Speciation of Iron in Humic Substances by X-ray Absorption Fine Structure and Its Effect on the Complexation between Humic Substances and Trace Metal Ions

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The chemical state of Fe in standard humic substances (HS) was determined by X-ray absorption fine structure. Iron(III) complexed with HS, which can inhibit complexation of other metal cations with HS, is the dominant form of Fe in HS. The degree of inhibition of complexation by Fe^{III} was evaluated using a model for complexation between various metal cations and HS. Our results suggest that contribution of Fe must be considered in the evaluation of complexation between metal cations and HS.

Complexation of various metal ions and humic substances (HS) has been widely studied to understand behavior of metal ions in natural environments where natural organic matter is abundant.[1] In such studies, standard and commercial HS materials extracted from natural soils, river waters, and peat bogs have often been employed.[2] These HS materials contain considerable amount of metals as impurities depending on the extraction methods.[3,4] Some of these metals cannot be removed from HS completely even after acid purification.[3] These metals can affect the complexation of target ions and HS.

For example, Fe is present in HS at a high concentration even after purification owing to the high affinity of Fe for HS.[3] However, it is often the case that the Fe species in standard and commercial HS is not known, while both iron(III) and iron(II) ions and Fe (hydr)oxides can be possible species.[5] It is reported that interaction between HS and Fe strongly affects the complexation between target ions and HS.[5–11] Since the effect on the complexation by iron(III) or iron(II) ion is clearly different from that by Fe (hydr)oxides,[5–9] speciation of Fe in HS is important to evaluate the effect. If iron(III) or iron(II) ion is complexed with the binding site, for example, it is likely that the stability constant for the ion can be smaller by the presence of Fe. However, many studies of the interaction between metal ions and HS using standard and commercial HS materials have not taken account of the effect of Fe originally contained in HS. Contribution of original Fe cannot be neglected because of its large abundance. Therefore, the aims of this study are the speciation of Fe in HS using X-ray absorption fine structure (XAFS) and evaluation of the inhibition and/or enhancement effect of Fe on the complexation of HS with other metal cations using a model.

In this study, Suwannee River humic and fulvic acids (SRHA and SRFA) widely used in previous studies[1,4,7,11,12] were received from the International Humic Substances Society (IHSS) and used without further purification. These HS samples were obtained by IHSS method: extraction with a hydrophobic resin (XAD-8) from river water, followed by separation into HA and FA fractions according to solubility with pH and freeze drying. Iron concentration in HS was determined by inductively coupled plasma mass spectrometry (ICP-MS) after decomposition of HS. Concentrations of Fe in SRHA and SRFA were 570 and 330 mg/kg, respectively.

The Fe K-edge XAFS spectra were measured at BL-12C, Photon Factory, Japan. The storage ring operating conditions were 2.5 GeV electron energy and 400–300 mA electron current. Emitted X-rays were monochromized with a Si(111) double crystal monochromator. The beam size was $0.8 \times 0.8\,\mathrm{mm}^2$ at the sample position. The spectra were detected in the fluorescence mode using a 19-element Ge semiconductor detector. Powdered HS samples were shaped into pellet form. Iron(II) sulfate, goethite, ferrihydrite, iron(III) oxalate, iron(III) citrate, Fe^{3+} adsorbed on acrylic acid (AA) resin, and Fe^{3+} adsorbed on iminodiacetic acid (IDA) resin were used as reference materials for XAFS spectra of Fe.

Figures 1a and 1b show Fe K-edge X-ray absorption near edge structure (XANES) spectra, which reflect oxidation state of Fe. The XANES spectra for FA and HA are similar to each other. It is likely that Fe exists as Fe^{III} in HS estimated from the energy position of the absorption edge of the XANES spectra. In particular, XANES spectra for HS are similar to those of

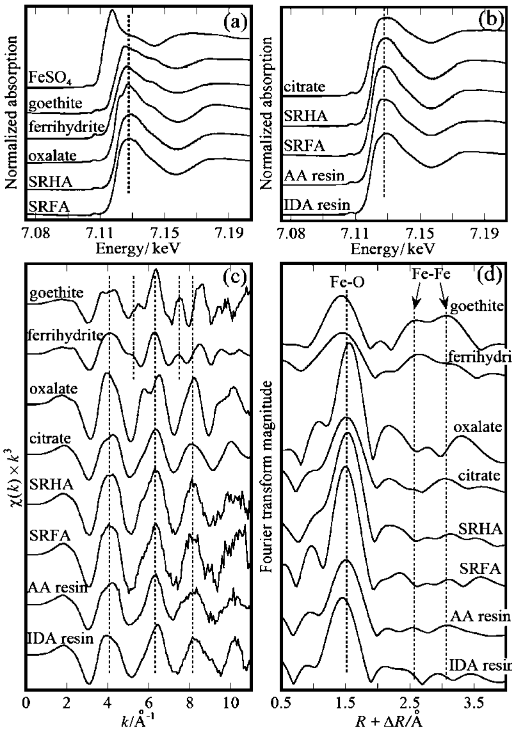

Figure 1. XAFS spectra for Fe. (a, b) Fe K-edge XANES, (c) k^3-weighted EXAFS, and (d) Fourier transform spectra of HS and reference samples.

Fe^{3+} adsorbed on AA and IDA resins based on the round shape of the XANES peak. Thus, it is suggested that carboxylate complex can be important as Fe species in HS.

Figure 1c shows the k^3-weighted Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra, which reflect local coordination structure of Fe. The EXAFS spectra for HA and FA are similar to each other, as were the XANES spectra. The spectra for HS show three peaks around 4.1, 6.3, and 8.2 $Å^{-1}$, resembling those for carboxylates and carboxylic resins, except for the second peak of oxalate. The spectra for Fe (hydr)oxides are different from Fe in HS in terms of frequency and amplitude, especially for two small peaks around 5.3 and 7.4 $Å^{-1}$. The k^3-weighted EXAFS spectra were converted into the Fourier transform spectra (Figure 1d). For the first peak around 1.5 Å corresponding to the Fe–O shell (details of the simulation are given in Supporting Information),[13] the coordination number and bond length for Fe (hydr)oxides, carboxylates, and carboxylic resins are similar to each other, resembling those for HS. This fact indicates that differences in coordination number and bond length for the first Fe–O shell among HS, Fe (hydr)oxides, carboxylates, and carboxylic resins are not so large. However, the next peaks around 2.6 and 3.0 Å, which correspond to Fe–Fe shells, are found in Fe (hydr)oxides. In the HS and carboxylate resin samples, however, distinct peaks were not found as the second shell, quite different from Fe (hydr)oxides. This fact indicates that the second neighboring atom is not Fe for Fe atom in HS. All the results for the XANES and EXAFS spectra for Fe among Fe (hydr)oxides, carboxylates, HS, and carboxylate resins strongly suggest that Fe in HS does not exist as Fe (hydr)oxides, but present as carboxylate complex, which can inhibit the complexation of other metal cations with HS.[5–7]

The degree of inhibition by Fe^{3+} for HS complexation with several metal cations was evaluated under the conditions of concentrations of the cations at 100 ng/dm^3 and 100 µg/dm^3 (Be^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, $UO_2{}^{2+}$, Al^{3+}, Eu^{3+}, and Th^{4+}) and HA concentration at 10 mg/dm^3 using the Windermere Humic Aqueous Model (WHAM ver. 6.0).[14] Because Fe concentration in HA (570 mg/kg) is much less than that of functional groups of HA, the net charge of HA in the presence of Fe is identical to that in the absence of Fe at all pH values. Therefore, Fe^{3+} in HA does not affect formation of outer sphere complexes, and competition by Fe^{3+} at the binding sites is the most important factor inhibiting complexation of trace metal cations. The degree of inhibition of complexation depends on the amount of Fe^{3+} ions loaded in HA. The Fe loading level, which is the ratio of Fe–HA complexes (mol) and dissociated ligands (equiv) in HA, was within the range from 1.6 to 5.7 mmol/equiv for HA at pH between 2 and 10, where the amount of dissociated ligands was calculated based on the results of pH titration.[12]

Figure 2 shows several examples of fraction of metal–HA complexes as a function of pH at a metal concentration of 100 ng/dm^3. Fractions of all metal–HA complexes decrease in the presence of Fe^{3+}. The degree of inhibition is significant for divalent cations. Fractions of metal–HA complexes in the presence of Fe^{3+} are up to 30–70% smaller than those in the absence of Fe^{3+} at identical pH values. On the other hand, for trivalent and tetravalent cations, differences in fraction of metal–HA complexes with and without Fe^{3+} are less than 10%. Based on the model, these facts are due to the differences in affinity for minor but stable biding sites in HA between Fe and other cations.[1,5,7,14] On the other hand, at a metal concentration of 100 µg/dm^3, the degree of inhibition is less than 10% for divalent and 3% for trivalent and tetravalent cations, that is, much smaller than that at a metal concentration of 100 ng/dm^3. Contribution of Al^{3+} originally contained in SRHA is not so large compared with Fe^{3+}, since concentration of Al^{3+} in SRHA (160 mg/kg) is smaller than that of Fe^{3+} (model calculations including the Al^{3+} effect are given in Supporting Information).[13]

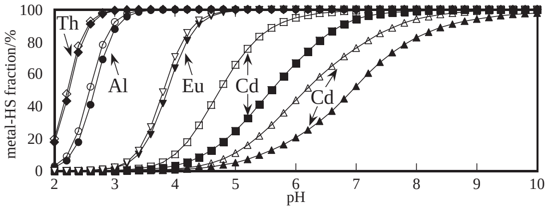

Figure 2. Metal–HA complex fractions for various metal cations calculated by WHAM at an ionic strength of 0.10 M. Closed and open symbols correspond to the values with and without Fe, respectively. All parameters for the model employed here were identical to reported values.[14]

Our results indicate that Fe exists as iron(III) carboxylate complexes in HS samples, which strongly inhibits complexation of divalent cations with HA. It is likely that stability constants of metal cations and HS are underestimated owing to the presence of Fe in HS. Therefore, contribution of Fe must be considered in the evaluation of complexation between metal cations and HS. The molar ratios of target ions and Fe^{3+} should be at least 100 for divalent cations and 10 for trivalent and tetravalent cations to prevent the underestimation. Under such conditions, average differences in metal–HA fractions with and without Fe^{3+} are less than 1%. To achieve such conditions, careful purification of HS is required.

This research was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science. XAFS measurement was performed with the approval of the Photon Factory, KEK (Proposal Nos. 2006G347 and 2007G670).

References and Notes

1 E. Tipping, *Cation Binding by Humic Substances*, Cambridge University Press, Cambridge, **2002**.
2 http://www.ihss.gatech.edu/.
3 J. I. Kim, G. Buckau, G. H. Li, H. Duschner, N. Psarros, *Fresenius J. Anal. Chem.* **1990**, *338*, 245.
4 L. L. Stookey, *Anal. Chem.* **1970**, *42*, 779.
5 A. J. Peters, J. Hamilton-Taylor, E. Tipping, *Environ. Sci. Technol.* **2001**, *35*, 3495.
6 N. Senesi, G. Sposito, J. P. Martin, *Sci. Total Environ.* **1986**, *55*, 351.
7 Y. Yamamoto, Y. Takahashi, H. Shimizu, *Geochem. J.*, under review.
8 A. W. P. Vermeer, J. K. McCulloch, W. H. Riemsdijk, L. K. Koopal, *Environ. Sci. Technol.* **1999**, *33*, 3892.
9 T. Saito, L. K. Koopal, S. Nagasaki, S. Tanaka, *Environ. Sci. Technol.* **2005**, *39*, 4886.
10 D. J. Mackey, A. Zirino, *Anal. Chim. Acta* **1994**, *284*, 635.
11 K.-K. Au, A. C. Penisson, S. Yang, C. R. O'Melia, *Geochim. Cosmochim. Acta* **1999**, *63*, 2903.
12 J. D. Ritchie, E. M. Perdue, *Geochim. Cosmochim. Acta* **2003**, *67*, 85.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
14 E. Tipping, *Aquat. Geochem.* **1998**, *4*, 3.

Published on the web (Advance View) February 21, 2009; doi:10.1246/cl.2009.278