 10 cm^3 of water. The soil texture was determined by the sedimentary technique.[31]

The Walkley-Black method[31] was introduced to determine the total organic carbon in soils. Total water-soluble organic carbon was determined in water soil extracts (50 g of moist soil with 50 cm^3 of distilled water)[29,30] by a TOC analyzer (high temperature, combustion oxidation method).

The total chromium and manganese in soil were determined by flame atomic absorption spectrometry after HNO_3, $HClO_4$, HF digestion.[32]

Determination of exchangeable Mn(II) and easily reducible Mn(IV) in soils. The $MgSO_4$-hydroquinone extraction proposed by Bartlett and James[28] and also employed in our previous studies[26] was used for determining easily reducible Mn(IV).

Determination of the total easily exchangeable chromium and Cr(VI). 2.00 g of moist Cr-treated soil samples were shaken for 30 minutes with 20 cm^3 of 0.15 mol dm^{-3} KH$_2$PO$_4$/Na$_2$HPO$_4$ buffer solution, centrifuged for 20 min at 10 000 rpm and decanted. The pH of the KH$_2$PO$_4$/Na$_2$HPO$_4$ extractant was adjusted to the pH of the particular soil. Samples were then filtered through cellulose nitrate membrane filters (pore size 0.1 μm)[32] and the concentration of total easily exchangeable chromium was determined by flame or electrothermal atomic absorption spectrometry.[27] Extractions were performed in duplicate at room temperature (295 ± 2K). Aliquots of these soil extracts were used for the determination of Cr(VI) by employing 1,5-diphenylcarbazide spectrophotometric method.[27,28]

Sequential extraction procedure for the determination of the total chromium in various sparingly soluble fractions of soils. In the past, a huge work on optimization of the sequential extraction procedure for the determination of chromium in easily and sparingly soluble fractions of soils was performed. On the basis of our previously published[25] and unpublished data, the described extraction procedure was found as the most efficient. It provided us with an appropriate information about behavior and distribution of the added aqueous soluble Cr(III) and Cr(VI) in various soils, although the European Community proposed a standardized three-step sequential extraction procedure.

After KH$_2$PO$_4$/Na$_2$HPO$_4$ extraction, a number of extractions employing various selective extractants were preformed. The following order of extractants was employed: for exchangeable chromium, ammonium chloride (NH$_4$Cl) was added to the solid residue and shaken for 4 h. Tetrasodium diphosphate (Na$_4$P$_2$O$_7$) (16 h) was employed to determine chromium in organic fraction and di-sodium ethylenediamine tetraacetic acid (Na$_2$EDTA) for chromium in carbonate fraction. Extraction with buffer solution of di-sodium disulphate (Na$_2$S$_2$O$_4$) was performed at 353 K for 0.25 h in two replicates to determine chromium in Fe and Mn oxides and hydroxides fraction. The last extractant used for extraction of chromium in sulfide fraction was nitric acid (HNO$_3$). Chromium in the residue (silicate minerals fraction) was determined after complete nitric acid

(HNO₃), perchloric acid (HClO₄) and hydrochloric acid (HCl) digestion[33] of the remaining solid sample.

All analyses were done in triplicate. Experimental results obtained on replicate samples of particular soil extracts demonstrate that the relative standard deviation of the sequential extraction procedure was generally better than ± 10%.

The scheme of the sequential extraction procedure is presented in Table 5.

Table 5. The sequential extraction procedure for the determination of chromium in various sparingly soluble fractions of soils.

soil fraction	extractant	conc. of extractant ($mol\ dm^{-3}$)	time of extraction (hours)
easily exchangeable	KH_2PO_4/Na_2HPO_4	0.15	2.0
exchangeable	NH_4Cl	1.0	4.0
organic	$Na_2P_2O_7$	0.10	16
carbonate	Na_2EDTA	0.05	16
Fe and Mn oxides and hydroxides	buffer solution of $Na_2S_2O_4$ at 353 K		0.25
sulfide	HNO_3	1.0	16
silicate minerals	digestion with mixture of $HF + HClO_4 + HNO_3$		

2.0 g of moist soil samples were shaken with 20 cm³ of extractant for appropriate time presented in Table 5. Extracts were than centrifuged (20 min, 10 000 rpm) and filtered through 0.45 μm membrane filters. In subsequent extractions, prior to the addition of the next extractant, each solid residue was washed with 10 cm³ of water (shaken 1 min, centrifuged at 10 000 rpm for 10 min, and decanted). The washing solution was then discarded. In easily exchangeable fraction, the filtrating through 0.1 μm membrane filters was applied to remove the colloidal particles.[27,34]

The concentrations of chromium in extracts were determined by flame or electrothermal atomic absorption spectrometry. Aliquots of extracts of easily exchangeable fraction of soils were used for determination of Cr(VI) by 1,5-diphenylcarbazide spectrophotometric method (LOD = 30 ng cm⁻³).[11,27,28]

Experimental design. A total of 1500 g of each of four moist natural soils (clay, peat, sand and cambisols) was mixed with an appropriate amount of an aqueous solution of Cr(VI) as $K_2Cr_2O_7$ or Cr(III) as $CrCl_3$, so that the final total concentration of chromium was twice the former value of the concentration of chromium in soils of the natural origin.

Duplicate samples were mixed using a plastic-coated metal mechanical stirring device to obtain the homogeneous thick paste, which was then placed in a 2.0 dm^3 shallow plastic container to achieve rapid evaporation of excess water. Homogenized samples were left thirty days under the constant moisture (periodical watering) and constant room temperature.

The fractionation of chromium was investigated thirty days after chromium application employing sequential extraction procedure presented in Table 5.

In addition to the total easily exchangeable chromium, Cr(VI) was also determined employing 1,5-diphenylcarbazide spectrophotometric method.[11,27,28]

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Povzetek

Na podlagi sekvenčne ekstrakcijske sheme smo določali vsebnost kroma v različnih lahko in slabo topnih fazah tal (glinasta, organska, peščena in pokarbonatna tla) 30 dni po dodatku Cr(VI) ali Cr(III) v obliki vodne raztopine. Določali smo celotne koncentracije kroma v posameznih fazah kontaminiranih tal (vezanega na organske molekule, vezanega na Fe in Mn okside in hidrokside, vezanega na karbonate, vezanega na sulfide in vezanega na silikatne minerale) in jih primerjali s koncentracijo kroma v posameznih fazah tal v naravnih nekontaminiranih tleh. V vseh treh vrstah tal smo določali tudi vsebnost vodotopnega Cr(VI).

Rezutati frakcionacije kroma v tleh kontaminiranih z vodotopnim Cr(VI) 30 dni po dodatku kažejo, da je v pokarbonatnih, glinastih in peščenih tleh večji del kroma ostal v vodotopni oziroma lahko izmenljivi obliki. V organskih tleh vodotopnega oziroma kroma v izmenljivi obliki nismo zaznali. V organskih tleh je bil krom predvsem vezan na organske molekule, v ostalih tleh pa je bilo največ kroma vezanega na Fe in Mn okside in hidrokside.

V tleh kontaminiranih z vodotopnim Cr(III) je bil krom večinoma vezan na organske molekule, vezan na Fe in Mn okside in hidrokside ter tudi na karbonate. Vsebnost izmenljivega kroma, je bila v primerjavi z organskimi tlemi, veliko višja v glinastih in pokarbonatnih tleh.