NOTICE: this is the author's version of a work that was accepted for publication in Environmental Science and Technology. A definitive version was subsequently published in *Environmental Science and Technology* **48**, 1753-1761, 2014. <http://dx.doi.org/10.1021/es404557e>

Chromium(III) complexation to natural organic matter: mechanisms and modeling

Jon Petter Gustafsson,^{*,†,‡} Ingmar Persson,[§] Aidin Geranmayeh Oromieh,[†] Joris W.J. van Schaik,[†] Carin Sjöstedt,^Δ Dan Berggren Kleja,^{†,⊥}

[†]Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, 750 07 Uppsala, Sweden

[‡]Division of Land and Water Resources Engineering, KTH Royal Institute of Technology, Brinellvägen 28, 100 44 Stockholm, Sweden

[§]Department of Chemistry, Swedish University of Agricultural Sciences, Box 7001, 750 07 Uppsala, Sweden

^ΔDepartment of Chemistry, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden

[⊥]Swedish Geotechnical Institute, Kornhamnstorg 61, 111 27 Stockholm, Sweden

Corresponding author

*Phone: +46 (0)18 671284, Fax: +46(0)18 673156, e-mail: jon-petter.gustafsson@slu.se

ABSTRACT

Chromium is a common soil contaminant, and it often exists as chromium(III). However, limited information exists on the coordination chemistry and stability of chromium(III) complexes with natural organic matter (NOM). Here, the complexation of chromium(III) to mor layer material and to Suwannee River Fulvic Acid (SRFA) was investigated using EXAFS spectroscopy and batch experiments. The EXAFS results showed a predominance of monomeric chromium(III)-NOM complexes at low pH (< 5), in which only Cr^{III}-C and Cr-O-C interactions were observed in the second coordination shell. At pH > 5 there were polynuclear chromium(III)-NOM complexes with Cr^{III}-Cr interactions at 2.98 Å and for SRFA also at 3.57 Å, indicating the presence of dimers (soil) and tetramers (SRFA). The complexation of chromium(III) to NOM was intermediate between that of iron(III) and aluminum(III). Chromium(III) complexation was slow at pH < 4 : three months or longer were required to reach equilibrium. The results were used to constrain chromium-NOM complexation in the Stockholm Humic Model (SHM): a monomeric complex dominated at pH < 5 , whereas a dimeric complex dominated at higher pH. The optimized constant for the monomeric chromium(III) complex was in between those of the iron(III) and aluminium(III) NOM complexes. Our study suggests that chromium(III)-NOM complexes are important for chromium speciation in many environments.

INTRODUCTION

Chromium is an element of significant environmental interest. It is a common contaminant from e.g. the use of chromite-ore processing residue (COPR) as a filling material¹, from tanning, and the use of chromium-copper-arsenic (CCA) salts for wood preservation. Under natural conditions, chromium exists as either chromium(III) or chromium(VI), of which the latter is considered more toxic.¹ The free hydrated chromium(III) ion, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, is stable only at low pH as it easily hydrolyzes to CrOH^{2+} and $\text{Cr}(\text{OH})_2^+$ in dilute solution, and it may also form a wide range of polynuclear complexes at higher pH or concentrations.² Natural organic matter (NOM) may constitute an important sink for chromium in the environment, due to the strong interaction with chromium(III), and to its ability to reduce chromium(VI) to chromium(III).³ Despite this, few studies have been published regarding the complexation of chromium(III) to NOM. This makes it difficult to properly calibrate the existing geochemical models for trace metal binding to NOM, such as Model VII,⁴ NICA-Donnan,⁵ and the Stockholm Humic Model (SHM).⁶ When generic values for complexation constants have been derived for these models,^{4,6-7} only data from one study has been available.^{4,8} Because of the limited availability of reliable chromium(III) complexation data, the use of complexation models to predict chromium(III) solubility in the environment remains uncertain.⁹⁻¹⁰

The objective of this study is to increase the knowledge on the chromium(III) speciation with NOM by use of EXAFS spectroscopy, and to use this information as a basis for calibrating an improved equilibrium-based model for chromium(III) binding to NOM. We chose to obtain structural information for two NOM samples: the Suwannee River Fulvic Acid, and the Risbergshöjden Oe soil sample, which represent aquatic and terrestrial NOM. A large number of batch experiments was also performed for the soil, to investigate the kinetics of the

chromium(III)-NOM complexation process, and to provide quantitative data for calibration of the SHM.⁶

MATERIALS AND METHODS

Samples. Chromium(III) complexation was investigated for two different organic samples: the IHSS Suwannee River Fulvic Acid I (SRFA) standard (see <http://www.humicsubstances.org>), and one organic soil sample. The elemental composition of the SRFA is 52.44 % C, 42.20 % O, 4.31 % H, 0.72 % N and 0.44 % S, and the charge density of carboxyl groups at pH 8.0 has been estimated to 11.44 meq g⁻¹ C.¹¹

The soil sample (Risbergshöjden Oe) is a mor sample from a Spodosol in central Sweden that has been described and used in a number of earlier investigations.¹²⁻¹³ The sample was collected in 2011, sieved through a 4 mm sieve to remove roots and coarse particulates, and homogenized. It was stored in its field-moist state at +5°C until further use. The water content was 68.5 %. The sample contained 45.0 % C and 1.3 % N on a dry-weight basis. By use of 0.1 M HNO₃ (1 g dry soil to 30 mL, shaking time 16 h), geochemically active concentrations of Al, Ca, Cr, Fe, K, Mg, Mn and Cu were determined after filtration through a 0.2 µm Acrodisc PF filter (Gelman Sciences) and analysis with ICP-MS using an ICP-SFMS Thermo Scientific instrument.

Experimental. Batch experiments were performed to study chromium(III) sorption to the soil as a function of pH, initial chromium(III) concentration, and competition from aluminum(III). A detailed description of the procedure can be found elsewhere.¹² Briefly, 1.00 g of field-moist sample was mixed with 30 mL solution of varying composition in 40-mL polypropylene bottles. The solution contained a background electrolyte of 0.01 M NaNO₃,

and different final pH values in the range of 2 to 7 were obtained by addition of HNO₃ or NaOH. After pH adjustment, metals were added to the suspensions using stock solutions of 10 mM Cr(NO₃)₃ or 10 mM Al(NO₃)₃. To one set of samples, chromium(III) nitrate was added to an intended final concentration of 100 µmol L⁻¹ Cr(III), equivalent to 0.31 mmol Cr(III) g⁻¹ dry soil. A second set of samples contained 1000 µmol L⁻¹ Cr(III) (equivalent to 3.1 mmol Cr(III) g⁻¹ dry soil) and in a third set of samples a mixture of 100 µmol L⁻¹ Cr(III) and 1000 µmol L⁻¹ aluminum(III) was added. The actual final concentrations were somewhat (2 %) lower due to dilution from interstitial water in the field-moist soil sample. All samples were made in duplicate.

The samples were equilibrated on an end-over-end shaker (Heidolph Reax II) in darkness at 10°C for different periods of time to investigate the effect of reaction time on the results. Thus, separate sets of samples were equilibrated for 1, 5, 34, 90 and 211 days. Once a week the caps were removed for a few minutes to ensure full aeration of the samples during the entire equilibration period. After equilibration, the samples were centrifuged and filtered through a 0.2 µm Acrodisc PF filter (Gelman Sciences). The pH was measured on the unfiltered supernatant using a PHM210 standard pH meter (MeterLab) equipped with a combination electrode, at 10°C. Filtered samples were divided in two subsamples. One subsample was acidified (1 % HNO₃) and sent to ALS Scandinavia AB, Luleå, Sweden, for analysis of major cations and metals using ICP-MS with an ICP-SFMS Thermo-Scientific instrument. In the second subsample, dissolved organic carbon (DOC) was determined using a TOC-5000a Analyzer (Shimadzu Corp.)

Separate batch experiment samples were prepared for EXAFS analysis. However, only samples with 3000 µmol L⁻¹ added Cr(III) were prepared. The samples were shaken for 47, 53 or 192 d and three pH levels were included, 2.5, 3.0 and 5.5. After equilibration, the samples were centrifuged as described above. The wet soil paste was stored at +5°C, brought to the

synchrotron and analysed within 3 days after centrifugation. Prior to EXAFS analysis, the soil paste was dewatered further by squeezing the sample between two Whatman ashless grade filter papers.

Chromium(III) complexation to SRFA was studied by means of EXAFS spectroscopy, at a Cr(III) concentration of 0.33 mmol g⁻¹ SRFA. A solution containing 3 mmol L⁻¹ Cr(NO₃)₃, 9 g L⁻¹ SRFA and 0.03 M NaNO₃ (final concentrations) was prepared in a polypropylene bottle. Aliquots were titrated with different additions of HNO₃ or NaOH to provide three different pH levels; 2.1, 3.6 and 5.5. The solutions were equilibrated for 202 days in darkness at 10 °C. At approximately weekly intervals, samples were mixed and pH was recorded. No systematic drift in pH with time could be detected. After equilibration, the samples were filtered using 0.2 µm Acrodisc PF filter (Gelman Sciences). Filtered solutions were analyzed for DOC and Cr, as described above. Filters (wrapped in polyethylene bags) and solutions were kept cold (+5°C) until analysis with EXAFS spectroscopy (max. 3 days after the end of the equilibration).

X-ray absorption spectroscopy. X-ray spectroscopic measurements of samples from the experiments of fulvic acid and of soil suspensions were performed at the Cr K edge. The measurements were conducted at the wiggler beam line I811 at MAX-Lab, Lund, Sweden, at different occasions during 2011 and 2012. The beam line was equipped with a Si[111] double crystal monochromator, the storage ring was operated at 1.5 GeV and a maximum current of 230 mA. Higher-order harmonics were reduced by detuning the second monochromator crystal to reflect 40 % of the maximum intensity at the high-energy end of the scans. Samples were collected in fluorescence mode using a Passivated Implanted Planar Silicon (PIPS) detector with a vanadium filter. All measurements were carried out at ambient room temperature. The samples were mounted with tape on aluminium frame holders. No

systematic changes were observed in individual scans of the same sample, indicating that there was no change in oxidation state or binding mode of chromium in the samples during the experiments. Internal energy calibration was made with a foil of metallic chromium assigned to 5,979 eV.¹⁴ Between 10 and 20 continuous scans of 5 min each were collected per sample, depending on the chromium concentration.

EXAFS data analysis. The primary treatment, energy calibration and averaging of scans was performed with EXAFSPAK.¹⁵ After this, the EXAFSPAK and GNXAS¹⁶⁻¹⁷ program packages were used for further data treatment. The GNXAS code is based on calculation of the EXAFS signal and subsequent refinement of the structural parameters.¹⁶⁻¹⁷ The GNXAS method accounts for multiple scattering (MS) paths by including the configurational average of all the MS signals to allow fitting of correlated distances and bond distance variances (Debye-Waller factors). A correct description of the distribution of the Cr-O distances in a coordination shell should in principle account for asymmetry.¹⁸⁻¹⁹

When modeling the higher shell contributions, the CN (coordination number) of the single-scattering (SS) Cr···C path was fixed at 2 and the CN of the corresponding multiple scattering (MS) Cr-O-C path was fixed at $2 \times 2 = 4$, while letting the Debye-Waller factors be adjusted during optimization. Further, the short SS Cr···Cr path at ~ 3.0 Å was fixed at CN = 0.5 (tetramer) or 1 (dimer) again letting the Debye-Waller factor vary, and for the second SS Cr···Cr path at ~ 3.6 Å the CN was fixed at 2.0. This is in agreement with the procedure for modeling Fe-EXAFS spectra used by Kleja et al.²⁰ The standard deviations given for the refined parameters were obtained from k^3 -weighted least squares refinements of the EXAFS function $\chi(k) \times k^3$, and do not include systematic errors of the measurements. These statistical

error values provide a measure of the precision of the results and allow reasonable comparisons of e.g. the significance of relative shifts in the distances.

To decide if a certain peak in the Fourier transform originates from a heavy or a light back-scatterer, wavelet transform (WT) analyses of the EXAFS spectra were performed.²¹ The wavelet transform is a 3-D image that combines the EXAFS-spectra in k -space and R -space (FT transform) with the WT modulus, and where the back-scattering of the heavy elements appear with a maximum of the envelope of the EXAFS function at higher R . Depending on the atomic number of the back-scatterer the maximum intensity in the envelope appears at increasing k values. The Morlet wavelet transform incorporated in the Igor Pro script was used (Wavelet2.ipf).²² k^3 -weighted EXAFS spectra were imported to the script, and a wavelet parameter combination of $\kappa = 6$ and $\sigma = 1$ was used, with a range of $R + \Delta R$ from 2 to 4 Å (corresponding to interatomic distances of ca. 2.5 to 4.5 Å). The k -range used was 2-11 Å⁻¹. Wavelet transform analysis was performed both on the pre-treated EXAFS data and on the modeled EXAFS spectrum. A model that results in close agreement with the WT modulus of the EXAFS data provides additional support for the EXAFS model interpretation.

Geochemical model. The geochemical software Visual MINTEQ ver. 3.1²³ was used as the modeling environment for chromium(III) speciation. This software contains data for a large number of solution complexes involving chromium(III), and most of these are from the NIST Critical Stability constants compilation²⁴, see also Table S2. It is important to note that Visual MINTEQ uses $\text{Cr}(\text{OH})_2^+$ as the main component for chromium(III), hence all reactions involving chromium(III) need to be defined using this component.

To describe the binding of chromium(III) to fulvic and humic acids in the soil suspensions, the SHM was used,⁶ as modified for solid-phase organic matter in soil suspensions.²⁵ The SHM is a discrete-site electrostatic model, in many ways similar to WHAM-Model VII

model⁴ except that it uses a different electrostatic submodel. The model is described in detail elsewhere.^{13, 25} The equations describing metal binding through mono-, bi- and tridentate complexes are shown in the Supporting Information section, as they are relevant for this paper.

For the soil suspensions, we assumed that 75 % of the ‘active’ solid-phase organic matter consisted of humic acid (HA), whereas 25 % was fulvic acid (FA).¹³ Furthermore, we assumed that 100 % of the dissolved organic matter in these suspensions was FA.¹³ To consider the effect of initially bound metals in the modeling, the input for ‘active’ aluminum, iron, major cations and trace metals was estimated from extraction with 0.1 mol L⁻¹ nitric acid (Table S1). For sodium and nitrate, the total concentrations were calculated from the added amounts.

For the proton binding parameters of HA and FA, the generic values for the SHM were used.¹² For the modeling only samples that had been equilibrated for 90 d were considered, as almost all of these were at equilibrium (see Results section). Modeling was done in two steps: 1) From the observed buffer curve, we optimized the suspension concentration of humic and fulvic acid that was ‘active’ with respect to cation binding, through the comparison of measured and simulated pH values for a given addition of acid or base. These concentrations determine the slope of the modeled buffer curve. 2) With all other complexation constants fixed at those obtained during earlier investigations (see Table S3), the two considered chromium(III) complexation constants for the three data sets with different combinations of chromium(III) and aluminium(III) were optimized until a satisfactory fit was obtained. The ΔLK_2 value for chromium(III) was constrained by analyzing the model fit at the lowest pH values in systems with 100 and 1000 $\mu\text{mol L}^{-1}$ Cr(III). The goodness-of-fit was analyzed using root-mean square errors (RMSE) of simulated vs. measured dissolved concentrations of chromium (logarithmically transformed values).

RESULTS AND DISCUSSION

Kinetics of Cr(III) complexation. At low pH and high Cr(III) concentration, equilibrium was reached only after long equilibration times (Figure 1), which can be attributed to the slow water exchange of the hydrated Cr^{3+} ion (see Supporting Information). At pH 2.3, it does not seem likely that equilibrium was reached even after 211 d in the system to which $1000 \mu\text{mol L}^{-1}$ Cr(III) had been added. At pH 3.2 equilibrium was probably reached after 90 d, whereas at pH 3.9 and higher equilibrium was reached within a month. The slow kinetics at low pH was less prevalent in the $100 \mu\text{mol L}^{-1}$ Cr(III) system (Figure 1); also the most acidic system (pH 2.3) had reached equilibrium after 90 d. In many cases an upward drift in the equilibrium concentrations was seen after long equilibration times; this is most likely due to the dissolution of organic C, which increased over the studied time period (Figure S1). Thus organically complexed Cr(III) in solution became increasingly important. The decrease in dissolved chromium between 90 d and 211 d at the highest pH level (6.6) in the $100 \mu\text{mol L}^{-1}$ Cr(III) system deviated from this pattern, for unknown reasons.

EXAFS spectroscopy. The EXAFS results for SRFA and soil samples are shown in Figure 2 and Table 1. Included in the plots for comparison are also the results obtained for the tetramer $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ in water at pH 3.7.² The EXAFS data for the SRFA systems were of much better quality for the particulate fraction collected on the membrane filters ($> 0.2 \mu\text{m}$) than for the solutions. Since the Cr:DOC ratio of the particulate fraction ($0.52\text{-}0.68 \text{ mmol g}^{-1}$) was similar to the solution Cr:DOC ratio ($0.62\text{-}0.67 \text{ mmol g}^{-1}$) at all three pH values, only data for the particulate fractions are presented.

241 For all samples, the first-shell analysis showed that chromium was coordinated to 6 O/N
 242 atoms (O and N cannot be distinguished by EXAFS spectroscopy). The Cr-O/N distances in
 243 the first coordination shell ranged from 1.96 to 2.00 Å (average 1.98 Å; Table 1). The refined
 244 Cr-O distances are in close agreement with those previously found in hydrated and
 245 hydrolyzed chromium(III) ions and complexes,^{2,26} showing that chromium(III) is six-
 246 coordinate in octahedral fashion in all samples studied. Further, the absence of any pre-edge
 247 peak in the XANES region showed that the chromium was present exclusively as
 248 chromium(III) in all samples.

249 For higher coordination shells the EXAFS model fit (Figure 3) and the WT analysis showed
 250 consistent differences in the coordination environment of chromium(III), depending on the pH
 251 value. At low pH (≤ 3.6) the EXAFS data for both SRFA and soil samples could be fitted
 252 with a model that included SS Cr^{III}-C and MS Cr-O-C paths at half-path lengths of ~2.85 and
 253 ~3.05 Å, respectively, but with no Cr^{III}-Cr paths. The absence of any heavier elements (such as
 254 Cr) in the higher coordination shells in the acidic samples was corroborated by WT analysis
 255 (Figure 3), as is indicated by the absence of any high-intensity regions at high k and R . These
 256 results are consistent with an interpretation according to which chromium(III) was bound
 257 monomerically to NOM in both SRFA and in the soil sample. Thus under acidic conditions,
 258 the coordination mode of chromium(III) to NOM is very similar to that of iron(III).²⁷⁻²⁸

259 At higher pH (> 5) the EXAFS model fit (which included SS Cr^{III}-C and MS Cr-O-C paths)
 260 needed to be complemented by SS Cr^{III}-Cr paths to provide acceptable descriptions to the data
 261 (Table 1). For all three such samples, a half-path length of ~2.98 Å was detected and
 262 attributed to a Cr^{III}-Cr interaction. For one of the samples, the SRFA sample at pH 5.5, a
 263 second half-path length could be identified at 3.57 Å. The WT analysis confirmed these
 264 results. In the WT plots, Cr^{III}-Cr interactions caused an envelope maximum at $k \sim 7 \text{ Å}^{-1}$ and at
 265 $R + \Delta R \sim 2.5 \text{ Å}$, which could be reproduced well in the model when the half-path Cr^{III}-Cr

length of ~ 2.98 Å was included. The signal was nearly absent from low-pH samples (Figure 3, Figure S2) but increased with higher pH values. In the SRFA pH 5.5 sample, the backscattering signal was greatest and extended beyond $R + \Delta R = 2.5$ Å, which was reproduced well when including also the second half-path Cr···Cr length at 3.57 Å.

Because simulations with Visual MINTEQ showed both the SRFA and soil systems to be at least three magnitudes undersaturated with respect to $\text{Cr}(\text{OH})_3(\text{s})$ under the experimental conditions,²⁹ the results at high pH are not easily explained by precipitation of a $\text{Cr}(\text{OH})_3$ -type mineral. However, the modeled Cr···Cr path parameters can be compared favorably to those of the dimer $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ and the tetramer $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$. As is shown in Table 1, these species also contain Cr···Cr interactions with half-path lengths of 2.98 Å and the latter also at 3.57 Å. Such half-path lengths can be attributed to the existence of di- or tetramers linked by double and single hydroxo bridges (c.f. Supporting Information). The soil samples at pH 5.5 did not contain any significant contribution from the 3.57 Å Cr···Cr path. This may indicate the predominance of dimers in these samples; however, the contribution of the long Cr···Cr path to the overall EXAFS signal is small, and therefore it is possible that the data quality did not permit the identification of such a Cr···Cr interaction.

It is not possible to determine the mean number of organic ligands binding to chromium(III). We have set this number to two based on results obtained for iron(III)-organic matter complexes,³⁰ as a refinement will anyhow give a very uncertain value. Furthermore, the mean Cr-O-C angle of ca. 125° is within the observed range for carboxylate-chromium(III) complexes in solid state, 120 - 135° .³¹

The EXAFS results show that polynuclear chromium(III)-organic complexes, consisting of di- and/or tetramers, are important at higher pH (at least at $\text{pH} > 5$). This is a different situation to the one for iron(III), for which polynuclear complexes have been absent from most studies except for a few.²⁸ One possible explanation is the high stability of cationic chromium(III)

hydroxo complexes relative to those of iron(III), which permits polynuclear chromium(III) complexes to be stable over a wide range of conditions, whereas iron(III) (hydr)oxides precipitate under similar conditions. However, at low pH and especially at low equilibrium chromium(III) concentrations (typical for many acidic organic soils), monomeric chromium(III)-organic complexes are still likely to predominate.

Equilibrium modeling. In agreement with the EXAFS results, two chromium(III)-organic complexes were defined (Table S3); one monomeric complex $(\text{RO})_2\text{Cr}^+$ bound bidentately to NOM, and one dimeric complex $(\text{RO})_3\text{Cr}_2(\text{OH})_2^+$ in which three carboxylic or phenolic acid groups are involved. This is likely an oversimplification (for example, there may be additional complexes such as hydroxylated monomeric complexes and tetrameric chromium(III) species), but the model can be refined as additional data becomes available.

To provide estimates of the ‘active’ HA and FA concentrations in the soil suspension, these were changed by trial-and-error until the model-calculated pH values were in agreement with the measured ones; the final fit (with an RMSE value of 0.13) is seen in Figure S3.

Dissolved chromium as a function of pH is shown in Figure 4. The data shown represents data collected after 90 d of equilibration; this should have led to equilibrium for all samples except possibly for the one at the lowest pH in the $1000 \mu\text{mol L}^{-1}$ Cr(III) data set. We assumed that this data point was sufficiently close to equilibrium to be included in the modeling. The results show that chromium(III) was strongly bound to the soil. Significant amounts of dissolved chromium were measured only at the lowest pH value. Already at pH 3.07 >98 % of the added chromium(III) was bound after adding $1000 \mu\text{mol L}^{-1}$. Also, the effect of competing Al^{3+} ions was rather small. Addition of $1000 \mu\text{mol L}^{-1}$ Al increased dissolved chromium from 4 to $10 \mu\text{mol L}^{-1}$ (out of $100 \mu\text{mol L}^{-1}$ added) at pH 2.3. Further, a minimum concentration of

dissolved chromium occurred at around pH 3.5. Above this pH value, dissolved chromium increased again, because of the increased dissolution of NOM (Figure 4).

The batch experiment data could be reasonably well explained with a model in which the monomeric complex predominated at low pH, particularly at low equilibrium concentrations of chromium(III) (Figure 5), whereas the dimeric complex $(RO)_3Cr_2(OH)_2^+$ dominated at higher pH. Organically bound chromium(III) predominated also in the dissolved phase, except at the lowest pH (Figure S4). Moreover the optimum value of the heterogeneity parameter ΔLK_2 was found to be 1.0, which is close to the one found for Al(III) (1.06).³² The optimized model is qualitatively in agreement with the EXAFS interpretation (Figure 5). However, the optimum value of the binding constant for the dimeric complex is uncertain, as the Cr(III) concentration in solution at high pH is governed primarily by the partitioning between dissolved and solid organic matter. Moreover, the goodness-of-fit was $RMSE = 0.16$ in $\log [Cr]$. This relatively high value is heavily impacted by the poor prediction of dissolved chromium at the highest pH (6.7) in the $100 \mu\text{mol L}^{-1}$ chromium(III) data set (removing this data point from the optimization gives an RMSE of 0.10). The reason for the poor description of this data point is not known; mobilization of chromium(III)-rich organic colloids to the water phase is one possible reason.

The value of the SHM equilibrium constant for the monomeric complex $(RO)_2Cr^+$ can be compared to those of the equivalent complexes for aluminum(III) and iron(III), $(RO)_2Al^+$ and $(RO)_2Fe^+$. The equilibrium constant for $(RO)_2Cr^+$ was defined based on the $Cr(OH)_2^+$ component, as required by Visual MINTEQ. After recalculation of the value when having Cr^{3+} as a component ($\log \beta = 9.84$),²⁹ $\log K_{Cr,b} = -2.34$. This means that the chromium(III) affinity to NOM is intermediate between that of aluminum(III) ($\log K_{Al,b} = -4.06$) and that of

iron(III)) ($\log K_{\text{Fe,b}} = -1.68$). This agrees rather well with the relationship between the first-hydrolysis constants ($\log K_{\text{MOH}} = -2.02$ for Fe(III), -3.57 for Cr(III) and -5.00 for Al(III)). Further, the optimized equilibrium constant for $(\text{RO})_2\text{Cr}^+$ is much larger than the one previously used in the SHM ($\log K_{\text{Cr,b}} = -3.75$ when using Cr^{3+} as a component), derived from the study of Fukushima et al.⁸ When accounting for the likely presence of a di- or tetrameric species the optimized $\log K_{\text{Cr,b}}$ the difference would be even greater. This will affect geochemical modeling calculations for chromium(III) considerably. We do not know the reason for this difference. Different origin of samples might be one explanation for the difference in results. Fukushima et al.⁸ used an isolated peat HA. Another explanation for the lower binding affinity is the short equilibration time used (30 h), which could have resulted in a pseudo-equilibrium situation.

Outlook. This study advances the understanding of chromium(III) binding to NOM. However, to arrive at reliable complexation constants for organic complexation models such as SHM, NICA-Donnan and WHAM-Model VII, we recommend additional studies under different reaction conditions. In such experiments it is important to consider the slow reaction kinetics of chromium(III), especially of the hydrated $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ion, which requires very long equilibration times.

ACKNOWLEDGMENTS

The study was founded by the Swedish Research Council (Vetenskapsrådet) (number 2008-4354). Portions of this research were carried out at beamline I811, MAX-lab Lund University, Sweden. Funding for the beamline I811 was kindly provided by The Swedish Research

Council and The Knut och Alice Wallenbergs Stiftelse. We thank Mirsada Kulenovic for skilful help at the laboratory and MAX-lab for beam time and help from the staff.

ASSOCIATED CONTENT

Supporting information

Coordination chemistry of chromium(III), metal complexation in the Stockholm Humic Model, initial concentrations in the soil suspensions (Table S1), inorganic equilibrium reactions for chromium(III) in Visual MINTEQ (Table S2), cation complexation reactions to soil organic matter in the Stockholm Humic Model (Table S3), dissolved organic C in soil suspensions (Figure S1), high resolution WT modulus for the second coordination shell (Figure S2), the pH as a function of the base-acid added (Figure S3), modeled speciation of dissolved chromium(III) (Figure S4). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

REFERENCES

- (1) James, B.R. The challenge of remediating chromium-contaminated soil. *Environ. Sci. Technol.* **1996**, 30 (6), 248A-251A.
- (2) Torapava, N.; Radkevich, A.; Davydov, D.; Titova, A.; Persson, I. Composition and structure of polynuclear chromium(III) hydroxo complexes. *Inorg. Chem.* **2009**, 48 (21), 10383-10388.
- (3) Wittbrodt, P.R.; Palmer, C.D. Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances. *Environ. Sci. Technol.* **1996**, 30 (8), 2470-2477.

- (4) Tipping, E.; Lofts, S.; Sonke, J.E. Humic ion binding Model VII: a revised parameterisation of cation-binding by humic substances. *Environ. Chem.* **2011**, 8 (3), 225-235.
- (5) Kinniburgh, D.G.; van Riemsdijk, W.H.; Koopal, L.K.; Borkovec, M.; Benedetti, M.F.; Avena, M.J. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry, and thermodynamic consistency. *Colloid Surf.* **1999**, A151 (1-2), 147-166.
- (6) Gustafsson, J.P. Modeling the acid-base properties and metal complexation of humic substances with the Stockholm Humic Model. *J. Colloid Interface Sci.* **2001**, 244 (1), 102-112.
- (7) Milne, C.J.; Kinniburgh, D.G.; van Riemsdijk, W.H.; Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **2003**, 37 (5), 958-971.
- (8) Fukushima, M.; Nakayasu, K.; Tanaka, S.; Nakamura, H. Chromium(III) binding abilities of humic acids. *Anal. Chim. Acta* **1995**, 317 (1-3), 195-206.
- (9) Khai, N.M.; Öborn, I.; Hillier, S.; Gustafsson, J.P. Modeling of metal binding in tropical Fluvisols and Acrisols treated with biosolids and wastewater. *Chemosphere* **2008**, 70 (8), 1338-1346.
- (10) Groenenberg, J.E.; Dijkstra, J.J.; Bonten, L.T.C.; de Vries, W.; Comans, R.N.J. Evaluation of the performance and limitations of empirical partition-relations and process-based multisurface models to predict trace element solubility in soils. *Environ. Poll.* **2012**, 166, 98-107.
- (11) Ritchie, J.D.; Purdue, E.M. Proton-binding study of standard and reference fulvic acids, humic acids and natural organic matter. *Geochim. Cosmochim. Acta* **2003**, 67 (1), 85-96.
- (12) Gustafsson, J.P.; van Schaik, J.W.J. Cation binding in a mor layer: batch experiments and modelling. *Eur. J. Soil Sci.* **2003**, 54 (2), 295-310.

- (13) Gustafsson, J.P.; Persson, I.; Kleja, D.B.; van Schaik, J.W.J. Binding of iron(III) to organic soils: EXAFS spectroscopy and chemical equilibrium modeling. *Environ. Sci. Technol.* **2007**, *41* (4), 1232-1237.
- (14) Thompson, A.; Attwood, D.; Gullikson, E.; Howells, M.; Kim, K.-J.; Kirz, J.; Kortright, J.; Lindau, I.; Pianetta, P.; Robinson, A.; Scofield, J.; Underwood, J.; Williams, G.; Winck, H. *X-ray Data Booklet*. Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, 2009.
- (15) George, G.N.; Pickering, I.J. *EXAFSPAK - A Suite of Computer Programs for Analysis of X-ray Absorption Spectra*, SSRL, Stanford, CA, 1993.
- (16) Filipponi, A.; Di Cicco, A. X-ray-absorption spectroscopy and n-body distribution functions in condensed matter. II. Data analysis and applications. *Phys. Rev. B: Condens. Matter* **1995**, *52* (21), 15135-15149.
- (17) Filipponi, A.; Di Cicco, A.; Natoli, C. R. X-ray-absorption spectroscopy and n-body distribution functions in condensed matter. I. Theory. *Phys. Rev. B: Condens. Matter* **1995**, *52* (21), 15122-15134.
- (18) Hedin, L.; Lundqvist, B. I. Explicit local exchange-correlation potentials. *J. Phys. C: Solid State Phys.* **1971**, *4* (14), 2064.
- (19) Filipponi, A. The radial distribution function probed by X-ray absorption spectroscopy. *J. Phys. Condensed Mat.* **1994**, *6* (41), 8415-8427.
- (20) Kleja, D.B.; van Schaik, J.W.J.; Persson, I.; Gustafsson, J.P. Characterization of iron in floating surface films of some natural waters using EXAFS. *Chem. Geol.* **2012**, *326-327*, 19-26.
- (21) Funke H.; Scheinost A.C. ; Chukalina M. Wavelet analysis of extended x-ray absorption fine structure data. *Phys. Rev. B* **2005**, *71* (9), 094110.
- (22) Chukalina M. Wavelet2.ipf, a procedure for calculating the Wavelet transform in IGOR Pro.
<http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM20/Software/Wavelets/IG>

[OR](#). Grenoble, France, 2010.

- (23) Gustafsson, J.P., 2013. Visual MINTEQ version 3.1.
<http://www2.lwr.kth.se/English/OurSoftware/vminteq/index.html>. Stockholm, Sweden, February 2013.
- (24) Smith, R.M.; Martell, A.E.; Motekaitis, R.J. *NIST Critically Selected Stability Constants of Metal Complexes Database. Version 7.0*. NIST Standard Reference Database 46. National Institute of Standards and Technology, US Department of Commerce, Gaithersburg, VA, 2003.
- (25) Gustafsson, J.P.; Kleja, D.B. Modeling salt-dependent proton binding by organic soils with the NICA-Donnan and Stockholm Humic models. *Environ. Sci. Technol.* **2005**, *39* (14), 5372-5377.
- (26) Lindqvist-Reis, P.; Díaz-Moreno, S.; Munoz-Páez, A.; Pattanaik, S.; Persson, I.; Sandström, M. On the structure of the hydrated gallium(III), indium(III) and chromium(III) ions in aqueous solutions. A large angle X-ray scattering and EXAFS study. *Inorg. Chem.* **1998**, *37* (26), 6675-6683.
- (27) Karlsson, T.; Persson, P. Complexes with aquatic organic matter suppress hydrolysis and precipitation of Fe(III). *Chem. Geol.* **2012**, *322-323*, 19–27.
- (28) Sjöstedt, C.; Persson, I.; Hesterberg, D.; Kleja, D.B., Borg, H., Gustafsson, J.P. Iron speciation in soft-water lakes and soils as determined by EXAFS spectroscopy and geochemical modelling. *Geochim. Cosmochim. Acta* **2013**, *105*, 172–186.
- (29) Ball, J.W.; Nordstrom, D.K. Critical evaluation and selection of standard state thermodynamic properties for chromium metal, its aqueous ions, hydrolysis species, oxides and hydroxides. *J. Chem. Eng. Data* **1998**, *43* (6), 895-918.
- (30) Karlsson, T., Persson, P. Coordination chemistry and hydrolysis of iron(III) in a peat humic acid studied by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **2010**, *74* (1), 30-40.
- (31) Allen, F. The Cambridge structural database. A quarter of a million crystal structures and

- rising. *Acta Crystallogr. Sect. B.* **2002**, 58, 380-388.
- (32) Gustafsson, J.P.; Tiberg, C.; Edkymish, A.; Kleja, D.B. Modelling lead(II) adsorption to ferrihydrite and soil organic matter. *Environ. Chem.* **2011**, 8 (5), 485-492.

378

379

380 **Table 1. Fitting Parameters of the EXAFS Spectra for Cr(III) Bound to Suwanee River**
381 **Fulvic Acid (SRFA) and to Soil at Room Temperature^a.**

Sample	Interaction	CN	$R / \text{\AA}$	$\sigma^2 / \text{\AA}^2$	S_o^2	$\Delta E / \text{eV}$	F
Cr ₄ (OH) ₆ (H ₂ O) ₁₂ ⁶⁺ pH 3.7 ^b	Cr-O	6	1.970(2)	0.0044(2)	0.87(1)	-3.2(1)	9.83
	MS (CrO ₆)	3×6	3.892(8)	0.012(2)			
	Cr···Cr	0.5	2.982(3)	0.0029(2)			
	Cr···Cr	2	3.591(4)	0.0080(4)			
SRFA pH 2.1	Cr-O	6	1.977(1)	0.0020(1)	0.74(1)	-2.9(2)	13.9
	MS (CrO ₆)	3×6	3.984(8)	0.0061(12)			
	Cr···C	2	2.842(13)	0.008(2)			
	Cr-O-C	4	3.05(3)	0.012(5)			
SRFA pH 3.6	Cr-O	6	1.977(1)	0.0021(1)	0.89(1)	-2.7(2)	14.5
	MS (CrO ₆)	3×6	3.977(7)	0.0057(12)			
	Cr···C	2	2.859(9)	0.011(3)			
	Cr-O-C	4	3.07(2)	0.014(5)			
SRFA pH 5.5	Cr-O	6	1.975(1)	0.0024(1)	0.88(2)	-4.8(3)	17.3
	MS (CrO ₆)	3×6	3.89(2)	0.012(4)			
	Cr···Cr	0.5	2.998(11)	0.004(1)			
	Cr···Cr	2	3.575(11)	0.009(1)			
	Cr···C	2	2.85(2)	0.008(1)			
	Cr-O-C	4	3.07(2)	0.012(2)			
Soil 47 d pH 3.0	Cr-O	6	1.973(1)	0.0012(1)	0.78(1)	-3.7(2)	15.2
	MS (CrO ₆)	3×6	3.951(5)	0.0033(5)			
	Cr···C	2	2.850(12)	0.0080(1)			
	Cr-O-C	4	3.05(2)	0.007(2)			
Soil 53 d pH 2.5	Cr-O	6	1.999(1)	0.0027(1)	0.78(2)	-1.0(2)	17.3
	MS (CrO ₆)	3×6	4.01(1)	0.007(2)			
	Cr···C	2	2.834(11)	0.006(2)			
	Cr-O-C	4	3.03(3)	0.008(4)			
Soil 53 d pH 5.6	Cr-O	6	1.974(1)	0.0029(2)	0.85(2)	-4.2(3)	13.0
	MS (CrO ₆)	3×6	3.96(2)	0.010(4)			
	Cr···Cr	1	2.947(7)	0.0063(6)			

	Cr...C	2	2.85(2)	0.007(1)			
	Cr-O-C	4	3.06(2)	0.011(2)			
Soil 192 d	Cr-O	6	1.964(1)	0.0014(1)	0.79(1)	-5.6(2)	15.0
pH 2.4	MS (CrO ₆)	3×6	3.933(8)	0.0022(8)			
	Cr...C	2	2.86(1)	0.004(2)			
	Cr-O-C	4	3.05(2)	0.007(2)			
Soil 192 d	Cr-O	6	1.978(2)	0.0015(4)	0.73(2)	-3.8(3)	13.1
pH 5.5	MS (CrO ₆)	3×6	3.976(11)	0.0054(16)			
	Cr...Cr	1	2.98(1)	0.004(1)			
	Cr...C	2	2.87(2)	0.009(3)			
	Cr-O-C	4	3.06(2)	0.014(3)			

^aCN = coordination number, R = mean half-path length, σ^2 = Debye-Waller factor, S_o^2 = amplitude reduction factor, ΔE = fitted energy-shift parameter, F = goodness-of-fit parameter in EXAFSPAK.¹⁵

^bData from Torapava et al.²

Figures

Figure 1. Dissolved chromium in soil suspensions as a function of time and pH level after initial additions of 100 and 1000 $\mu\text{mol Cr(III) L}^{-1}$.

Figure 2. Left: stacked k^3 -weighted K -edge EXAFS spectra for chromium for (a) $\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}^{6+}$ in water, (b) SRFA at pH 2.1, (c) SRFA at pH 3.6, (d) SRFA at pH 5.5, (e) soil at pH 3, 47 d, (f) soil at pH 2.5, 53 d, (g) soil at pH 5.6, 53 d, (h) soil at pH 2.4, 192 d, and (i) soil at pH 5.6, 192 d. Lines are raw data and dashed lines are best fits. Right: Fourier Transforms (FT magnitudes) of the k^3 -weighted EXAFS spectra. Lines are raw data and dashed lines are best fits. The vertical dotted line highlight the Cr-O distance as found by EXAFS analysis.

Figure 3. High resolution Morlet WT modulus for the second coordination shell ($\kappa = 6$, $\sigma = 1$, k -range 2.0-11.0 $\text{\AA}^{-1}$) for pretreated and normalized raw EXAFS spectra (left column) and modeled EXAFS spectra (right column) with the fitting parameters given in Table 1.

Figure 4. Dissolved chromium (left) and dissolved organic C (right) as a function of pH in the Risbergshöjden soil suspensions. Points are observations and lines are model fits with the SHM.

Figure 5. Calculated chromium(III) speciation as a function of pH in the Risbergshöjden soil suspensions after addition of 100 $\mu\text{mol Cr(III) L}^{-1}$ (left) or 1000 $\mu\text{mol Cr(III) L}^{-1}$ (right). The lines are model fits with the SHM. The lower thick line separates the sorbed from the dissolved phases, whereas the upper thick line represents the final Cr(III) concentration after additions (98.5 and 984 $\mu\text{mol Cr(III) L}^{-1}$ respectively).

TOC / ABSTRACT ART

Chromium(III) complexation to natural organic matter: mechanisms and modeling

J.P. Gustafsson, I. Persson, A.G. Oromieh, J.W.J. van Schaik, C. Sjöstedt, D.B. Kleja

Supporting information

Number of pages: 12

Contents

Coordination chemistry of chromium(III) (text)

The slow water exchange of chromium(III) (text)

Equations describing metal complexation in the Stockholm Humic model (text)

Table S1. Initial concentrations in the soil suspensions

Table S2. Inorganic equilibrium reactions for chromium(III) in Visual MINTEQ

Table S3. Cation complexation reactions to soil organic matter in the Stockholm Humic Model

Figure S1. Dissolved organic C in soil suspensions

Figure S2. High resolution WT modulus for the second coordination shell

Figure S3. The pH as a function of the base-acid added

Figure S4. Modeled speciation of dissolved chromium(III)

References

Coordination chemistry of chromium(III)

Chromium(III) maintains six-coordination in octahedral fashion in almost all hydrolysis complexes studied in the solid state. The coordination chemistry of hydrolyzed chromium(III) in the solid state is strongly dominated by two types of complexes, a dimeric with a double hydroxo bridge, and a trimeric with three chromium(III) binding to a single oxo group.¹ These types are easy to distinguish from EXAFS studies as the mean Cr····Cr distances are significantly different, 2.98 and 3.30 Å, respectively. However, additional types of hydrolysis complexes are reported. Dimeric complexes with a single oxo bridge ($d(\text{Cr}\cdots\text{Cr})=3.60$ Å),²⁻⁸ as well as triple hydroxo bridges ($d(\text{Cr}\cdots\text{Cr})=2.67$ Å).⁹⁻¹⁴ There are also examples where dimeric complexes with a single and additionally two carboxylate groups bridging the chromium(III) ions,¹⁵⁻¹⁸ or double hydro bridge with an additional carboxylate group bridging the chromium(III) ions.¹⁹⁻²⁰ This causes a slight shortening to 3.50 and 2.90 Å, respectively. A type of complex of particular interest is tetrameric with one double and four single hydroxo bridges. Both a complex with only water as additional ligands,²¹ as well as organic ligand,²² are reported. Only one trimeric complex with one double and two single hydroxo bridges is reported indicating this kind of complex to be less stable than the corresponding dimers and tetramers. This shows that hydrolyzed chromium(III) has a good ability to bind different kind of organic ligands including carboxylates, phenolates, amino acids and amines, common in DOM, as also found in this study of natural samples. The trimeric complex with a single oxo group has not yet been observed in natural samples, while the corresponding iron(III) complexes have been reported occasionally.²³⁻²⁴ The probable reason is that iron(III) is more easily hydrolyzed than chromium(III), pK_a values of 2.5 and 3.5, respectively, and that trimeric complexes with a single oxo group require higher pH to form than the hydroxo complexes.

The slow water exchange of chromium(III)

The hydrated chromium(III) ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, is known for its kinetic inertness of water exchange, $k=2.36\cdot 10^{-6}$ s⁻¹, $t_{1/2}=81.6$ h, while the water exchange rate of the $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ complex is ca. 75 times faster, $k=1.78\cdot 10^{-4}$ s⁻¹, $t_{1/2}=1.08$ h, at 298.15 K.²⁵ The water exchange of the hydrolyzed dimeric complex, $[(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$, is even faster, $k=3.6\cdot 10^{-4}$ s⁻¹, $t_{1/2}=0.53$ h.²⁶ This shows that kinetics of chromium(III) accelerate with increasing number of hydroxo groups bound in comparison to the hydrated chromium(III) ion. However, the reactions are still very slow and a long time is required before a true equilibrium is reached.

Equations describing metal complexation in the Stockholm Humic model

The SHM allows metals to bind as monodentate, bidentate or tridentate complexes. The following reaction shows the formation of a monodentate complex involving a divalent metal ion M^{2+} :

The equilibrium constant $K_{M,m}$ is defined according to:

$$K_{Ca,m} = \frac{\{ROM^+\}\{H^+\}}{\{ROH\}\{M^{2+}\}} \cdot \exp\left(-g_f \cdot \frac{F(0.5\Psi_o - 1.5\Psi_d)}{RT}\right) \quad (2)$$

where g_f is the so-called gel-fraction parameter, whereas F is the Faraday constant, R is the gas constant, T is the absolute temperature, and Ψ_o and Ψ_d are electrostatic potentials in the o - and d -planes, respectively.²⁷ The relative contributions of o - and d -plane charge for the complexes considered are shown in Table S2. To account for heterogeneity of site affinity for metal complexation the parameter ΔLK_2 is introduced:

$$\log K_{M,m,x} = \log K_{M,m} + x \cdot \Delta LK_2, \quad x = 0, 1, 2 \quad (3)$$

This allows each site to be subdivided into three subsites with differing affinity for metal-humic complexation; x is set to 0 for 90.1 % of the sites, to 1 for 9 % and to 2 for 0.9 %. Monodentate complexes can be formed with proton sites 1, 2, 3, 4, *i.e.* with the carboxylic acid sites.²³ When the metal binds to two surface sites, a bidentate complex is formed. For aluminium(III), the reaction is described as follows:

$$K_{Al,b} = \frac{\{(RO)_2Al^+\}\{H^+\}^2}{\{ROH\}^2\{Al^{3+}\}} \cdot \exp\left(-g_f \cdot \frac{F(-0.2\Psi_o + 1.2\Psi_d)}{RT}\right) \cdot S_{bid} \quad (5)$$

$$\log K_{Al,b,x} = \log K_{Al,b} + 2x \cdot \Delta LK_2, \quad x = 0, 1, 2 \quad (6)$$

The extra term S_{bid} is used to correct the constant for the bidentate coordination.²⁸ This correction is done automatically in the Visual MINTEQ software. Bidentate complexes may involve both carboxylate and phenolate sites; the combinations of proton-binding sites used in

the SHM were detailed in Gustafsson et al.²³ A bidentate complex similar to that for aluminium(III) was considered also for chromium(III), see Table S2.

Tridentate complexes are defined in a similar fashion. As the EXAFS results indicated that an organically bound di- or polymeric chromium(III) species was important at high pH, we assumed that this could be reflected in the model by a $\text{Cr}_2(\text{OH})_2^+$ dimer that formed a tridentate complex. The reaction is written as follows:

$$K_{\text{Cr,t}} = \frac{\{(\text{RO})_3\text{Cr}_2(\text{OH})_2^+\} \{\text{H}^+\}}{\{\text{ROH}\}^3 \{\text{Cr}(\text{OH})_2^+\}^2} \cdot \exp\left(-g_f \cdot \frac{F(0.2\Psi_o + 0.8\Psi_d)}{RT}\right) \cdot S_{\text{trid}} \quad (8)$$

$$\log K_{\text{Cr,t,x}} = \log K_{\text{Cr,t}} + 3x \cdot \Delta LK_2, \quad x = 0, 1, 2 \quad (9)$$

where S_{trid} comprise terms needed to correct the constant for tridentate coordination;²⁸ again this correction is carried out automatically in Visual MINTEQ. Also, the combinations of proton-binding sites used in the SHM for tridentate complexes were detailed in Gustafsson et al.²³

Note that the assignment of bidentate and tridentate complexes in the SHM does not necessarily mean that the structure of the complexes are in reality bidentate or tridentate. This is because the modeling results are sensitive to the proton exchange stoichiometry but are usually not much dependent on the actual number of ROH groups in equations 4 and 7.

Table S1. Initial Concentrations in the Soil Suspensions

Parameter ^a	Value
Active humic acid (g L ⁻¹)	1.935
Active fulvic acid (g L ⁻¹)	0.645
Ca ²⁺ (μmol L ⁻¹)	662
Mg ²⁺ (μmol L ⁻¹)	136
K ⁺ (μmol L ⁻¹)	120
Mn ²⁺ (μmol L ⁻¹)	31.5
Al ³⁺ (μmol L ⁻¹)	228
Fe ³⁺ (μmol L ⁻¹)	35
Cr(OH) ₂ ⁺ (μmol L ⁻¹)	0.02
Cu ²⁺ (μmol L ⁻¹)	0.63

^a For cations the concentrations shown are geochemically active concentrations before any additions. For extraction methods see text.

Table S2. Inorganic Equilibrium Reactions for Chromium(III) in Visual MINTEQ

Reaction	log <i>K</i> at 25°C	Δ <i>H</i> _r (kJ mol ⁻¹)
<i>Solution complexes</i>		
Cr(OH) ₂ ⁺ + 2H ⁺ ↔ Cr ³⁺ + 2H ₂ O	9.84 ^a	93.62 ^b
Cr(OH) ₂ ⁺ + H ⁺ ↔ CrOH ²⁺ + H ₂ O	6.27 ^a	41.91 ^b
Cr(OH) ₂ ⁺ + H ₂ O ↔ Cr(OH) ₃ (aq)	-6.35 ^a	n.a. ^c
Cr(OH) ₂ ⁺ + 2H ₂ O ↔ Cr(OH) ₄ ⁻	-17.81 ^a	n.a. ^c
2Cr(OH) ₂ ⁺ + 2H ⁺ ↔ Cr ₂ (OH) ₂ ⁴⁺ + 2H ₂ O	14.68 ^a	n.a. ^c
3Cr(OH) ₂ ⁺ + 2H ⁺ ↔ Cr ₃ (OH) ₄ ⁵⁺ + 2H ₂ O	18.77 ^a	n.a. ^c
Cr(OH) ₂ ⁺ + NO ₃ ⁻ + 2H ⁺ ↔ CrNO ₃ ⁺ + 2H ₂ O	8.21 ^d	65.4 ^d
<i>Solid phase</i>		
Cr(OH) ₃ (s) + H ⁺ ↔ Cr(OH) ₂ ⁺ + H ₂ O	-0.49 ^a	-16.9 ^a

^aBall and Nordstrom²⁹

^bNIST³⁰

^cNot available, set to 0 in the simulations

^dMINTEQA2 ver. 3.0³¹.

Table S3. Cation Complexation Reactions to Soil Organic Matter in the Stockholm Humic Model (SHM)^a

Reaction	$(\Delta z_0, \Delta z_1)^b$	$\log K$	ΔLK_2
$2\text{ROH} + \text{Al}^{3+} \leftrightarrow (\text{RO})_2\text{Al}^+ + 2\text{H}^+$	(-0.2,1.2)	-4.06	1.06
$2\text{ROH} + \text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow (\text{RO})_2\text{AlOH} + 3\text{H}^+$	(-0.2,0.2)	-9.45	1.06
$\text{ROH} + \text{Ca}^{2+} \leftrightarrow \text{ROCa}^+ + \text{H}^+$	(-0.5,1.5)	-2.2	0.3
$2\text{ROH} + \text{Cr}(\text{OH})_2^+ \leftrightarrow (\text{RO})_2\text{Cr}^+ + 2\text{H}_2\text{O}$	(-0.2,1.2)	7.5	1.0
$3\text{ROH} + 2\text{Cr}(\text{OH})_2^+ \leftrightarrow (\text{RO})_3\text{Cr}_2(\text{OH})_2^+ + \text{H}^+ + 2\text{H}_2\text{O}$	(0.2,0.8)	12.2	1.0
$2\text{ROH} + \text{Fe}^{3+} \leftrightarrow (\text{RO})_2\text{Fe}^+ + 2\text{H}^+$	(-0.2,1.2)	-1.68	1.7
$2\text{ROH} + \text{Fe}^{3+} + \text{H}_2\text{O} \leftrightarrow (\text{RO})_2\text{FeOH} + 3\text{H}^+$	(-0.2,0.2)	-4.6	1.7
$\text{ROH} + \text{Mg}^{2+} \leftrightarrow \text{ROMg}^+ + \text{H}^+$	(-0.5,1.5)	-2.5	0.3

^aReactions for Ca^{2+} and Mg^{2+} are from Gustafsson *et al.*²³, those for Fe^{3+} are from Sjöstedt *et al.*³², those for Al^{3+} are from Gustafsson *et al.*³³, and those for $\text{Cr}(\text{OH})_2^+$ are from this study.

^bThe change of charge in the *o*-, and *d*-planes respectively.

Figure S1. Dissolved organic C in soil suspensions as a function of time and pH level after initial additions of 100 and 1000 μmol Cr(III) L⁻¹.

Figure S2. High resolution Morlet WT modulus for the second coordination shell ($\kappa = 6$, $\sigma = 1$, k -range 2.0-11.0 $\text{\AA}^{-1}$) for pretreated and normalized raw EXAFS spectra (left column) and modeled EXAFS spectra (right column) with the fitting parameters given in Table 1. The y axis is uncorrected for phase shift (~ 0.43 $\text{\AA}$).

Figure S3. The pH as a function of the base – acid added (as NaOH or as HNO₃) for the systems under study. The points are observations, and the lines are fits after optimization of the concentration of active humic and fulvic acid when using the final Cr(III) binding parameters of Table S2.

Figure S4. Modeled speciation of dissolved chromium(III) after initial additions of 100 (left) and 1000 $\mu\text{mol Cr(III) L}^{-1}$ (right). Black points connected by solid lines represent inorganic Cr(III) species, whereas red points connected by dashed lines are organically bound Cr(III) species. Only species present in concentrations above $10^{-15} \text{ mol L}^{-1}$ according to Visual MINTEQ were included in the figure.

References

- (1) Allen, F. H. The Cambridge Structural Database: a Quarter of a Million Crystal Structures and Rising. *Acta Crystallogr. Sect. B* **2002**, 58, 380–388.
- (2) Di Vaira, M.; Mani, F. Crystal and molecular structure of a dinuclear chromium(III) complex with a linear oxygen bridge. *Inorg. Chem.* **1984**, 23, 409–412.
- (3) MacLeod, K. C.; Patrick, B. O.; Smith, K.M. Reactivity of chromium μ -oxo compounds: catalyst regeneration and atom transfer processes. *Inorg. Chem.* **2012**, 51, 688–700.
- (4) Darensbourg, D. J.; Moncada, A. I.; Choi, W.; Reibenspies, J. H. J. Mechanistic studies of the copolymerization reaction of oxetane and carbon dioxide to provide aliphatic polycarbonates catalyzed by (sale)CrX complexes. *Am. Chem. Soc.* **2008**, 130, 6523–6533.
- (5) Gademann, K.; Chavez, D. E.; Jacobsen, E. N. Highly enantioselective inverse-electron-demand hetero-Diels-alder reactions of α - β unsaturated aldehydes. *Angew. Chem., Int. Ed.* **2002**, 41, 3059–3061.
- (6) Kaas, K. The crystal structure of Δ, Δ - μ -hydroxo-bis[bis(ethylenediamine)hydroxochromium(III)] triperchlorate monohydrate. *Acta Crystallogr., Sect. B* **1979**, 35, 1603–1607.
- (7) Glerup, J.; Weihe, H.; Goodson, P. A.; Hodgson, D. J. Structural and magnetic characterization of an adamantane-like complex ion of chromium(III) and 1,3,5-triaminocyclohexane, $[\text{Cr}_4(\text{tach})_4(\text{OH})_6]^{6+}$. *Inorg. Chim. Acta* **1993**, 212, 281–288.
- (8) Dean, R. K.; Granville, S. L.; Dawe, L. N.; Decken, A.; Hattenhauer, K. M.; Kozak, C. M. Structure and magnetic behaviour of mono- and bimetallic chromium(III) complexes of amine-bis(phenolate) ligands. *Dalton Trans.* **2010**, 39, 548–559.
- (9) Wieghardt, K.; Chaudhri, P.; Nuber, B.; Weiss, J. New triply hydroxo-bridged complexes of chromium(III), cobalt(III), and rhodium(III): crystal structure of tris- μ -hydroxo-bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] triiodide trihydrate. *Inorg. Chem.* **1982**, 21, 3086–3090.
- (10) Wieghardt, K.; Guttman, M.; Ventur, D.; Gebert, W. Z. Complexes of chromium containing 1,5,9-triazacyclododecane: Synthesis, magnetism, and crystal structure of tri- μ -hydroxo-bis[(1,5,9-triazacyclododecane) chromium (III)] tribromide · dihydrate; Kinetics and mechanisms of its bridge-cleavage with hydroxide. *Allg. Anorg. Chem.* **1985**, 527, 33–44.
- (11) Sugawara, K.; Hikichi, S.; Akita, M. A peroxochromium complex, $\text{Tp}^{\text{iPr}}_2\text{Cr}(\text{O}_2)_2$, obtained by oxidative dehydrative condensation between a dihydroxochromium complex and $\text{H}_2\text{O}_2[\text{Tp}^{\text{iPr}}_2 = \text{hydrotris}(3,5\text{-diisopropylpyrazolyl})\text{borato}]$. *Dalton Trans.* **2003**, 22, 4346–4355.
- (12) Glerup, J.; Larsen, S.; Weihe, H. Magnetism, spectroscopy and structure of tri- μ -hydroxobis{[N,N',N''-trimethyl-1,1,1-tris(aminomethyl)ethane]chromium(III)} chloride tetrahydrate. *Acta Chem. Scand.* **1993**, 47, 1154–1161.
- (13) Kalsbeek, N.; Larsen, S. Crystal structure of tri- μ -hydroxobis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] dithionate tetrahydrate. *Acta Chem. Scand.* **1999**, 53, 149–154.
- (14) Niemann, A.; Bossek, U.; Wieghardt, K.; Butzlaff, C.; Trautwein, A. X.; Nuber, B. A new structure–magnetism relationship for face-sharing transition-metal complexes with d^3 – d^3 electronic configuration. *Angew. Chem., Int. Ed.* **1992**, 31, 311–313.
- (15) Ciornea, V.; Shova, S.; Novitchi, G.; Ganzhu, D.; Kazheva, O. N.; Gulea, A.; Simonov, Y. A. Heterometallic Compounds with the Binuclear Complex Anion $[\text{Cr}_2(\text{OH})(\text{Ac})(\text{Nta})_2]^{2-}$: Synthesis and Structure. *Russ. J. Coord. Chem.* **2009**, 35, 817–823.
- (16) Andersen, N. H.; Dossing, A.; Molgaard, A. Synthesis, crystal structure, and magnetic properties of μ -hydroxo-bis[pentakis(acetonitrile)chromium(III)] tetrafluoroborate: An acetonitrile analogue

- to "acid rhodo". *Inorg. Chem.* **2003**, *42*, 6050-6055
- (17) Brudenell, S. J.; Crimp, S. J.; Higgs, J. K. E.; Moubaraki, B.; Murray, K. S.; Spiccia, L. Binuclear chromium(III) complexes bridged by hydroxide and acetate groups. *Inorg. Chim. Acta* **1996**, *247*, 35-41
 - (18) Ross, S.; Weyhermüller, T.; Bill, E.; Wieghardt, K.; Chaudhuri, P. (μ -hydroxo)bis(μ -acetato)dimetal complexes: structural and magnetochemical characterization of the Cr(III)Ni(II) and the Cr(III)Cr(III) species. *Inorg. Chim. Acta* **2002**, *339*, 71-76.
 - (19) Chen, X.Y.; Xia, J.; Zhao, B.; Cheng, P.; Yan, S.P.; Liao, D.Z.; Jiang, Z.H.; Song, H.B.; Wang, H.G. A macrocyclic chromium(III) complex with mixed hydroxo and carbonato bridges: crystal structure and magnetic properties of $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CO}_3)\text{Cr}(\text{tacn})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (tacn=1,4,7-triazacyclononane). *J. Coord. Chem.* **2004**, *57*, 231-237.
 - (20) Wieghardt, K.; Schmidt, W.; Van Eldik, R.; Nuber, B.; Weiss, J. Synthesis and kinetics of the decarboxylation of two carbonate-bridged complexes of chromium(III) and rhodium(III). Crystal structure of μ -carbonato-di- μ -hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] diiodide hydrate. *Inorg. Chem.* **1980**, *19*, 2922-2926.
 - (21) Drljaca, A.; Hardie, M. J.; Raston, C. L.; Spiccia, L. Self-assembled superanions: ionic capsules stabilized by polynuclear chromium(III) aqua cations. *Chem. Eur. J.* **1999**, *5*, 2295-2299.
 - (22) Flood, M. T.; Marsh, R. E.; Gray, H. B. J. Magnetism and structure of $[\text{Cr}_4(\text{OH})_6(\text{en})_6]^{6+}$ [hexakis(ethylenediamine)hexa- μ -hydroxytetrachromium(III) ion]. *Am. Chem. Soc.* **1969**, *91*, 193-194.
 - (23) Gustafsson, J. P.; Persson, I.; Berggren Kleja, D.; van Schaik, J. W. J. Binding of iron(III) to organic soils: EXAFS spectroscopy and chemical equilibrium modeling. *Environ. Sci. Technol.* **2007**, *41*, 1232-1237.
 - (24) Mikutta, C.; Kretzschmar, R. Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances. *Environ. Sci. Technol.* **2011**, *45*, 9550-9557.
 - (25) Xu, C.-F.; Krouse, H. R.; Swaddle, T. W. Conjugate base pathway for water exchange on aqueous chromium(III): variable-pressure and -temperature kinetic study. *Inorg. Chem.* **1985**, *24*, 267-270.
 - (26) Crimp, S. J.; Spiccia, L.; Krouse, H. R.; Swaddle, T. W. Early stages of the hydrolysis of chromium(III) in aqueous solution. 9. Kinetics of water exchange on the hydrolytic dimer. *Inorg. Chem.* **1994**, *33*, 465-470.
 - (27) Gustafsson, J.P. Modeling the acid-base properties and metal complexation of humic substances with the Stockholm Humic Model. *J. Colloid Interface Sci.* **2001**, *244* (1), 102-112.
 - (28) Venema, P.; Hiemstra, T.; van Riemsdijk, W.H. Multisite adsorption of cadmium on goethite. *J. Colloid Interface Sci.* **1996**, *183*, 515-527.
 - (29) Ball, J.W.; Nordstrom, D.K. Critical evaluation and selection of standard state thermodynamic properties for chromium metal, its aqueous ions, hydrolysis species, oxides and hydroxides. *J. Chem. Eng. Data* **1998**, *43* (6), 895-918.
 - (30) Smith, R.M.; Martell, A.E.; Motekaitis, R.J. *NIST Critically Selected Stability Constants of Metal Complexes Database. Version 7.0*. NIST Standard Reference Database 46. National Institute of Standards and Technology, US Department of Commerce, Gaithersburg, VA, 2003.
 - (31) Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J. *MINTEQA2/PRODEFA2, Geochemical assessment model for environmental systems: version 3.11 databases and version 3.0 user's manual*; Environmental Research Laboratory, U.S. Environmental Protection Agency: Athens, GA, 1991.
 - (32) Sjöstedt, C.; Persson, I.; Hesterberg, D.; Kleja, D.B.; Borg, H.; Gustafsson, J.P. Iron speciation in soft-water lakes and soils as determined by EXAFS spectroscopy and geochemical modelling.

Geochim. Cosmochim. Acta **2013**, *105*, 172–186.

- (33) Gustafsson, J.P.; Tiberg, C.; Edkymish, A.; Kleja, D.B. Modelling lead(II) adsorption to ferrihydrite and soil organic matter. *Environ. Chem.* **2011**, *8* (5), 485-492.