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Modification of the NH_2 column method for chromium speciation in surface water and soil water

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Abstract

A new application of the NH_2 column method has been tested for speciation of Cr(VI) in soil water and surface water. Soil water and surface water samples were collected from two sites near the world's largest stainless steel production plant, Outokumpu Tornio Works, about 10 km south of the City of Tornio, Finland. Dissolved chromium species [Cr(VI) and Cr(III)] were quantified immediately from the water samples with the NH_2 (aminopropyl-modified silica) column method and a graphite furnace atomic absorption spectrophotometer (GFAAS) and then three months later after the collection. The sum of Cr species concentration determined by the method was equal to total dissolved Cr concentration measured by inductively coupled plasma mass spectrometry (ICP-MS). The method was precise and selective for environmental water samples at low concentrations, and it fractionated Cr species with 100 % specificity without noteworthy interference from other metals. Some difficulties appeared with Cr standard solutions made with deionised water. In addition, the soluble form of Cr(VI) was preserved in a stable form for three months both in the refrigerator and freezer, and almost all the dissolved Cr was in the Cr(VI) form.

Key words: chemical analysis, chromium, chemical fractionation, concentration, soil water, surface water, Finland

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1. Introduction

The toxicity of chromium depends on its chemical form. In natural waters, chromium mostly occurs in two oxidation states: Cr(III) and Cr(VI). Environmental conditions like temperature, chemical composition, oxidation-reduction and pH control the occurrence of chromium species. Trivalent chromium is an essential nutrient and relatively non-toxic, unlike Cr(VI), whose certain compounds are known to be carcinogenic (Costa, 1997; O'Brien & G. Wang, 1989). Trivalent chromium exists as insoluble Cr(III)oxides or soluble Cr(III)hydroxide-cations, and Cr(VI) as soluble chromate or dichromate anions in natural waters. Furthermore, Cr(III) has a tendency to become absorbed or complexed by organic molecules, which obviously results in lower bioavailability and therefore in a lower toxicity rating (Bartlett & James, 1988; Farmer et al., 2002). In contrast, an oxyanion Cr(VI) is highly mobile in soil and water systems and weakly sorbed to inorganic surfaces (Kotas & Stasicka, 2000; Pantsar-Kallio et al., 2001). Hexavalent Cr is sensitive to reduction in acidic media and supposedly is reduced to Cr(III) by organic matter (Stollenwerk & Grove, 1985; Farmer et al., 2002). However, Cr(III) easily oxidises to Cr(VI) in a strongly alkaline media (Pilley et al., 2003). Thus, a proper identification of Cr species is required to evaluate the occurrence and toxicity risks of Cr, its chemical transformation in water, soil and air, as well as its distribution and transport in the environment.

Current and upcoming legislation in the European Union directly and indirectly forces countries to come up with methods to determine the accurate concentration of Cr(VI) in the environment, along with its potential bioavailability and health effects on a case-by-case basis (Zarogiannis, 2005). In most environmental studies, only total Cr has been analysed (Reimann et al., 1998; Salminen et al., 2004; Salminen et al., 2005; Tenhola et al., 2004). Despite of a number of methods that have been developed for Cr speciation in aquatic environments, one of the most commonly used methods is based on the coloured complex formation of Cr(VI) with diphenylcarbazide (DPC) (Ball & Mc Cleskey, 2003). Nonetheless, when the concentration of Cr is relatively low, the method may have interference effects caused by organic carbon, humic and fulvic substances, and the presence of coloured species or complexes such as iron with DPC. Adsorbing organic ligands and high metal concentrations, especially Fe and Mn, are common in the surface water composition of Finnish mine environments (Lahermo et al., 1996).

The main goal of the present study is to modify a column application for Cr(III) and Cr(VI) of low concentrations in water media. The application tested here is the NH_2 column method, which selectively sorbed Cr(VI) while Cr(III) remains unsorbed. Originally, it was developed to determine Cr(VI) levels in infant milk products by Lameiras et al. (1998) and Soares et al. (2000). They found that the method was precise and accurate with good sensitivity for low Cr(VI) concentration. Secondly, it is purpose to examine the effect of storage conditions (freezer and refrigerator) on the oxidation states of Cr in laboratory.

2. Experimental

2.1. Site description

The study site locates in the Kemi-Tornio area, northern Finland, where chromium concentrations are naturally high in subsoil (82 – 95 mg kg^{-1}), topsoil (76 – 88 mg kg^{-1}) and stream water (0.7 – 1.0 µg l^{-1}, Salminen et al., 2005). Water samples were collected in the surroundings of the Outokumpu Tornio Works, which is the largest stainless steel production site in the world and locates about 10 km south of the City of Tornio. The works consists of units of ferrochrome production and stainless steel production and the Kemi Cr mine (25 km southeast), where chromite is mined and the ore is then shipped to the Tornio works.

2.2. Materials, supplies and reagents

Water samples were collected with a PE(polyethylene)-decanter into the plastic LDPE (Low density polyethylene)-bottles using Nitrilite® Silky Ultra-Clean gloves (Ansell) for a clean environment and carried in the cool boxes with the cool batteries. The volume of the bottles was 100 ml, 250 ml and 500 ml. Bottles were factory-new. Concentrated Suprapur nitric acid (65 % HNO_3 by Merck) was used in the acidification of the water samples. Dissolved chromium was measured from the water samples, which were filtered through a 0.45 µm pore size filter (GD/XP syringe filter with polypropylene prefilter and PVDF (polyvinylidene fluoride) -membrane by Whatman) with a 50 ml BD (Becton Dickinson) Plastipak™ disposable syringe.

All the laboratory supplies (tips, volumetric pipettes (class AS, Hirschmann), volumetric flasks, decanters, etc.) were acid washed with freshly prepared 10% nitric acid, soaked for one day in deionised water, rinsed a third time with pure laboratory water and dried in a thermo closet at 50°C. All the digital pipettes (Finnpipette) were calibrated before use. Samples were filtered through the aminopropyl-modified silica ion-exchange columns, Chromabond NH_2 (3ml, 500mg) by Macherey-Nagel, with vacuum equipment (Baker). Filtered Cr(III), and eluted Cr(VI), water samples were collected in glass tubes (Kimax) with the caps.

For the activation and elution phases of the NH_2 column method, the following solutions were prepared and used: 1 mol l^{-1} and 2 mol l^{-1} Suprapur nitric acid (Merck), ultra-pure laboratory water (resistivity 18.2 MΩ cm^{-1}, the PURELAB Ultra system of ELGA). A standard solution of Cr(VI) was prepared by dissolving 2.828 g potassium dichromate ($K_2Cr_2O_7$) in 1 litre of deionised water. Potassium dichromate was Merck's reagent for ACS and ISO analysis. A chromium(III) standard solution was prepared from a 1000 mg l^{-1} reference solution (Romil Ltd) for AA, ICP and IC calibration (exp. Jan 2007). Working solutions (20, 40, 60 µg l^{-1}) of Cr(III) and Cr(VI) were made from the standard solutions by dilution on the same day the NH_2 column procedure and filtering were done. The pH of the deionised water, which went through the column in the activating phase, was measured with colour-fixed indicator sticks (pH 0 – 14).

2.3. Instrumentation

Element concentrations of chromium (dissolved, total) were analysed by inductively coupled plasma mass spectrometry (ICP-MS), Thermo Elemental X7, equipped with Collision Cell Technology (CCT/ED). Dissolved chromium and chromium species were quantified by graphite furnace atomic absorption spectrometer (GFAAS), Perkin Elmer SIMAA 6000 with use of end cap transverse heated graphite tubes (End Cap THGA). The instrumental conditions of the GFAAS are summarized in Table 1.

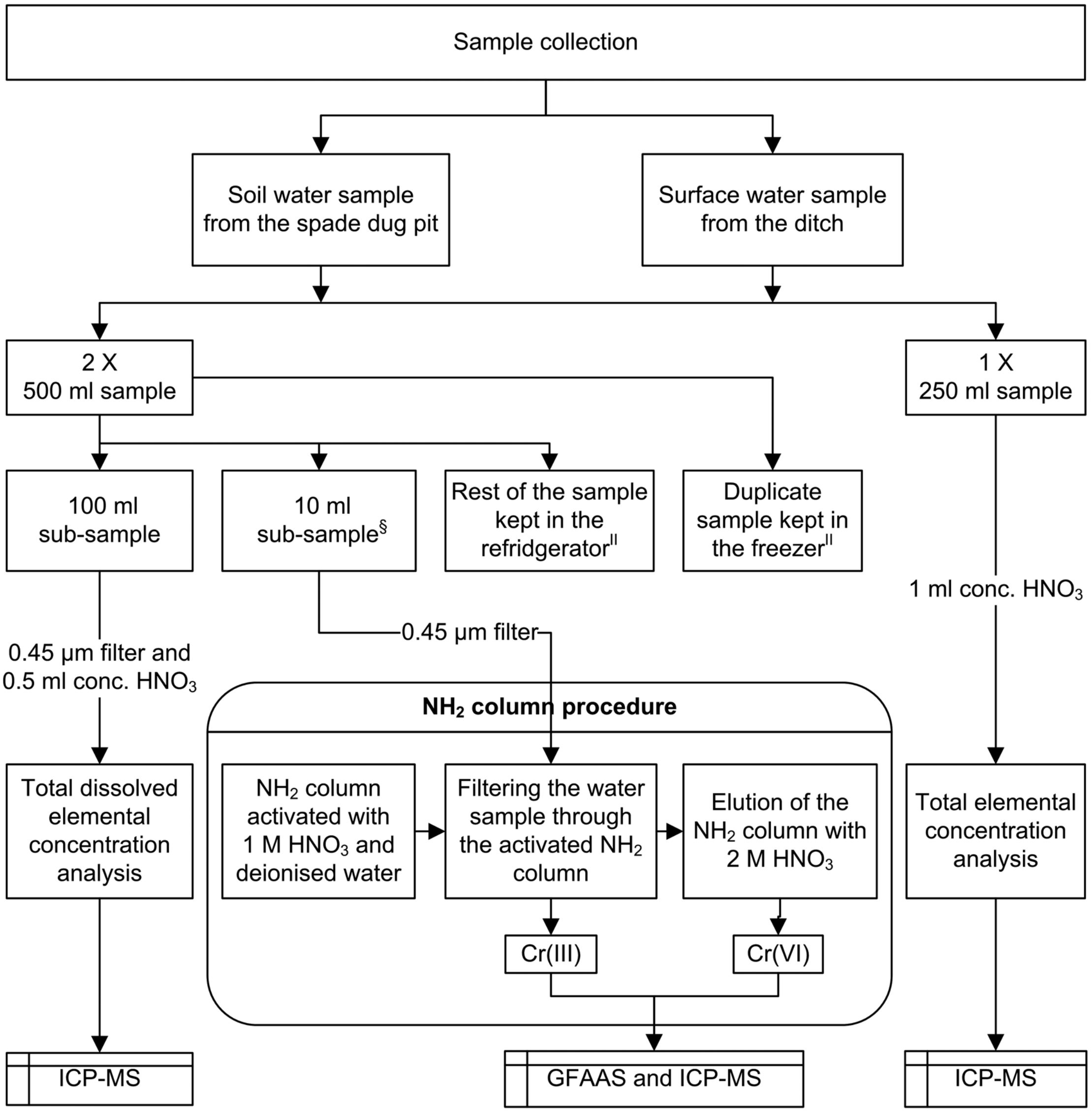
Table 1. Instrumental operating conditions.

Parameter	Value
Wavelength / nm	357.9
Two step drying, temperatures / °C	110 and 160
Ashing temperature / °C	1500
Atomization temperature / °C	2350
Read time / s	4.5
Read delay / s	0.0
Chemical modifier	3 µg Mg
Sample Injection volume / µl	20
Inert gas	Argon
Background correction	Zeeman
Measurement mode	Peak Area
Linear range / µg l-1	up to 20
Slit / nm	0.7
Standard deviation / µg l-1	0.012
Detection limit / µg l-1	0.25

2.4. Sampling and field measurements

The sampling sites were selected based on earlier studies by Hookana (2005). At the sites, water soluble Cr(VI) was detected on the surface of lingonberries and lettuces (Hookana, 2005). Fieldwork was carried out at the beginning of May 2005. Soil water and surface water samples were collected from two sites near the Outokumpu Tornio Works. The first sampling site was inside the factory area and the other was at the nearest coniferous forest, about 2 km northeast of the works. At the forest site, the snow was melting and in the factory area the snow had already melted away. The ground was thawed and the groundwater level was high.

Soil water samples and the duplicate soil water were taken from 30 cm deep and 40 – 50 cm wide spade-dug pits, which were filled by the soil water within half an hour after digging. Surface water samples were collected in the nearest ditches. Two water duplicates of 500 ml were taken from both media and at the both sampling sites. The 250 ml samples were pre-treated in the field, while the 500 ml samples were pre-treated later in the laboratory. Water samples were stored in the refrigerator and freezer



§ The 10 ml sub-sample has been taken in August. In May, the portions of the sub-samples were 50 ml (surface water) and 30 ml (soil water).

|| The 500 ml water samples were also treated later in August and September.

Fig. 1. Schematic presentation of the water samples treatment.

at the Geolaboratory of the Geological Survey of Finland (present Labtium Oy) in Kuopio. The schematic presentation of the water sample amounts and treatments are in Fig. 1.

After the sampling, pH, oxidation-reduction (redox), electric conductivity (EC) and temperature (T) of the water were measured with the portable field instruments. The measurements were done in situ from the water in sampling pits and in ditches. A blank sample was not taken during the field experiment.

In October of 2006, two humus samples were collected for spiking analysis. One of the samples was taken at the same coniferous forest site as the water samples, and the other was taken about 8 km northeast of the plant area. The moist samples were stored in polyethylene bags at 4 °C until the water extraction.

2.5. Sample pre-treatment and element measurements

After sample collection, the soil water and surface water samples were immediately pre-treated in the Outokumpu Tornio Works' laboratory (Fig. 1). At the same time, 50 ml portions of surface water samples were used in the NH_2 column procedure. Soil water samples were filtered for Cr(VI) analysis after three days settling because of the large amount of organic material and fine mineral particles. The rest of the soil water samples were left in the refrigerator for three months to settle. In August, the samples of settled soil water, refrigerated soil water and surface water duplicates were filtered and acidified similarly to the samples in the Outokumpu laboratory and used for total dissolved Cr analysis. In September, duplicate filtering was done to the soil water samples kept in the refrigerator and freezer and to the surface water sample stored in the freezer.

The 250-ml volume of soil water and surface water samples were pre-treated in the field in May (Fig. 1). Later, in the geolaboratory of the GTK (present Labtium Oy), these water samples were digested by adding 5-ml volume of Suprapur nitric acid and heated in a water bath at 90 ± 2 °C for six hours. After heating, the water samples were cooled overnight and the next day centrifuged for element measurement (total concentration). In August and September, the heating treatment with acid was also done to both soil water and surface water samples stored in the refrigerator and freezer.

The filtrates for total dissolved elemental concentration analysis and acid-treated samples for the total elemental concentration analysis were analysed by ICP-MS in the accredited geolaboratory of the GTK (present Labtium Oy) at Espoo.

2.6. NH_2 column pre-treatment and chromium analysis

The NH_2 column procedure includes activation, filtering and elution (Fig. 1). NH_2 columns were activated with 2 x 3 ml 1 M Suprapur HNO_3 and washed with 2 x 3 ml ultra pure laboratory water. After activating, the pH of washing deionised water was controlled. The filtered (0.45 µm) water samples were poured into the NH_2 column and filtered with a vacuum. In May, the volume of the filtrates was 50 ml of surface water and 30 ml of soil water, and the columns were eluted 2 to 3 times with 6 ml of 2 M nitric acid. In August, the volume of the samples of soil water and surface water, and the elution volume of nitric acid was 10 ml. Furthermore, 25 µl of nitric acid was added to the filtrates to ensure that Cr(III) remained in the solution. The chromium concentrations of the filtrates and elutes were measured with GFAAS and, in May, with ICP-MS as a comparative measurement in the accredited geolaboratory of the GTK (present Labtium Oy) at Kuopio.

The selectivity of the NH_2 column was tested with the standard working solutions of Cr(III) and Cr(VI) made with deionised water. Concentrations of the solutions were 20, 40 and 60 µg l^{-1}. The procedure with the standards was the same as for the samples: a 10 ml sample was filtered first, and then the column was eluted with 10 ml of 2 M nitric acid. Results are given as means ± standard deviation (SD) of three replicates (Table 2). The efficiency of the NH_2 column to specify Cr(III) from the Cr(III)-complexes with organic matter was also tested by the standard addition method. A 0.5 ml of 1 mg l^{-1} standard solution of Cr(III) was added to the filtered (0.45 µm) water extract of humus matter. An aqueous soil extract was prepared by shaking 25 g of the moist humus sample with 100 g of pure laboratory water in a round shaker at 50 rpm for two hours, at room temperature. Ten millilitres of the spiked sample was filtered through the NH_2 column, eluted with 10 ml of 2 M nitric acid and analysed with ICP-MS.

Table 2. (a) The concentration and recovery of chromium species (μg l^{-1}) in the working standard solutions of Cr(III) and Cr(VI), and (b) the recovery (%) of Cr(III) obtained from the spiking experiment of aqueous soil extract (LS ratio 4:1) using the NH_2 column method (see also the text). Mean recovery is calculated as following: Standard solution (compared to Cr concentration in standard working solution) = [Filtrate Cr(III) or Eluent Cr(VI)/ standard solution Cr]*100.

Oxidation state of Cr	Working solution of Cr (μg l^{-1})	Filtrate, mean ±SD (μg l^{-1})	Eluent, mean ±SD (μg l^{-1})	Mean recovery (%)	n
Cr(III)	20	10.8 ± 0.47	0.50 ± 0.05	53.8	3
	40	28.4 ± 0.92	0.20 ± 0.07	71.0	3
	60	45.2 ± 0.12	0.14 ± 0.06	75.3	3
	Blank	0.10 ± 0.03			
Cr(VI)	20	2.8 ± 0.5	13.2 ± 2.7	65.8	3
	40	2.8 ± 0.5	29.3 ± 5.2	73.3	3
	60	2.8 ± 2.3	40.3 ± 1.6	67.1	3
	Blank		1.9 ± 0.4		

Sample of the extract	Cr(III)-add (μg l^{-1})	Cr-add in filtrate (μg l^{-1})	Cr-add in eluent (μg l^{-1})	Cr recovery in filtrate (%)
Forest	50	46.9	2.5	94
Reference site	50	47.9	4.3	96
Reference site, duplicate	50	47.2	4.5	94
Tap water	50	47.6	0.0	95

3. Results and discussion

3.1. Chromium speciation with standard and spiked solutions

Results from the test with both Cr(III) and Cr(VI) diluted working standard solutions (20, 40 and 60 μg l^{-1}) showed that the recovery of the standards varied between 53.8 % and 75.3 % for both chromium species (Table 2a). Concentrations of the Cr working solutions were measured before and after filtering through the column. However, the concentrations of Cr(III) in the unfiltered working solutions were much lower than in the filtrates. Obviously, Cr in the diluted standard solutions of Cr(III) adhered to the sides of the glass container, resulting in a low concentration of Cr. This interpretation is based on the fact that the addition of the Suprapur nitric acid slightly increased the concentration of Cr(III) in the unfiltered working standard solutions. The difference between the Cr(VI) working standard solutions and Cr(VI) concentrations in the eluents was not significant when considering the standard deviation.

Due to the low recoveries of aquatic working solutions of Cr species, the aqueous soil extract from the humus sample was spiked with a standard solution of Cr(III) (50 μg l^{-1}). The recoveries of Cr(III) in the filtrates was 94 – 96 % (Table 2b). This indicates that the lack of organic shielding material in the deionised water of the standard solutions obviously causes the low recoveries from aquatic working solutions. Cr species from the aquatic working solution may diffuse inside the column's solid stationary phase particle's pore and are not therefore able to leach out from the column with nitric acid-solvent, unlike those of the spiked soil extracts and environmental water samples with the high organic matter content (see chapter 3.2).

Lameiras et al. (1998) and Soares et al. (2000) did not use deionised water for a calibration curve because of the difficulties adapting the pH in the deionised water matrix. This may be true for the spiked standard solution of this study. Instead, Lameiras et al. (1998) and Soares et al. (2000) spiked the milk samples with standard Cr solutions. It was assumed

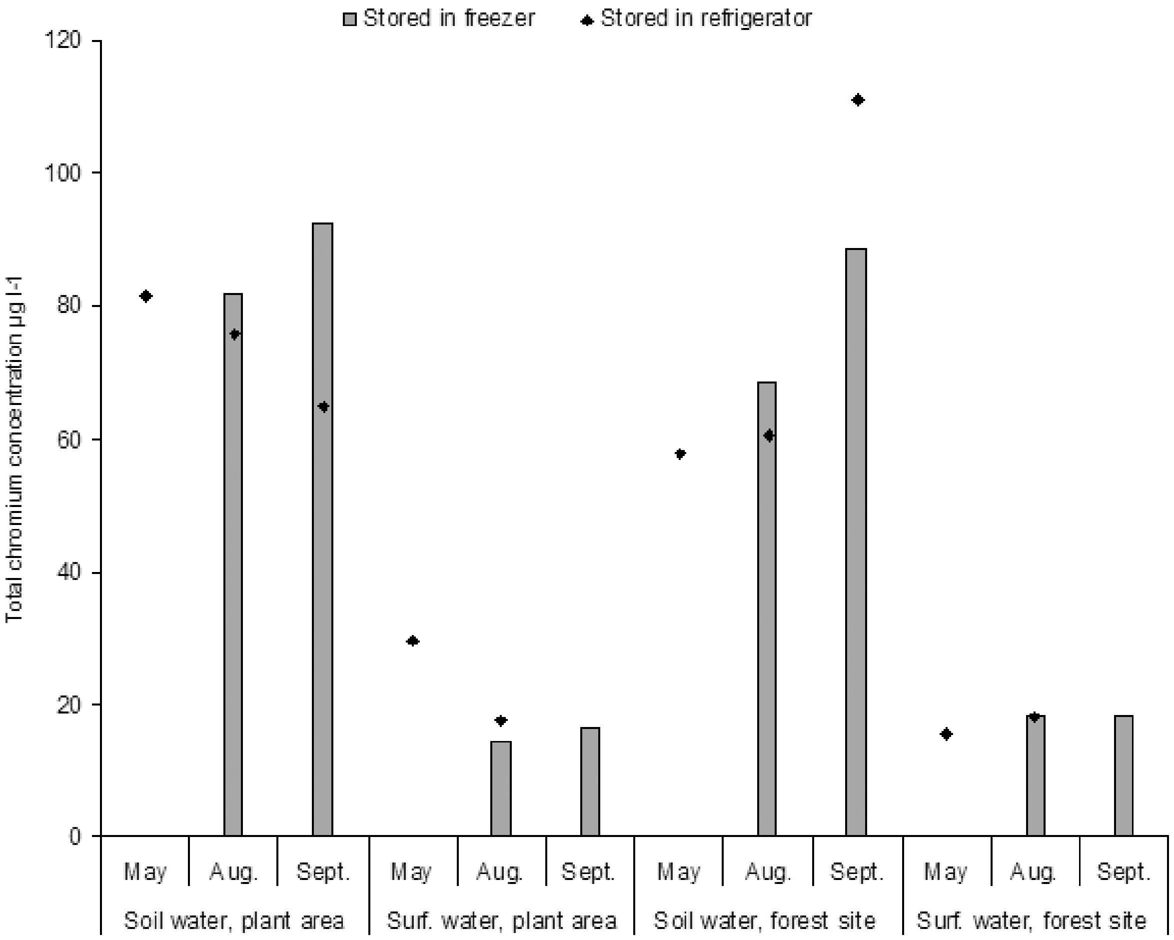


Fig. 2. Total Cr concentration (µg l^{-1}) of the soil water and surface water samples measured in May, August and September 2005, Tornio, Finland. Keys: Plant area refers to the sampling site in the factory area of the Outokumpu Tornio Works and forest site to the sampling site in the forest area about 2 km from the works. The number of samples stored in the fridgerator was 10 and in the freezer 8.

that the use of a Finnish surface water sample as a matrix for spiking may cause interferences due to the variable content of organo-Fe complexes, and fractionating problems of the standard solution.

According to the results, the NH_2 column separates organically bound Cr(III)-complexes, and Cr(III)-complexes will not significantly replace aquatic Cr(VI)-complexes in the elution stage of the method. The results also confirmed that the NH_2 column separates Cr(VI) from Cr(III) from water samples of the low Cr concentration.

3.2. Total and dissolved chromium concentration of surface water and soil water samples

In the plant area, total Cr concentrations of the soil water were between 65 µg l^{-1} and 90 µg l^{-1} and in the surface water between 15 µg l^{-1} and 30 µg l^{-1} (Fig. 2). At the forest site, the total concentrations were, on average, somewhat lower than in the plant area, and similarly soil water contained more chromium than surface water.

The concentration of dissolved Cr was markedly lower than the total Cr concentration at both study

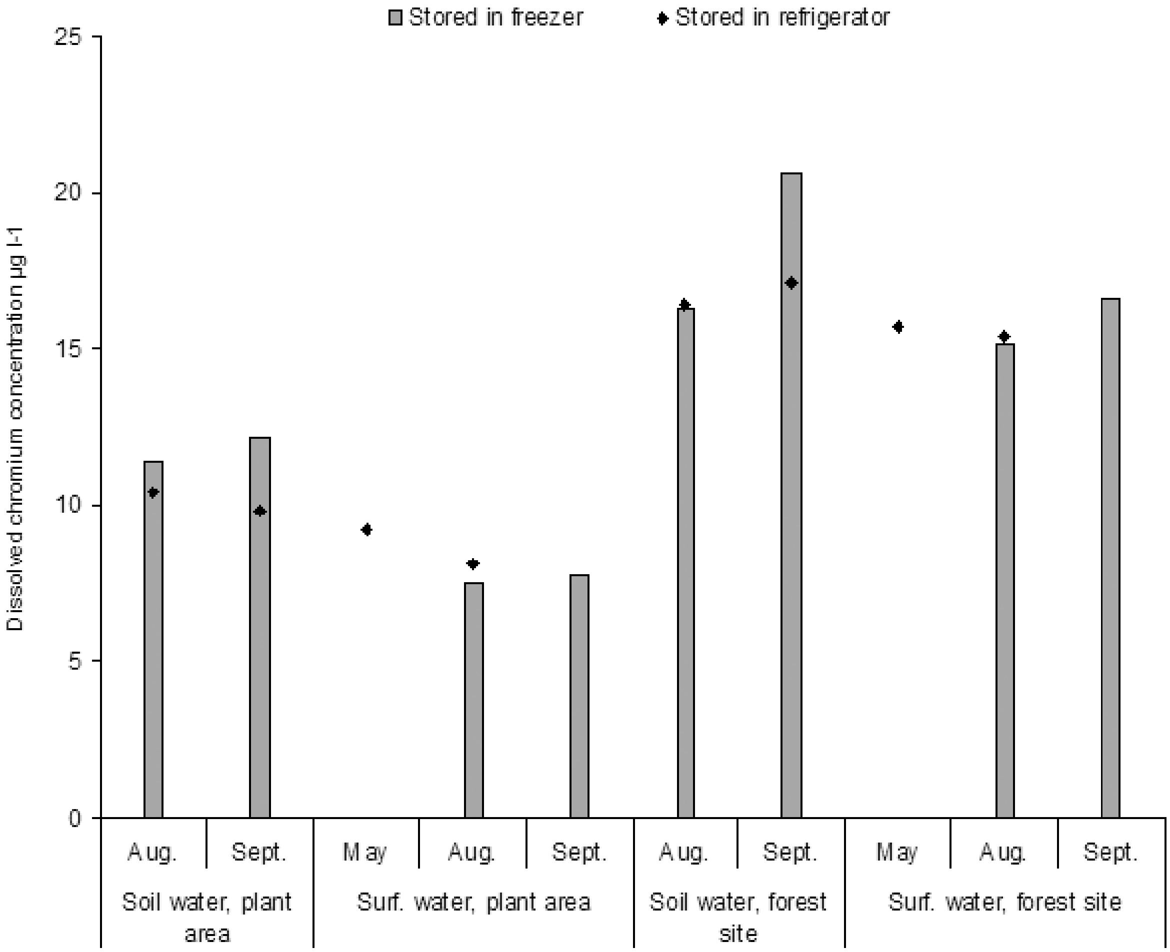


Fig. 3. Total dissolved Cr concentration (µg l^{-1}) in the soil water and surface water samples measured in May, August and September 2005, Tornio, Finland. See keys in Figure 2. The number of samples stored in the fridgerator was 8 and in the freezer 8.

sites. This indicates that Cr in soil water and surface water is predominantly bound in solid particles, as hydrated oxides, complexed by organic matter and/or Fe-precipitates of soils (Farmer et al., 2002; Räisänen et al., 1997). In contrast to the total Cr contents, the concentrations of dissolved Cr in soil water were higher (mean 17 µg l^{-1}) at the forest site than in the plant area (10 µg l^{-1}, Fig. 3). The same trend was also seen in the surface water.

The sample preserving time did not show an unambiguous effect on the Cr concentrations (Figs. 2 – 3). The variation was within the uncertainty in instrumental measurement (15 %). In addition, the concentration of dissolved chromium was the same regardless of the storage method. Moreover, the Cr concentrations were stable during the four months. That was unexpected for the dissolved chromium concentration. Any change in dissolved Cr concentration was not observed even after a harsh shaking procedure.

3.3. Chromium speciation in surface water and soil water samples

In the plant area, mean dissolved Cr(VI) concentration of soil water was about 12 µg l^{-1}, and in the surface water about 9 µg l^{-1} (Table 3). At the forest site, the Cr(VI) concentration in the soil water was about

Table 3. Mean concentrations and standard deviations of the dissolved Cr and Cr species in soil water and surface water samples analysed with the NH$_2$ column method. The concentration of dissolved Cr in water samples was measured during the period from May to September, and Cr(III)-filtrates and Cr(VI)-eluates in May and in August in 2006.

Collection site of the sample	Sample	Time of the measurement	Cr in filtrate (µg l^{-1})	n	Cr in eluent (µg l^{-1})	n	Cr, stored in refrigerator (µg l^{-1})	Cr, stored in freezer (µg l^{-1})	n
Plant Area	soil water	May	0.63 ± 0.44	2	12.1 ± 0.85	2			
	soil water, refrigerator	Aug.	0.80 ± 0.12	2	12.9 ± 0.15	3			
	soil water, freezer	Aug.	1.12 ± 0.42	2	13.1 ± 2.33	2			
	soil water, total dissolved	May–Sept.					10.1 ± 0.42	11.8 ± 0.49	2
	surface water	May	0.43 ± 0.09	2	8.44 ± 0.83	2			
	surf. water, refrigerator	Aug.	0.90	1	8.83	1			
	surf. water, freezer	Aug.	0.72	1	8.49	1			
	surf.water, total dissolved	May–Sept.					8.67 ± 0.77	7.67 ± 0.17	2
Forest site	soil water	May	0.61	1	17.4 ± 1.37	2			
	soil water, refrigerator	Aug.	1.44	1	15.6	1			
	soil water, freezer	Aug.	1.19	1	15.8	1			
	soil water, total dissolved	May–Sept.					16.8 ± 0.49	18.5 ± 3.04	2
	surface water	May	1.51 ± 1.10	2	15.0 ± 1.04	2			
	surf. water, refrigerator	Aug.	1.28 ± 0.09	3	17.0 ± 0.00	2			
	surf. water, freezer	Aug.	1.03 ± 0.13	2	16.9 ± 0.14	2			
	surf.water, total dissolved	May–Sept.					15.6 ± 0.21	15.9 ± 1.06	2

16 µg l^{-1} and in surface water about 15 µg l^{-1}. At both sites, the mean concentrations of Cr(III) were below 2 µg l^{-1}. However, one subsample of soil water from the forest site gave an anomalously high Cr(III) concentration, 8 µg l^{-1}. With this value, the average Cr(III) concentration for the soil water of the forest site would be 3.5 mg l^{-1}.

The summed recoveries of the Cr species were equal to the total concentration of dissolved chromium (Table 3). The recovery of the dissolved chromium measured by ICP-MS was between 95 % and 108 % and by GFAAS between 108 % and 119 %, which can be considered comparable within the uncertainty. Nevertheless, results showed that the dissolved chromium was almost entirely in the hexavalent form. After the elution stage, Cr(VI) concentrations contained a positive elution error, approximately 2 µg l^{-1}.

Assuming that dissolved Cr in the surface water was almost entirely Cr(VI), measurable concentrations of Cr(VI) in soil water were unexpected. We presumed that the organic carbon in the litter and humus layer would reduce Cr(VI) to Cr(III). According to the DPC-method, water samples that contain high levels of organics or sulphides can cause rapid reduction of soluble Cr(VI) to Cr(III) (US EPA, 1994). Even then, the ratio of Cr(VI) to Cr(III) in dissolved solutions remained unchanged during the preservation time. Similar findings regarding the slow reducing time of Cr(VI) to Cr(III) have been presented in Cr(VI) studies for milk products (reduced in 48 hours) (Soares et al., 2000).

3.4. Suitability of the NH$_2$ column application for chromium species

The NH$_2$ column was able to separate Cr(III) as [$Cr(NO_3)_3$] and Cr(VI) as [$K_2Cr_2O_7$], but the recoveries of Cr species (53.8 – 75.3 %) and standard deviations remained unexplained and exceptionally low.

In contrast, the recoveries of soil water and surface water samples were comparable to the concentrations of the total dissolved Cr.

Adjustment of the pH during the NH_2 procedure with Cr working standard solutions may also be more important than presumed. Deionised water's acidity was measured after the activating. The pH was 4-5, which is somewhat lower than the pH of the soil water and surface water samples. Nevertheless, the NH_2 column procedure includes several uncertainties. Chromate can be sorbed differently in the NH_2 column than dichromate, which results in the low recoveries of Cr standard solutions. Secondly, the influence of the deionised water on the redox state of the Cr(VI) compounds is not well understood. Another question is connected to the dilution of the Cr standard solutions and the stability of Cr species.

Despite of the abovementioned uncertainty factors, the NH_2 column fractionates Cr species with almost 100 % specificity for the Tornio area environmental water samples used in the present study. The elution stage raised the Cr(VI) concentration about 2 $\mu g\ l^{-1}$ in the both environmental water samples and the deionised working standard solutions. The positive error may be the result of Suprapur nitric acid, which contains a maximum 1.0 $\mu g\ l^{-1}$ Cr, in addition to dissolving particles from the column material and the instrumental limit of quantification. After the reduction of the elution stage's error, the recoveries of Cr species were over 92 % as measured by GFAAS.

Furthermore, other possible factors include where the organic material in water samples (going through the filter) presses too hard, and the overload of the NH_2 column, which was seen once as occasional high Cr(III) concentration, 8 $\mu g\ l^{-1}$ after NH_2-filtration. Also, the duplicate water samples taken from different bottles than the initial water samples may be a reason for the poor precision of the Cr concentration. The incomplete melting of the duplicate soil water samples frozen occurred in the second measurement (in September), can also be a possible error factor. The significance of the errors mentioned above is impossible to statistically quantify due to the small number of samples in the present study.

3.5. Comparison of methods

The DPC-method (USEPA 218.6, for drinking water, groundwater and industrial wastewater) emphasizes that samples must be filtered and adjusted to pH 9 – 10 in the field (Ball and Mc Cleskey, 2003), stored at 4 °C and analysed within 24 hours of collection (USEPA, 1994) to ensure that the dissolved Cr species remain unchanged. Anionic species such as chloride and sulphate may cause interference in DPC-method (USEPA, 1994), but according to Ball and Izbicki (2004), the most serious interference with USEPA DPC-method is caused by Fe. Concentrations of Fe(II) and Fe(III) 50 times greater than Cr(VI) dramatically decrease the recovery of Cr(VI) in the DPC-method (Ball and Izbicki, 2004). In the present study, concentrations of dissolved iron in soil water and surface water samples were almost 60-fold at maximum and 8-fold at minimum compared to the concentration of Cr(VI). Therefore, the NH_2 column method appears to be less sensitive to the interferences of other metals or sulphates, and easier to use (no pH adjusting) with longer preservation time of water samples (over 24 hours) than the DPC-method commonly used in Finland.

According to the results, the application of the NH_2 column method is adequate for identifying Cr(VI), especially at low concentrations and without interference from other metals or sulphate. Furthermore, the results showed a clear relation between the dissolved chromium and the sum of Cr species, Cr(III) and Cr(VI), measured. This relation allows us to quantify the concentration of Cr(VI) by deducting the concentration of Cr(III) from the total concentration of the dissolved Cr instead of the elution stage measurement. The deducting will significantly decrease the cost of the Cr speciation and will quicken the analysis procedure.

Further study is needed for chromium species fractionation in environmental water samples using the NH_2 column method, especially for more precise results for chromium distribution and behaviour in the aquatic environment (soil water, surface water and groundwater). Amount and availability of interfering agents and the problem with the Cr standard solution remained unsolved. The pure deionised water may not be the right matrix for the NH_2 column or the pH will need adjusting during procedure.

4. Conclusion

The NH_2 column method application was successful for the determination of Cr(VI) and Cr(III) in environmental water samples. The NH_2 column procedure is precise and selective for soil water and surface water samples with low concentration of chromium species. Other metals or sulphates, or high dissolved organic material do not interfere with the speciation of Cr species. The sum of Cr species concentrations was approximately equal to the total dissolved Cr concentration. This finding suggests that the concentration of Cr(VI) can be quantified by deducting the concentration of Cr(III) from the total concentration of the dissolved Cr instead of the elution stage measurement. The fractionation of the Cr species from the standard solutions showed difficulties with the unacceptably low recoveries, which will need further experimentation.

The results showed that Cr(VI) is not so sensitive to reduce Cr(III) during sampling, transport and storage. Overall, the case study shows that the dissolved chromium in the environmental water is in the form of Cr(VI). This is true even though the concentrations in soil and surface waters are small ($< 25\ \mu g\ l^{-1}$). The findings reveal a misunderstanding of the Cr behaviour in the northern hemisphere. Furthermore, the NH_2 column application will offer a good possibility for the studying the chromium species in the Finnish mining and metal industry environment.

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