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

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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*(Cr····Cr)=3.60 Å),[2-8] as well as triple hydroxo bridges (*d*(Cr····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, [$Cr(H_2O)_6^{3+}$], is known for its kinetic inertness of water exchange, k=2.36·10^{-6} s^{-1}, t$_{½}$=81.6 h, while the water exchange rate of the [$Cr(OH)(H_2O)_5^{2+}$] complex is ca. 75 times faster, k=1.78·10^{-4} s^{-1}, t$_{½}$=1.08 h, at 298.15 K.[25] The water exchange of the hydrolyzed dimeric complex, [$(H_2O)_4Cr(OH)_2Cr(H_2O)_4$]$^{4+}$, is even faster, k=3.6·10^{-4} s^{-1}, t$_{½}$=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+}:

$$\mathrm{ROH} + \mathrm{M}^{2+} \rightleftarrows \mathrm{ROM}^{+} + \mathrm{H}^{+} \quad ; \quad K_{\mathrm{M,m}} \tag{1}$$

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

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

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:

$$\log K_{\mathrm{M,m,x}} = \log K_{\mathrm{M,m}} + x \cdot \Delta LK_2, \qquad x = 0, 1, 2 \tag{3}$$

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:

$$2\mathrm{ROH} + \mathrm{Al}^{3+} \rightleftarrows (\mathrm{RO})_2\mathrm{Al}^{+} + 2\mathrm{H}^{+} \quad ; \quad K_{\mathrm{Al,\,b}} \tag{4}$$

$$K_{\mathrm{Al,b}} = \frac{\{(\mathrm{RO})_2\mathrm{Al}^{+}\}\{\mathrm{H}^{+}\}^2}{\{\mathrm{ROH}\}^2\{\mathrm{Al}^{3+}\}} \cdot \exp\left(- g_f \cdot \frac{F(-0.2\Psi_o + 1.2\Psi_d)}{RT} \right) \cdot S_{bid} \tag{5}$$

$$\log K_{\mathrm{Al,b,x}} = \log K_{\mathrm{Al,b}} + 2x \cdot \Delta LK_2, \qquad x = 0, 1, 2 \tag{6}$$

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 $Cr_2(OH)_2^+$ dimer that formed a tridentate complex. The reaction is written as follows:

$$3\mathrm{ROH} + 2\mathrm{Cr(OH)_2^+} + 2\mathrm{H_2O} \rightleftarrows (\mathrm{RO})_3\mathrm{Cr_2(OH)_2^+} + \mathrm{H^+} + \mathrm{H_2O} \; ; \; K_{\mathrm{Cr,t}} \tag{7}$$

$$K_{\mathrm{Cr,t}} = \frac{\{(\mathrm{RO})_3\mathrm{Cr_2(OH)_2}^+\}\{\mathrm{H}^+\}}{\{\mathrm{ROH}\}^3\{\mathrm{Cr(OH)_2}^+\}^2} \cdot \exp\left(-g_f \cdot \frac{F(0.2\Psi_o + 0.8\Psi_d)}{RT}\right) \cdot S_{trid} \tag{8}$$

$$\log K_{\mathrm{Cr,t,x}} = \log K_{\mathrm{Cr,t}} + 3x \cdot \Delta LK_2, \qquad x = 0, 1, 2 \tag{9}$$

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 *K* at 25°C	ΔH_r (kJ mol^{-1})
Solution complexes		
$Cr(OH)_2^{+} + 2H^{+} \leftrightarrow Cr^{3+} + 2H_2O$	9.84[a]	93.62[b]
$Cr(OH)_2^{+} + H^{+} \leftrightarrow CrOH^{2+} + H_2O$	6.27[a]	41.91[b]
$Cr(OH)_2^{+} + H_2O \leftrightarrow Cr(OH)_3(aq)$	-6.35[a]	n.a.[c]
$Cr(OH)_2^{+} + 2H_2O \leftrightarrow Cr(OH)_4^{-}$	-17.81[a]	n.a.[c]
$2Cr(OH)_2^{+} + 2H^{+} \leftrightarrow Cr_2(OH)_2^{4+} + 2H_2O$	14.68[a]	n.a.[c]
$3Cr(OH)_2^{+} + 2H^{+} \leftrightarrow Cr_3(OH)_4^{5+} + 2H_2O$	18.77[a]	n.a.[c]
$Cr(OH)_2^{+} + NO_3^{-} + 2H^{+} \leftrightarrow CrNO_3^{+} + 2H_2O$	8.21[d]	65.4[d]
Solid phase		
$Cr(OH)_3(s) + H^{+} \leftrightarrow Cr(OH)_2^{+} + H_2O$	-0.49[a]	-16.9[a]

[a] Ball and Nordstrom[29]

[b] NIST[30]

[c] Not available, set to 0 in the simulations

[d] MINTEQA2 ver. 3.0[31].

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
$2ROH + Al^{3+} \leftrightarrow (RO)_2Al^{+} + 2H^{+}$	(-0.2,1.2)	-4.06	1.06
$2ROH + Al^{3+} + H_2O \leftrightarrow (RO)_2AlOH + 3H^{+}$	(-0.2,0.2)	-9.45	1.06
$ROH + Ca^{2+} \leftrightarrow ROCa^{+} + H^{+}$	(-0.5,1.5)	-2.2	0.3
$2ROH + Cr(OH)_2^{+} \leftrightarrow (RO)_2Cr^{+} + 2H_2O$	(-0.2,1.2)	7.5	1.0
$3ROH + 2Cr(OH)_2^{+} \leftrightarrow (RO)_3Cr_2(OH)_2^{+} + H^{+} + 2H_2O$	(0.2,0.8)	12.2	1.0
$2ROH + Fe^{3+} \leftrightarrow (RO)_2Fe^{+} + 2H^{+}$	(-0.2,1.2)	-1.68	1.7
$2ROH + Fe^{3+} + H_2O \leftrightarrow (RO)_2FeOH + 3H^{+}$	(-0.2,0.2)	-4.6	1.7
$ROH + Mg^{2+} \leftrightarrow ROMg^{+} + H^{+}$	(-0.5,1.5)	-2.5	0.3

[a] Reactions 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 $Cr(OH)_2^{+}$ are from this study.

[b] The change of charge in the *o*-, and *d*-planes respectively.

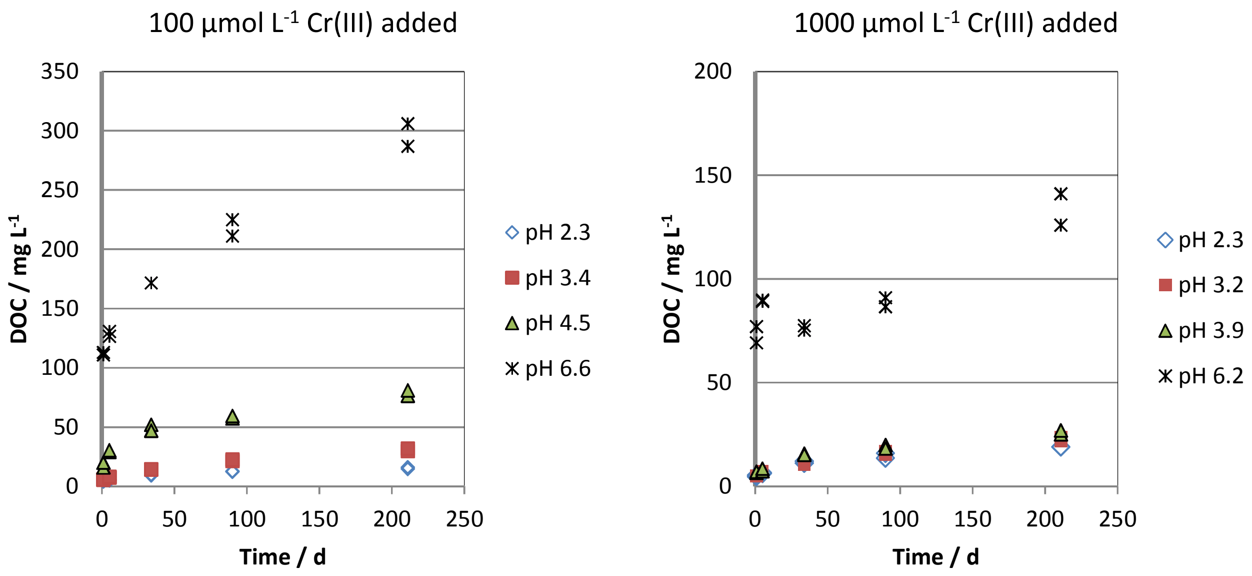

Figure S1. Dissolved organic C in soil suspensions as a function of time and pH level after initial additions of 100 and 1000 µmol Cr(III) L^{-1}.

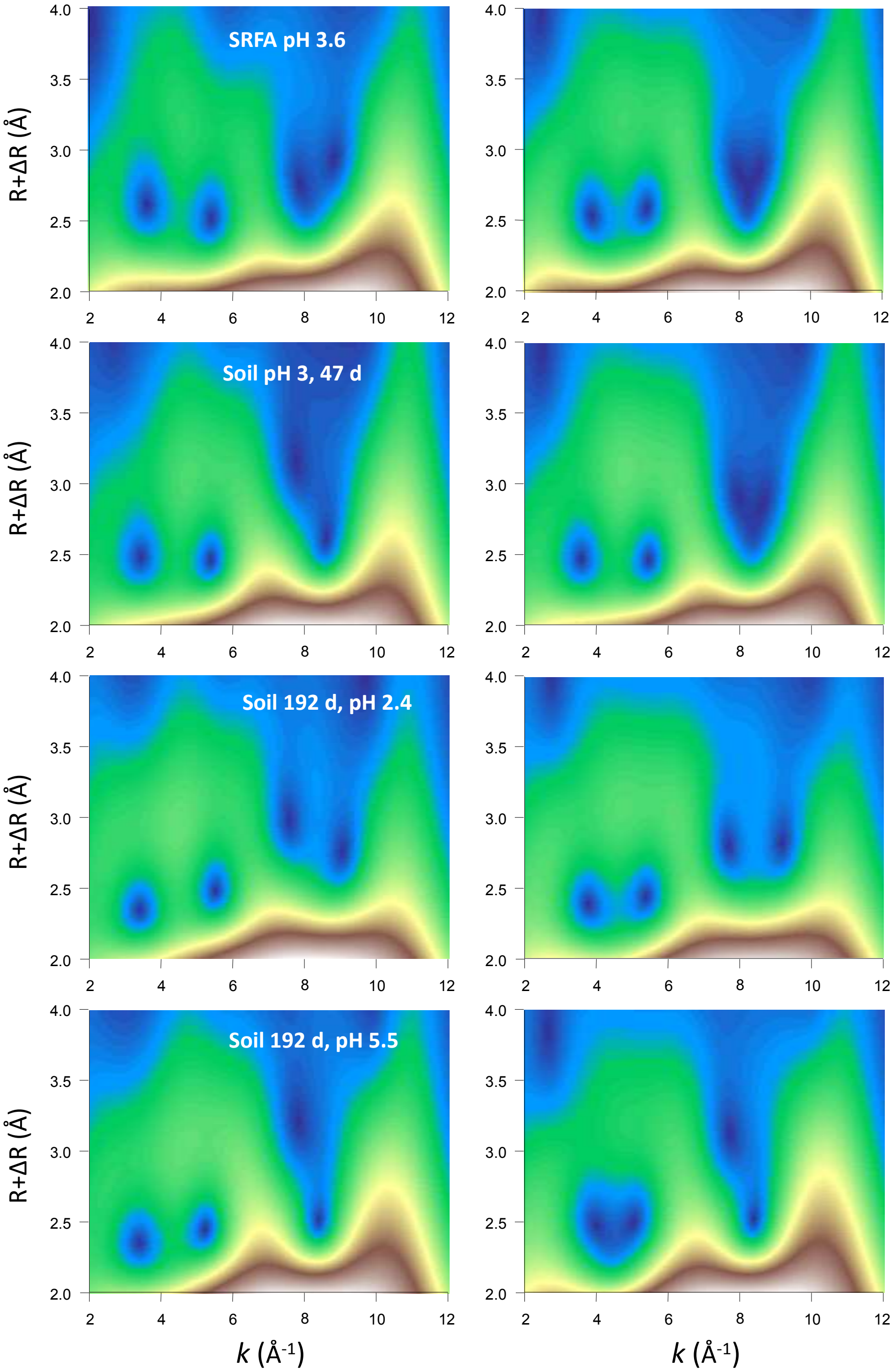

Figure S2. High resolution Morlet WT modulus for the second coordination shell (κ = 6, σ = 1, *k*-range 2.0-11.0 Å^{-1}) for pretreated and normalized raw EXAFS spectra (left column) and modeled EXAFS spectra (right column) with the fitting parameters given in Table 1. The y axis is uncorrected for phase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

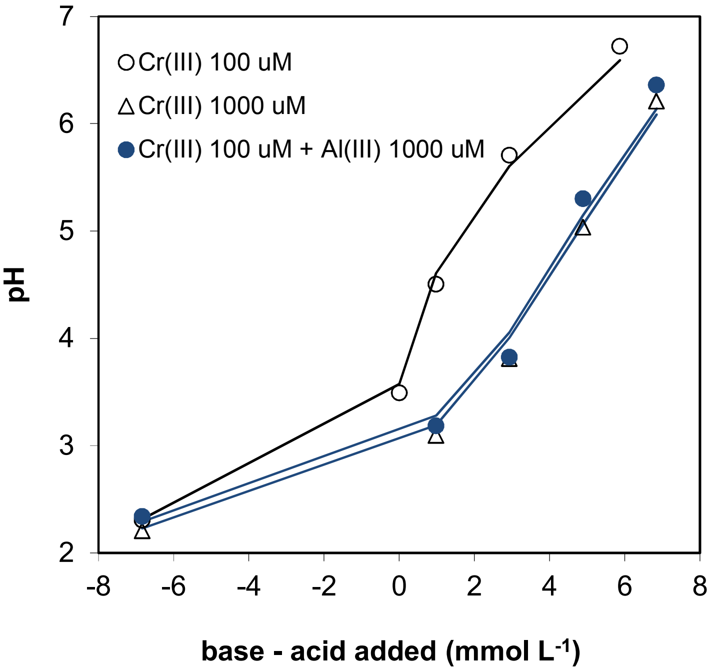

Figure S3. The pH as a function of the base – acid added (as NaOH or as HNO_3) for the systems under study. The points are observations, and the lines are fits after optimization of the concentration of active humic and fulvic acid when using the final Cr(III) binding parameters of Table S2.

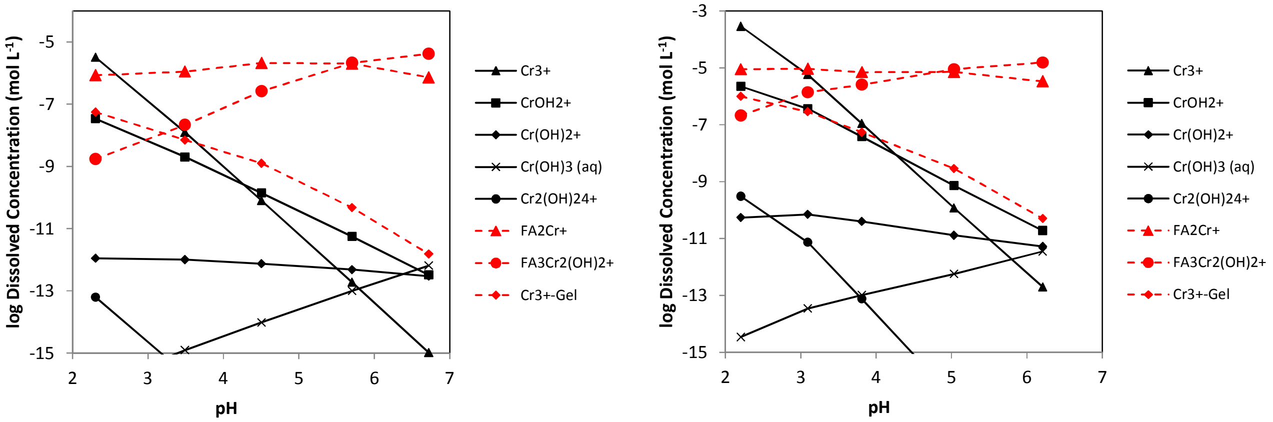

Figure S4. Modeled speciation of dissolved chromium(III) after initial additions of 100 (left) and 1000 µmol Cr(III) L^{-1} (right). Black points connected by solid lines represent inorganic Cr(III) species, whereas red points connected by dashed lines are organically bound Cr(III) species. Only species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

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