Speciation study of Cr(VI/III) reacting with humic substances and determination of local structure of Cr binding humic substances using XAFS spectroscopy

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X-ray absorption fine structure (XAFS) analysis was applied to elucidate Cr(VI/III) speciation during reaction with standard humic acid materials extracted from Japanese soils. The degree of reduction of Cr(VI) by humic acids differed for different degrees of humification. Adsorption of Cr(III) to humic substances was higher for higher carboxylic humic substance contents. After reduction experiments of Cr(VI) by humic acids, Cr binding with humic acids has a trivalent state. Nevertheless, a substantial amount of Cr(VI) remains in solution. The X-ray absorption near-edge structure (XANES) spectra of the Cr(VI) experimental system were almost identical to those of Cr(III) adsorbed onto humic acids in a low-pH condition. However, during adsorption of Cr(III) by humic acids, Cr was partly precipitated as $Cr(OH)_3 \cdot nH_2O$. Its concentration was higher for higher pH. XANES spectra of Cr(VI/III) reacted with different humic acids showed no systematic differences, indicating that the binding form of Cr to humic substances is common, irrespective of differences in functional group concentrations. Linear combination fitting using XANES spectra of reference compounds to HA–Cr samples suggests that 50% hydrated Cr(III) was adsorbed onto HA and that the remainder of Cr(III) was bound to carboxylic acid of HA.

The local structure of Cr binding to humic acids was characterized using extended X-ray absorption fine structure (EXAFS) spectroscopy. The EXAFS features of Cr binding to humic acids were similar to those of Cr^{3+} aquo ions having simple octahedral symmetry of the oxygen coordination sphere. They show no clear presence of carboxylic group of humic acids around the Cr site. Scattering from the C atom might not be visible because the backscatter amplitude of a C atom becomes weak steeply with increasing wavenumber (*k*) and because it is smaller than those of the O atom and the Cr atom. Considering the linear combination fitting results of XANES spectra, the structural mode of Cr binding with HA is $R-COO-Cr-(OH_2)_5$.

Keywords: hexavalent chrome, humic acid, XANES, EXAFS, oxidation state, speciation analysis

INTRODUCTION

Chromium is widely used for applications such as stainless steel materials, plate processing, tanning, and pigments. Although Cr(III), a necessary ionic species for living organisms, is less toxic and less soluble than Cr(VI), the latter has high oxidizing ability and presents risks of skin inflammation, tumor, and carcinogenesis. For that reason, reduction-oxidation processes of Cr in natural waters and soil environments have continued to attract intense scientific interest. Especially, reduction of Cr(VI) by Fe(II) and organic materials such as humic and fulvic acids (HA and FA) in soil environments is an interesting phenomenon presenting important implications for environmental problems (Wittbrodt and Palmer, 1996, 1997; Kožuh et al., 2000). Reduction-oxidation studies of Cr in soils have mainly targeted estimation of the reduction kinetics and stability constants (complexation capacities), or have addressed the presence of Cr(VI) (Fukushima et al., 1995; Wittbrodt and Palmer, 1995, 1996, 1997; Nakayasu et al., 1999; Kožuh et al., 2000). Information about the detailed chemical structure of Cr in nature is also necessary for complete understanding of toxicity and stability. However, determining a chemical state of Cr during or after a reaction process of Cr(VI) and soils is challenging because the soil system is too complex for speciation studies of Cr. Analysis using X-ray absorption fine structure (XAFS) spectroscopy is effective for determination of a valence state and a chemical form of metals in heterogeneous materials because it yields information with elemental selectivity obtained through

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Table 1. HA and Cr(VI/III) concentrations and Cr species* in the initial experimental solutions

HA concentration	83 µg/ml	83 µg/ml	83 µg/ml	83 μ g/ml	83 µg/ml	83 µg/ml
Initial Cr(VI) concentration	2.1 µg/ml	$2.1 \ \mu \text{g/ml}$	2.1 µg/ml	—	_	—
Initial Cr(III) concentration	—	—	_	$2.1 \ \mu \text{g/ml}$	2.1 µg/ml	$2.1 \ \mu \text{g/ml}$
pH	2.0	4.0	6.0	2.0	4.0	6.0
$Cr_2O_7^{2-}$	100%	100%	100%		—	—
Cr ³⁺		_	_	98%	39%	<1%
CrOH ²⁺			_	2%	61%	71%
$Cr(OH)_2^+$	—	—	—	<1%	<1%	28%

**Chromium(III)* speciation is calculated using the solubility equilibriums of Cr(III) hydroxide listed below (Fukushima et al., 1995): $Cr(OH)_{3(s)} + 3H^{+} = Cr^{3+} + 3H_2O \log K_I = 9.76, (1)$

 $Cr(OH)_{3(s)}^{(0)} + 2H^+ = CrOH^+ + 2H_2O\log K_2 = 5.96, (2)$

 $Cr(OH)_{3(s)} + H^+ = Cr(OH)_2^+ + H_2O \log K_3 = -0.44.$ (3)

non-destructive observations. Peterson *et al.* (1997), Kappen *et al.* (2008), and Elzinga and Cirmo (2010), after conducting speciation studies of Cr(VI) in soils, reported that Cr(III), reduced from Cr(VI) in soils or present in chromite ore wastes, adsorbs onto Fe-minerals or precipitates as Cr_2O_3 and $Cr(OH)_3 \cdot nH_2O$. The unreduced Cr(VI) persists as CaCrO₄ and PbCrO₄.

In contrast, few reports have described Cr binding with humic substances, which are ubiquitous in natural water and soil, acting as an important electron donor for Cr(VI). Covelo *et al.* (2004) reported that Cr sorption by humic substances is more rapid than that of Cu, Cd, Ni, or Zn. Therefore, Cr(III) reduced from Cr(VI) is likely to bind to humic substances in a first-order reaction before precipitating as Cr(OH)₃·*n*H₂O or adsorbing onto minerals, as Peterson *et al.* (1997), Kappen *et al.* (2008), and Elzinga and Cirmo (2010) have reported.

As a preliminary study, we examined speciation of Cr(VI/III) reacting with commercially available humic substances (Ohta et al., 2011). We reported that 1) humic substances adsorb Cr(III) reduced from Cr(VI), 2) Cr(III) has binding forms of two kinds to humic substances (inner sphere complex and outer sphere complex), and 3) a substantial amount of $Cr(OH)_3 \cdot nH_2O$ precipitates with humic substances. Nevertheless, the origins and chemical properties of commercially available humic substances are too uncertain to elucidate how differences in chemical properties of humic substances contribute to Cr(VI) reduction and Cr(III) absorption processes and the local coordination sphere of Cr binding to HA. Subsequently, we used humic substances accredited as standard samples by the Japanese Humic Substances Society (JHSS). In the present study, we specifically examine the relation between the chemical properties of humic acids and the speciation of Cr(VI/III) reacting with humic substances. We use XAFS spectroscopy to determine the binding structure of Cr on humic substances and to evaluate its stability.

MATERIALS AND EXPERIMENTAL METHODS

Humic substances

For this study, HA of two kinds was purchased from the Japanese Humic Substances Society were used. The soil-derived samples of Dando and Inogashira humic acids (HA) were extracted respectively from Dystric Cambisol and Umbric Andosol. Chemical properties of these samples were reported by Kuwatsuka et al. (1992), Watanabe et al. (1994), and Watanabe et al. (2004), who described that chemical compositions (C, H, O, and N) do not differ greatly between Dando HA and Inogashira HA. However, the ¹³C CPMAS NMR spectra implied that Dando HA has higher alkyl C concentration and lower aromatic C concentration than Inogashira HA has. Moreover, the OH group is somewhat richer in Dando HA, and the carbonyl group is more abundant in Inogashira HA. The composition of N species in HA, as determined using X-ray photoelectron spectroscopy, suggests higher aromatic N content and lower peptide N concentration in Inogashira HA than in the Dando HA. These features suggest that Inogashira HA is the highest class and Dando HA is the lowest class in terms of the degree of humification.

Experimental methods

A 0.1 mg/ml stock solution was made for each humic sample by dissolving 50 mg of the HA in 500 ml Milli-Q (MQ) water with 5 ml of 1 mol/l NaOH solution. Then 50 ml of each HA stock solution (0.1 mg/ml) was placed in a 60 ml PFA vessel. In the reduction experiments, an additional 2.5 ml of 50 μ g/ml Cr(VI) (K₂Cr₂O₇) solution was added to the PFA vessel. In the adsorption experiments, a 2.5 ml of 50 μ g/ml of Cr(III) (Cr(NO₃)₃) solution was added to the vessel. The pH values of the experimental solutions were adjusted to 2.0, 4.0, and 6.0 using dilute HCl and NaOH. Solutions were finally diluted to 60 ml using MQ water. The HA and Cr(VI/III) concentrations in the initial experimental solutions were set to be 83 μ g/ml and 2.1 μ g/ml, respectively (Table 1). The Cr(VI) species were unchanged over the experimental pH range, but Cr(III) species in the initial experimental solution were changed by pH. The Cr³⁺, CrOH²⁺, and Cr(OH)₂⁺ were the most dominant species in the pH = 2–6 condition. Table 1 also shows the Cr(III) speciation in the experimental solution, as calculated using the solubility equilibria of Cr(III) hydroxide (Fukushima *et al.*, 1995). The Cr³⁺ was the dominant species in pH = 2 solution. The CrOH²⁺ was the major species in both pH = 4 and pH = 6 solutions.

The reactant vessels were covered with aluminum foil to prevent photoreaction. The reactant vessels were shaken at 80 rpm using a turn-overturn mechanical shaker for 1, 2, 8, 14, and 28 days. An aliquot of 10 ml experimental solutions was isolated from vessels after measuring pH. The remaining solutions were adjusted to within 0.1 pH units of the initial values using dilute HCl and NaOH. A few drops of 2 mol/l HCl were added to aliquots to precipitate HA. The HA was aggregated in such acidic conditions and is precipitated (Stevenson, 1994). A few minutes later, solutions were centrifuged at 3000 rpm for 15 min. Cr(III) was not dissolved (dissociated) from HA in this process because Cr-HA bonding was expected to exhibit substitution inertness: Cr bound to HA was replaced only slightly with other anions (Ohashi et al., 2005). The acidified aliquot (about 0.02 mol/l HCl) might accelerate the reduction of Cr(VI) by HA further. However, that does not present a serious problem because the reaction time is no more than about 20 min. Furthermore, the same procedure was applied to all samples. Although this process might yield systematic error for the reduction properties, no problem arises in comparing the reduction rate and XAFS spectra among HA samples. The precipitate was filtered using a 0.1 μ m PTFE membrane filter and was dried under vacuum at room temperature. The dried samples on the filter were put in a plastic bag and stored in a refrigerator at about 4°C before analysis.

The sample materials, on the filter, were placed in a refrigerator until XAFS measurement. The concentration of Cr(VI) remaining in filtrates was determined immediately at 540 nm luminescence wavelength as Cr(VI)-diphenylcarbazide complex, for which the luminescence was measured using a spectrophotometer (6C; Hirama Rika Kenkyujo Ltd.) with a 1 cm glass-flowing cell. The proportion of reduction of Cr(VI) was calculated as the ratio of the concentration of Cr(VI) remaining in a solution to the initial Cr(VI) concentration. In the Cr(III) experimental system, the concentration of Cr(III) remaining in filtrates was determined using ICP-AES (IRIS; Thermo Jarrell Ash). The percentage of adsorption of Cr(III) on HA was estimated from the {[total Cr(III]] – [Cr(III) remaining in a solution]}/[total Cr(III)], where

the brackets signify the Cr concentration. We confirmed that the Cr(III) was not oxidized to Cr(VI) by humic acids in the experimental condition at pH = 2-8 (Ohta *et al.*, 2011).

Ohta *et al.* (2011) reported that a substantial amount of $Cr(OH)_3 \cdot nH_2O$ precipitates in the adsorption process of Cr(III) on HA. For direct comparison of $Cr(OH)_3 \cdot nH_2O$ precipitation associated with HA samples, the $Cr(OH)_3 \cdot nH_2O$ precipitated matter was synthesized from 1 µg/ml of Cr(III) solution adjusted at pH = 8.0. The solution was stirred gently in a flask for 72 hr with magnetic stirrers. The suspended precipitate was filtered using a 0.1 µm PTFE membrane filter. Then it was dried under vacuum at room temperature.

Measurement of Cr K-edge XAFS spectra

The Cr K-edge XAFS spectra were recorded in fluorescence mode at the BL-12C of the Photon Factory in the Institute of Material Structure Science, High Energy Accelerator Research Organization (Nomura and Koyama, 1996). The KEK-PF storage ring was operated at 2.5 GeV with a 450 mA maximum current. A Si(111) doublecrystal monochromator was used to produce a monochromatic X-ray beam. The monochromator was calibrated at the sharp pre-edge peak of Cr(VI) at 5989 eV using K₂Cr₂O₇ powder in the transmission mode, as in an earlier study (Tsuno et al., 2006). A bent cylindrical mirror focuses the beam into an area smaller than 1×1 mm (Nomura and Koyama, 1996). The HA sample on the filter in a plastic bag was equipped on the aluminum sample holder. The sample holder frame was positioned at 45° to the incident light. The fluorescence X-ray (Cr K α : 5.4 keV) was measured using a 19-element pure-Ge solidstate detector (Nomura, 1998) mounted at a right angle to the incident light. The XAFS spectra of all samples were measured at room temperature. The energy region around the Cr-K α fluorescence was selected from elastic scattering using single-channel analyzers. Detuning was performed by reducing the incident flux to 70%. Multiple scans (typically two or three times) were conducted for each sample and averaged.

XAFS includes two different regions: X-ray absorption near-edge structure (XANES) region and the extended X-ray absorption fine structure (EXAFS) regions. Analyses of the XANES and EXAFS spectra were performed using a computer program (REX2000; Rigaku Corp.). The XANES spectra were collected over a range (5950–6080 eV) and used for the speciation study of Cr binding with HA. Especially, the sharp pre-edge peak attributable to the 1s \rightarrow 3d-4p hybrid orbital transition (de Groot *et al.*, 2009) is extremely sensitive to the presence of Cr(VI) and estimation of the ratio of Cr(VI) and Cr(III) (e.g., Bajt *et al.*, 1994; Peterson *et al.*, 1997). For comparison, XANES spectra of several commercially provided com-

pounds were also obtained: potassium dichromate $(K_2Cr_2O_7)$, chrome oxide (Cr_2O_3) , chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$), chromium hydroxide $(Cr(OH)_3 \cdot nH_2O)$, chromium acetate $(Cr(CH_3COO)_3)$, and chromium acetylacetonate (Cr(C₅H₈O₂: acac)₃). In addition, 1000 μ g/ml Cr³⁺ solution with 0.1 mol/l HNO₃ $(Cr^{3+}_{(aq)})$, was measured in fluorescence mode. The preedge background absorption is subtracted by extrapolating a linear polynomial fitted to the pre-edge absorbance though the post-edge region. The spectra subtracted from the pre-edge background absorption were normalized by the intensity at the fundamental absorption edge. The fundamental absorption edges estimated from EXAFS spectra of various samples listed in the following sentence were 5998.8-5999.5 eV. Consequently, we fixed them as 5999.0 eV for all samples.

The EXAFS spectra provide a local coordination sphere of a metal. In this study, EXAFS analysis was applied to the Cr(VI) reacting with Dando and Inogashira HA at pH = 2, Cr(III) reacting with Dando HA at pH = 6, $Cr^{3+}_{(aq)}$, $Cr(acac)_3$, and the synthetic $Cr(OH)_3 \cdot nH_2O$ precipitate. The measured EXAFS spectra were converted from energy to k space first. The EXAFS oscillation was determined using pre-edge subtraction, cubic-spline removal, and data normalization. The pre-edge background absorption was then subtracted by extrapolating a linear polynomial fitted to the pre-edge absorbance though the post-edge region. The isolated atomic contribution to the absorption coefficient is regarded as the smooth background in the EXAFS region with a cubic spline curve. The EXAFS signals were Fourier-transformed using a Hanning window function to yield a radial structure function (RSF). A peak appearing in an RSF was isolated and back-transformed to k space. The coordination number, the interatomic distance, the threshold energy value, and the Debye-Waller factor for the isolated shell surrounding an absorber in an unknown material were determined using least-squares fitting of the Fourier-filtered EXAFS function. The backscattering amplitudes and phase shifts of oxygen, chromium, and carbon were calculated theoretically from α -CrOOH (Christensen *et al.*, 1977) and $Cr(acac)_3$ (Morosin, 1965), which was used as a model compound, using FEFF 8.20 (Ankudinov et al., 2002). An estimate of the amplitude reduction factor was determined as 0.97 using FEFF 8.20. That value was set for modeling.

RESULTS

Reduction of Cr(VI) by HA and adsorption of Cr(III) to HA

Figure 1a portrays the reduction process of Cr(VI) by Dando HA and Inogashira HA. As described in previous reports (Wittbrodt and Palmer, 1995, 1997), the concen-



Fig. 1. a) Reduction of Cr(VI) by Dando HA and Inogashira HA. b) Absorption of Cr(III) to Dando HA and Inogashira HA.

trations of Cr(VI) remaining in solutions decreased with reaction time and the reduction rate of Cr(VI) increased continuously with decreasing pH. The Dando HA reduced Cr(VI) more efficiently than Inogashira HA in all pH conditions. The Inogashira HA has a higher degree of humification than Dando HA has (Watanabe *et al.*, 2004). In other words, Inogashira HA is more oxidized in the natural environment than Dando HA is. Therefore, the difference in efficiency of Cr(VI) reduction between Dando HA and Inogashira HA is attributable to the difference in chemical properties.



Fig. 2. XANES spectra of seven reference materials and synthetic $Cr(OH)_3 \cdot nH_2O$ precipitates. Spectra are shifted upward and downward for clarity.

Figure 1b depicts the percentage of Cr(III) absorbed on HA. The percentage of absorption of Cr(III) increased with reaction time and with increasing pH. The Inogashira HA adsorbed Cr(III) more efficiently than Dando HA in all pH conditions. The Cr(III) binding capacity is correlated with the carboxylic contents in humic substances (Fukushima et al., 1995). Actually, Inogashira HA has larger contents of carboxyl group than Dando HA has (Watanabe et al., 1994, 2004). The alcoholic and phenolic hydroxyl groups and amino acids are also a possible binding site for Cr. Their contents in Inogashira HA are lower than that of Dando HA (Watanabe et al., 1994), which is the opposite trend from that of the percentage of absorption of Cr(III) presented in Fig. 1b. Consequently, the adsorption capacity of hydroxyl group in HA is weaker than that of carboxyl group in HA.

XANES spectra of Cr compounds and Cr reacting with HA

Figure 2 presents Cr K-edge XANES spectra of several chromium compounds. The XANES spectra of $K_2Cr_2O_7$ have a sharp pre-edge at 5988 eV and a broad peak around 6030 eV. A sharp pre-edge peak is assigned at the $1s \rightarrow 3d$ -4p hybrid orbital transition (de Groot *et al.*, 2009). The trivalent chromium compounds also have a small pre-edge peak at 5985 eV ($1s \rightarrow 3d$ -4p excitation) that is much smaller than the main peak at 6003– 6007 eV. The XANES spectra of a 1000 μ g/ml of Cr³⁺ solution resemble those of Cr(NO₃)₃·9H₂O, but the concave portion around 6009 eV is rather inconspicuous. The



Fig. 3. XANES spectra of Dando HA and Inogashira HA reacting with Cr(VI) and Cr(III). Dotted lines represent the fitting results of samples using Cr(VI/III) reacting with HA at pH = 2and synthetic $Cr(OH)_3$ ·nH₂O precipitate as endmembers. Spectra are shifted upward and downward for clarity.

XANES spectra of synthetic $Cr(OH)_3 \cdot nH_2O$ and reagent $Cr(OH)_3 \cdot nH_2O$ are mutually similar, but the main peak of the reagent material is more sharply defined than that of the synthetic material. Although both $Cr(CH_3COO)_3$ and $Cr(acac)_3$ are organic Cr compounds, their XANES spectra mutually differ. The $Cr(CH_3COO)_3$ has a broad peak at 6007 eV. The $Cr(acac)_3$ has bimodal peaks at 6001 eV and 6011 eV. The Cr_2O_3 has duplicate peaks at 6002 eV and 6006 eV, which is a different feature from those of XANES spectra of the other reagents. Because XANES spectra are sensitive to valence states and chemical species, they are useful for fingerprint analysis.

The XANES spectra for Cr reacting with HA obtained



Fig. 4. XANES spectra of the Wako, Aldrich, Dando, and Inogashira HA reacting with Cr(VI) in pH = 2 conditions. Data for the former two samples were referred from Ohta et al. (2011). The dotted line shows the linear combination fitting results of XANES spectra of samples using $Cr(NO_3)_3 \cdot 9H_2O$, $Cr(CH_3COO)_3$, and $Cr(acac)_3$ as endmembers. Spectra are shifted upward and downward for clarity.

in this study are presented in Fig. 3. Because XANES spectra of samples did not change over time (1, 2, 8, 14, and 28 days), data for the samples reacting with Cr(VI/III) for 28 days, except for the Dando HA sample reacting with Cr(VI) in pH = 2 solution for 14 days, are portrayed in Fig. 3. The mean errors (2σ ; n = 5) estimated from XANES spectra of HA reacting with Cr(VI/III) at pH = 2–6 for 1, 2, 8, 14 and 28 days were $\pm 0.6-1.9\%$ over the range of 5950–6080 eV and $\pm 0.4-2.2\%$ at the maximum intensity (at the main peak). The results suggest that the fitting of XANES spectra has high reliability even though the scanning range was narrow (5950–6080 eV).

As depicted in Fig. 3, no sample that had been reacted with Cr(VI) exhibited the intense pre-edge peak characteristic of Cr(VI) (5988 eV), which suggests that Cr(III) that had been reduced from Cr(VI) bound to HA, but that unreacted Cr(VI) remained in the experimental solutions. Park et al. (2008) reported the same results, although they examined the reaction of Cr(VI) with brown seaweed. They concluded that Cr(III) reduced from Cr(VI) was bound to the carboxyl groups of the brown seaweed (Ecklonia sp.). The XANES spectra were almost identical for two experimental systems: HA reacting with Cr(VI) and with Cr(III). Figure 4 shows the XANES spectra among different humic substances (Wako, Aldrich, Dando, and Inogashira HAs) in pH = 2 experimental solution containing Cr(VI). The Wako and Aldrich HAs are commercially available humic substances. Their XANES data were referred from Ohta et al. (2011). The Cr binding to



Fig. 5. a) XANES spectra of the Wako HA reacting with Cr(VI)at pH = 2 and with Cr(III) in pH = 4, 6 and 8 conditions and $Cr(OH)_3 \cdot nH_2O$ precipitates. b) XANES spectra of the Dando HA reacting with Cr(III) in pH = 4 and 6 conditions and $Cr(OH)_3 \cdot nH_2O$ precipitates. Data for the former samples were referred from Ohta et al. (2011). Spectra are shifted upward and downward for clarity.

these HA is in a trivalent state, although unreacted Cr(VI) remained in experimental solutions. No evidence shows that Cr XANES spectra differ among those for the four reactant HAs (Fig. 4). It is possible, however, that Cr(VI) sorbed on HA is reduced completely to Cr(III) by X-ray radiation during the measurement. We assume that the photoinduced reduction did not occur immediately for the dried samples. Additionally, it takes 11 min for measuring the whole XANES region and only 150 s for measuring within the pre-edge region including the pre-edge peak at 5899 eV, which is sensitive to the presence of Cr(VI). Actually, XANES spectra, especially the pre-edge region around 5899 eV, of all Cr(VI)-HA samples showed no change in repeated measurements. Therefore, the absence of Cr(VI) on HA in XANES spectra is not caused by Xray radiation.

Ohta *et al.* (2011) reported that the IR spectra of Wako HA reacting with Cr(III) and Cr(VI) show increased intensity of IR bands at 3400 cm⁻¹, 1608 cm⁻¹, and 1384 cm⁻¹. The increased intensity of IR band at 3400 cm⁻¹ is

Sample	Dando HA	Dando HA	Inogashira HA	Inogashira HA	Aldrich HA	Wako HA
HA concentration	83 µg/ml	83 µg/ml	83 µg/ml	83 µg/ml	90 µg/ml	90 µg/ml
Initial Cr(VI) concentration	$2.1 \ \mu \text{g/ml}$	—	2.1 µg/ml	—	23 µg/ml	23 µg/ml
Initial Cr(III) concentration	—	$2.1 \ \mu \text{g/ml}$	—	2.1 µg/ml	—	—
рН	2.0	2.0	2.0	2.0	2.0	2.0
XANES fitting						
R-factor	0.023 (0.022)	0.023 (0.023)	0.024 (0.023)	0.021 (0.021)	0.023 (0.022)	0.022 (0.021)
Cr(NO ₃) ₃ ·9H ₂ O	46% (41%)	53% (48%)	55% (49%)	57% (47%)	49% (44%)	50% (45%)
Cr(CH ₃ COO) ₃	54% (59%)	47% (52%)	45% (51%)	43% (53%)	51% (56%)	50% (55%)
R-factor	0.017 (0.019)	0.017 (0.018)	0.017 (0.018)	0.015 (0.018)	0.018 (0.020)	0.014 (0.016)
$Cr(NO_3)_3 \cdot 9H_2O$	49% (45%)	53% (50%)	54% (50%)	56% (49%)	52% (48%)	51% (47%)
Cr(acac) ₃	51% (55%)	47% (50%)	46% (50%)	44% (51%)	48% (52%)	49% (53%)
R-factor	0.016 (0.016)	0.017 (0.017)	0.017 (0.017)	0.014 (0.016)	0.017 (0.017)	0.014 (0.014)
$Cr(NO_3)_3 \cdot 9H_2O$	42% (38%)	49% (45%)	50% (46%)	53% (43%)	46% (40%)	46% (40%)
$Cr(CH_3COO)_3$	18% (25%)	12% (20%)	10% (19%)	9% (22%)	17% (26%)	13% (22%)
Cr(acac) ₃	40% (37%)	39% (35%)	40% (35%)	38% (35%)	37% (34%)	41% (38%)

Table 2. Fitting result of Cr XANES data of HA reacting with Cr(VI/III) at pH = 2 by a linear combination of $Cr(NO_3)_3 \cdot 9H_2O$, $Cr(CH_3COO)_3$, and $Cr(acac)_3$ spectra

Blanket means the result of a linear combination fitting using $Cr^{3+}_{(aq)}$ spectra as a substitute for $Cr(NO_3)_3$ ·9H₂O spectra to XANES spectra of HA–Cr samples.

R-factor describes the fit quality.

explained by the presence of hydrated Cr forming an outer sphere complex with HA by reference to the ESR and IR data of Cu adsorbed onto HA (Senesi et al., 1986). The change of the remaining IR bands is interpreted as the inner sphere complex formation of Cr(III) and carboxyl groups (Fukushima et al., 1995). The fractions of two binding forms were determined from XANES spectra. Ohta et al. (2011) fitted a linear combination of XANES spectra of Cr(NO₃)₃·9H₂O and Cr(CH₃COO)₃ to the spectra of Cr-HA samples. The Cr(NO₃)₃·9H₂O is a hydrated compound with high ion binding property. Its XANES spectrum is useful as a model of pseudo-outer-sphere complexes of Cr(III) and HA. Chromium acetate is substituted for Cr-carboxylate binding, although HA contains both aromatic and aliphatic carboxylic acids. The same fitting process was done for four samples. Their proportions were estimated as roughly one-to-one (see Table 2).

The $Cr(acac)_3$ is useful as an possible endmember of the inner sphere complex, although the acetylacetonate $(C_5H_8O_2: acac)$ is not a carboxyl group but a ketone group. When $Cr(acac)_3$ was used as an additional endmember of a model of the inner sphere complex, XANES fitting of Cr(III) binding with HA was improved. The fitting results obtained using the three endmembers are portrayed in Fig. 4. The respective percentages of the three endmembers are presented in Table 2. Results suggest that the proportions of the outer sphere ($Cr(NO_3)_3.9H_2O$) and the inner sphere ($Cr(CH_3COO)_3$ and/or $Cr(acac)_3$) complexes were estimated as roughly one-to-one for all samples. The ratios of binding forms do not differ greatly among the three fitting models (Table 2). Incidentally, when the XANES spectrum of $Cr^{3+}_{(aq)}$ is used as a substitute for those of $Cr(NO_3)_3 \cdot 9H_2O$, a model of pseudo-outersphere complexes, the estimated ratios do not differ greatly (Table 2).

Cr hydroxide precipitates associated with HA samples

Trivalent chromium ion is hydrolyzed easily and precipitates as Cr hydroxide (e.g., Richard and Bourg, 1991). Kappen *et al.* (2008) reported that $Cr(OH)_3 \cdot nH_2O$ precipitates in the reduction process of Cr(VI) in soils at the experimental pH of 4–6. The same phenomenon appears in our experimental system (Ohta et al., 2011). Figure 5 shows XANES spectra of Wako HA reacted with Cr(VI) at pH = 2 and with Cr(III) at pH = 4-8, and XANES spectra of Dando HA reacted with Cr(III) at pH = 4-6. The intensity in the region of 6010-6020 eV weakened continuously with the increase of the experimental pH level. The XANES features of Wako HA reacted with Cr(III) at pH = 8 and Cr(OH)₃·nH₂O are mutually similar. The percentages of Cr hydroxide precipitates in Aldrich and Wako HA experimental systems were about 10% at pH = 4, about 30% at pH = 6 and about 50% at pH = 8 (Ohta et al., 2011). To prevent precipitation of Cr(OH)₃·nH₂O, Cr concentrations were reduced to less than one-tenth of those adopted by Ohta et al. (2011). The experiments were conducted in a lower pH range (2–6). Consequently, XANES spectra Dando HA experimental system (also Inogashira

Sample	HA concentration	Initial Cr concentration	pН	$Cr(OH)_3 \cdot nH_2O$ (reagent)	R-factor	$Cr(OH)_3 \cdot nH_2O$ (synthetic)	R-factor
Dando HA	83 µg/ml	Cr(III): 2.1 µg/ml	4.0	10%	0.010	11%	0.010
	83 µg/ml	Cr(III): 2.1 µg/ml	6.0	25%	0.010	26%	0.011
	83 µg/ml	Cr(VI): 2.1 µg/ml	4.0	<5%	0.004	n.d.	n.d.
	83 µg/ml	Cr(VI): 2.1 µg/ml	6.0	<5%	0.006	5%	0.006
Inogashira HA	83 μ g/ml	Cr(III): 2.1 μ g/ml	4.0	13%	0.007	11%	0.006
0	83 μg/ml	Cr(III): 2.1 μ g/ml	6.0	18%	0.010	17%	0.008
	83 µg/ml	Cr(VI): 2.1 µg/ml	4.0	<5%	0.006	<5%	0.006
	83 µg/ml	Cr(VI): 2.1 µg/ml	6.0	n.d.	n.d.	n.d.	n.d.
Aldrich HA	90 μ g/ml	Cr(III): 45 μ g/ml	4.0	7%*	0.008	25%	0.006
	90 µg/ml	Cr(III): 45 µg/ml	6.0	31%*	0.008	49%	0.004
	90 µg/ml	Cr(III): 45 μ g/ml	8.0	46%*	0.012	64%	0.010
Wako HA	90 µg/ml	Cr(III): 45 μ g/ml	4.0	12%*	0.007	28%	0.004
	$90 \mu \text{g/ml}$	Cr(III): 45 μ g/ml	6.0	30%*	0.010	45%	0.010
	90 μg/ml	Cr(III): 45 μ g/ml	8.0	50%*	0.013	73%	0.011

Table 3. Fitting result of Cr XANES data of HA reacting with Cr(VI/III) at pH = 4-8 by a linear combination of $Cr(OH)_3 \cdot nH_2O$ and HA reacting with Cr(VI/III) at pH = 2

R-factor describes the fit quality.

n.d.: not determined.

*The data are from Ohta et al. (2011).

HA experimental system) has slight variation over the experimental pH range (Fig. 5).

The fraction of $Cr(OH)_3 \cdot nH_2O$ associated with HA is determined from a linear combination fit using HA reacted with Cr(VI) or Cr(III) at pH = 2 and synthetic $Cr(OH)_3 \cdot nH_2O$ (or reagent $Cr(OH)_3 \cdot nH_2O$) as endmembers. The fitting results are depicted in Fig. 3 and are presented in Table 3. The percentage of $Cr(OH)_3 \cdot nH_2O$ in the Cr(III) experimental system increases from 10-13% to 17-26% with increasing pH level. Those values are lower than data of the previous report, although the newly calculated ratios obtained using the synthetic $Cr(OH)_3 \cdot nH_2O$ are larger than those estimated using reagent Cr(OH)₃·nH₂O (Ohta et al., 2011). In contrast, the contribution of $Cr(OH)_3 \cdot nH_2O$ precipitation to solid phases in the Cr(VI) experimental systems is negligible (less than 5%). We conclude that $Cr(OH)_3 \cdot nH_2O$ precipitation does not occur in the Cr(VI) experimental system.

Structural analysis of Cr reacting with HA using EXAFS spectra

Figure 6 depicts the EXAFS signals weighted by k^3 and the RSFs of Cr(VI) reacting with Dando and Inogashira HA. For comparison, EXAFS spectra of 1000 μ g/ml Cr³⁺ solution (Cr³⁺_(aq)), Cr(acac)₃, and the synthetic Cr(OH)₃·*n*H₂O precipitate are also depicted in Fig. 6. The EXAFS oscillations of Cr³⁺_(aq) and Dando and Inogashira HA reacting with Cr(VI) are expressed as a simple sine curve. The result reveals the existence of the first shell local order around the Cr site. Actually, their RSFs have one major peak at about 1.6 Å (phase shift is uncorrected) and some small ripples beside the main peak. In contrast, the EXAFS oscillations of $Cr(acac)_3$ and synthetic $Cr(OH)_3 \cdot nH_2O$ precipitate are not expressed as a simple sine curve, especially in the regions of 7–11 Å⁻¹. Their RSFs have the first peak at 1.6 Å (phase shift is uncorrected) and a small second peak at 2.5-2.7 Å (phase shift is uncorrected) (Fig. 6b). The second peak is assumed to represent scattering from the C atom or the Cr atom. As depicted in Fig. 3, a part of Cr precipitates as $Cr(OH)_3 \cdot nH_2O$ in the Cr(III) experimental system. Although the EXAFS oscillation of Dando HA reacting with Cr(III) at pH = 6 is apparently expressed as a simple curve, its RSF shows the small second peak at a similar distance to that of the synthetic $Cr(OH)_3 \cdot nH_2O$ precipitate.

The results of curve-fitting using theoretical parameters calculated using FEFF 8.20 are also portrayed in Fig. 6 and Table 4. The EXAFS data for $Cr^{3+}_{(aq)}$ and HA reacting with Cr(VI) were fitted simply using a singleshell model. The Cr–O distance of $Cr^{3+}_{(aq)}$ determined here was 1.98 Å, which is consistent with the hydration structure of Cr^{3+} ion having regular octahedral (Cr–O distance of 1.98–2.00 Å) (Ohtaki and Radnai, 1993). The second peak found in RSF of Cr(acac)₃ was fitted using the two Cr–C shells model because the Cr–Cr bond does not exist in the range of RSF (Morosin, 1965). When the coordination numbers of the shorter and longer Cr–C bonds were fixed at six and three, respectively, each determined



Fig. 6. EXAFS signals weighted by k^3 (a) and radial distribution functions (b) of samples: [1] 1000 µg/ml Cr³⁺ solution with 0.1 *M* HNO₃; [2] Cr(acac)₃; [3] the synthetic Cr(OH)₃·nH₂O; [4] Inogashira HA reacting with Cr(VI) at pH = 2; [5] Dando HA reacting with Cr(VI) at pH = 2; [6] Dando HA reacting with Cr(III) pH = 6. Dotted lines represent curves fitted using theoretical parameters calculated using FEFF 8.20. Spectra are shifted upward and downward for clarity.

Cr-C distance was 2.91 Å and 3.19 Å. In addition, the Cr–O and Cr–Cr distances of the synthetic $Cr(OH)_3 \cdot nH_2O$ precipitate were, respectively 2.00 Å and 2.99 Å. Those data are consistent with the structural data of synthetic $Cr(OH)_3 \cdot nH_2O$ reported previously by Manceau and Charlet (1992), which has the presence of Cr-O at 1.99 Å and Cr–Cr at 2.98 Å. The $Cr(OH)_3 \cdot nH_2O$ precipitate can be compared with Cr oxyhydroxides such as α -CrOOH and γ -CrOOH. The α -CrOOH possesses a layered structure and γ -CrOOH is an amorphous-like material, whose respective coordination numbers of the Cr-Cr shell are 6.0 and 1.5 (Christensen, 1976; Manceau and Charlet, 1992; Fendorf et al., 1994). The coordination numbers determined for the synthetic $Cr(OH)_3 \cdot nH_2O$ precipitate of Manceau and Charlet (1992) and this study are 1.9 and 1.4, respectively, which means that the structural parameters of the synthetic $Cr(OH)_3 \cdot nH_2O$ are consistent with those of γ -CrOOH.

The bonding distances of the Cr atom and the O atom in the first coordination sphere of humic samples are 1.99 Å, which is a similar length to that of Cr^{3+} aqueous ions and synthetic $Cr(OH)_3 \cdot nH_2O$ precipitate. The coordination numbers of the Cr–O shell are determined to be 5.9– 6.4 for all samples. The IR spectra of Cr–HA complexes reported previously indicate the presence of hydrated Cr^{3+} ion and Cr–carboxylate binding (Fukushima *et al.*, 1995; Ohta *et al.*, 2011). The XANES study also yields the same result (Fig. 4 and Table 2). Xia *et al.* (1997) reported that Co, Ni, Cu, and Zn form the inner sphere complex with the carboxyl group of humic and fulvic acids. They reported the presence of the second shell representing scattering from the C atom in the EXAFS spectra. Unexpectedly, the second shell arising from the Cr–C bond was not recognized in the RSFs of Dando and Inogashira HA samples reacting with Cr(VI) different from the RSF feature of $Cr(acac)_3$ (Fig. 6). Even if the Cr–C shell in EXAFS were included in analyses for these samples, the goodness-of-fit for these samples would not be improved at all.

The RSF of Dando HA reacting with Cr(III) in the pH = 6 condition has a small second peak that is assigned as scattering not from the C atom but from the Cr atom (Fig. 6). The Cr–Cr distance of Dando HA reacting with Cr(III) in the pH = 6 condition is 2.94 Å. The estimated coordination numbers were 0.7 for Dando HA reacting with Cr(III) (Table 4). Fendorf *et al.* (1994) reported that Cr(III) forms a monodentate complex with a SiO₂ surface and that Cr hydroxides having γ -CrOOH type local structure are nucleated on the surface. The coordination number of Cr–Cr of Cr sorbed on SiO₂ was 2.3–2.9, which is much larger than that of γ -CrOOH. The determined coordination numbers of Cr–Cr for the Dando HA sample are much smaller than those values. Therefore, the surface nucleation of Cr(OH)₃·nH₂O possibly does not occur.

Table 4. EXAFS Curve-fitting summary of $Cr^{3+}_{(aq)}$, Cr acetylacetonate $(Cr(acac)_3)$, synthetic Cr hydroxides, and Cr(VI/III) reacting with HA for coordination numbers (N), interatomic distances (R), shifts of threshold energy (ΔE_0), and the Debye–Waller factors (σ^2)

Sample	Shell	N	<i>R</i> (Å)	$\Delta E_0 (\text{eV})$	$\sigma^2 \times 10^3 (\text{\AA}^{-2})$	k-range (Å ⁻¹)	R-factor
Cr ³⁺ _(aq)	Cr–O	6.4 ± 0.2	1.979 ± 0.002	-8.6 ± 0.5	2.92 ± 0.03	2.6-13.0	3.872
Cr(acac) ₃	Cr–O	6*	1.986 ± 0.002	-4.3 ± 0.5	2.50 ± 0.04	2.5-13.0	3.699
	Cr–C	6*	2.91 ± 0.02	-10.3 ± 2.4	1.1 ± 0.4		
	Cr–C	3*	3.19 ± 0.04	-10.3 ± 2.4	1.8 ± 0.4		
$Cr(OH)_3 \cdot nH_2O$ (synthetic)	Cr–O	6.1 ± 0.3	1.996 ± 0.002	-7.0 ± 0.5	3.36 ± 0.04	2.7-13.2	2.770
	Cr–Cr	1.4 ± 0.3	2.99 ± 0.01	-11.4 ± 1.9	3.4 ± 0.4		
Inogashira HA reacting with $Cr(VI)$ at $pH = 2$	Cr–O	6.1 ± 0.3	1.986 ± 0.003	-6.6 ± 0.5	4.10 ± 0.04	2.6-13.0	1.869
Dando HA reacting with $Cr(VI)$ at $pH = 2$	Cr–O	5.9 ± 0.2	1.990 ± 0.003	-5.9 ± 0.5	3.25 ± 0.04	2.6-13.0	0.820
Dando HA reacting with $Cr(III)$ at $pH = 6$	Cr–O	6.4 ± 0.2	1.988 ± 0.002	-5.4 ± 0.5	3.84 ± 0.03	2.6-13.2	3.176
	Cr–Cr	0.7 ± 0.3	2.94 ± 0.02	-7.1 ± 4.1	5.0 ± 1.3		

*The coordination numbers were fixed in the EXAFS analysis.

The error was obtained from the square root of the diagonal elements in the covariance matrix that was estimated in the fitting calculation. R-factor describes the fit quality.

DISCUSSION

Structural model of Cr binding with HA

Concentrations of the functional groups differ between Dando HA and Inogashira HA. Results show that Dando HA has a greater reducing ability for Cr(VI) but a weaker affinity to Cr(III) than Inogashira HA has (Figs. 1a and 1b). Nevertheless, the XANES spectra resemble each other. Furthermore, similar XANES spectra were obtained for the Wako and Aldrich HA samples (Fig. 4 and Table 2). It is expected that the percentage of the inner sphere complex determined from XANES spectra increases continuously with increasing carboxylic contents in HA. The actual percentages do not differ greatly among the four HA samples (Table 2).

In contrast, EXAFS spectra of HA samples reacting with Cr show no presence of carboxylic group of HA around the Cr site. They are similar to EXAFS spectra of $Cr^{3+}_{(aq)}$, which is a model of hydrated Cr forming the outer sphere complex (Fig. 6). Scattering from the C atom might not be visible because the backscatter amplitude of a carbon atom becomes weak steeply with increasing wavenumber (k) and is smaller than those of the O atom and the Cr atom. An earlier report described that Co, Ni, Cu, and Zn form the inner sphere complex with humic and fulvic acids (Xia et al., 1997). The IR spectra of Cr-HA complexes indicate the presence of Cr-carboxylate binding (Fukushima et al., 1995). Therefore, we assume that Cr also binds with the carboxylate of HA, although scattering from the C atom is not visible in EXAFS spectra of HA-Cr samples.

The inconsistency among IR, XANES, and EXAFS spectra suggests that Cr–HA binding is not explained by the simple mixing of inner sphere and outer sphere com-

plexes. In other words, the binding model of 50% of Cr sorbed on HA electrostatistically (outer sphere complex) and the remainder of Cr bound to organic ligands (inner sphere complex), which is concluded from XANES analysis, is not reasonable. EXAFS analyses suggest that the Cr binding with HA is surrounded by six oxygen atoms (Table 4). The results might indicate that three bonds out of six Cr-O bonds are covalent bonds and that the other three Cr-O bonds are weaker electrostatic interaction (hvdrated waters). The coordination number of the Cr-C shell for this model is expected to be three. In this case, the Cr-C shell would be visible in the EXAFS spectra, even if the backscatter amplitude of C atom were weak. However, the Cr-C shell does not appear on the EXAFS spectra (Fig. 6). Accordingly, the ratio of the inner sphere and outer sphere complexes determined from XANES spectra is not comparable to the number of Cr-O bonds. For those reasons, the structural mode of Cr binding with HA determined from EXAFS spectra should be expressed as R-COO-Cr-(OH₂)₅. The proposed model consistently elucidates IR spectra and XANES spectra of HA reacting with Cr. The changes found in some IR bands are expected to be explained by the formation of inner sphere complex of hydrated Cr and carboxyl group of HA. Even if adsorption of Cr on HA increases with the increase of carboxyl groups in HA (see Fig. 1), then the ratio of the apparent outer sphere and inner sphere complexes obtained from XANES spectra remains unchanged. They remain roughly one-to-one (Table 2).

Formation of $Cr(OH)_3 \cdot nH_2O$ precipitation associated with HA

XANES and EXAFS spectra suggest that $Cr(OH)_3 \cdot nH_2O$ precipitation occurs not in the Cr(VI) ex-

perimental system but in the Cr(III) experimental system. Of the total Cr concentration, 50–90% existed as Cr(VI) in solution (Fig. 1a). The lower concentration of Cr(III) reduced from Cr(VI) in a solution engenders lower level precipitation of $Cr(OH)_3 \cdot nH_2O$. Alternatively, it is possible that CrOH²⁺ and Cr(OH)₂⁺ species in solutions bound directly to HA because the concentrations of those species increase continuously with increasing pH (Richard and Bourg, 1991; Fukushima et al., 1995) (see Table 1). The XANES spectra of CrOH²⁺ and Cr(OH)₂⁺ complexes with HA might resemble the XANES spectra of $Cr(OH)_3 \cdot nH_2O$. However, the proportions of Cr^{3+} , $CrOH^{2+}$ and $Cr(OH)_2^+$ are controlled simply by pH, and are independent of total Cr(III) concentrations in solutions (Table 1). In addition, the presence of the Cr-Cr shell for Dando HA reacting with Cr(III) does not support the simple adsorption of CrOH²⁺ and Cr(OH)₂⁺ on HA. Therefore, the absence of $Cr(OH)_3 \cdot nH_2O$ precipitation in the Cr(VI) experimental system is explained simply by the low concentrations of Cr(III) reduced from Cr(VI).

CONCLUSION

Humic substances (Dando HA and Inogashira HA) provided by the Japanese Humic Substances Society were reacted with Cr(VI/III) in various pH conditions. The Dando HA has greater reducing ability for Cr(VI), but a weaker affinity to Cr(III) than Inogashira HA has. These results are explained by differences in their chemical properties. However, the differences of chemical properties are not reflected in XANES spectra of Cr(VI/III) reacting with these humic acids. XANES spectra of humic acids reacting with Cr(VI) have no sharp pre-edge peak indicating the presence of Cr(VI). Nevertheless, a significant amount of Cr(VI) remained in solution. No systematic difference of XANES spectra was found between the Cr(VI) and Cr(III) experimental systems. The Cr partly precipitates as $Cr(OH)_3 \cdot nH_2O$ with increasing pH because Cr(III) is less soluble in solution.

The XANES spectra of Cr binding with HA are explained by a linear fitting model of the inner sphere complex with carboxyl group and the outer sphere complex of hydrated Cr^{3+} . However, EXAFS spectra of HA reacting with Cr(VI) in low pH are similar to EXAFS spectra of Cr^{3+} aquo ions having the simple octahedral symmetry of the oxygen coordination sphere. The Cr binding with HA is surrounded by six oxygen atoms. Finally, we concluded that Cr forms a monodentate complex with carboxyl groups in HA and that the remaining oxygen atoms are the consistent atoms of water model cues.

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