

# REMOVAL AND FRACTIONATION CHARACTERISTICS OF DISSOLVED IRON IN ESTUARINE MIXING ZONE

TERASHIMA M.<sup>1</sup> AND NAGAO S.<sup>2</sup>

<sup>1</sup> *Research Institute for Humanity and Nature*

<sup>2</sup> *Faculty of Environmental Earth Science, Hokkaido University*

## 1. INTRODUCTION

The elucidation of fate of iron in estuaries is a key subject for understanding the impact of iron in river water on the bio-productivity in marine environments. In previous studies, more than 90% of the total dissolved iron, defined as the fractions below 400 or 700 nm, has been found to be removed in estuaries via the coagulation induced by an increase in salinity (Sholkovitz, 1976, 1978; Sholkovitz and Copland, 1981). On the other hand, only less than 10% of the dissolved iron remains in the aqueous phase even at salinity of seawater level. Although this fraction may serve as a nutrient for the phytoplankton in marine environments, available information on the chemical form determining the bioavailability is incomplete.

In river water systems, humic substances (HSs), which comprise more than 50% of the dissolved organic carbon (Thurman, 1985), are one of major factors determining the chemical form of iron. For example, the iron in river waters can dissolve as the complexes with HSs (Waite and Morel, 1984; da Silva et al., 1998; Tipping et al., 2002) and the suspended particles such as iron (hydro)oxides protected by HSs (Tipping, 1981). In the estuarine system, such difference in the form may result in the fractionation between the complexes and suspended particles during the mixing with seawater, because the coagulation characters will be significantly different from each other. In general, the colloidal coagulation can preferentially occur in colloids with larger size and higher charge density, obeying the DLVO theory (Hunter, 2001). In previous works, the average hydrodynamic radius of HSs have been evaluated to be below 10 nm (Lead et al., 2000; Ngo Manh et al., 2001; Pranzas et al., 2003; Benedetti et al., 2003), but a few hundred nm for the suspended particles of iron (Nomizu et al., 1988; Baalousha et al., 2006). Thus, these findings suggest that the complexes of iron with HSs could preferentially remain in the aqueous phase in the estuarine condition.

In this work, to clarify the chemical form of iron remaining in the estuary, the removal and fractionation characteristics of iron and HSs in the Bekanbeushi River in Hokkaido were investigated on the basis of the mixing with artificial seawater. The size exclusion chromatography – UV detection (SEC–UV) was applied to monitor the concentration or to identify the removed fraction of HSs (Nagao et al., 2001). The size fractionations of iron and HSs were performed to clarify the form as well as size fractions of remaining iron. Moreover, the size distribution of iron complexes with fulvic acid (FA), which was isolated from the Bekanbeushi River water, was characterized by the size fractionation, and the removal characteristic was elucidated to verify the stability in the estuarine condition.

## 2. REMOVAL CHARACTERISTICS OF FE AND HS IN BEKANBEUSHI RIVER WATER

Fig.1 shows the concentration of dissolved iron in the river water sample as a function of salinity. The concentration gradually decreased with increasing salinity. At the salinity of seawater level (33.7), approximately 86% of the total dissolved iron was removed, while the remaining 14% remained in the aqueous phase. This result shows that no the dissolved iron in the river water is completely removed in the estuarine condition. On the other hand, only 20% of the absorbance at 280 nm wavelength in the water sample disappeared at the salinity of 33.7. In addition, the degree of disappearance was good agreement with the result of SEC measurements. These indicate that the majority of HSs in the river water sample dissolves stably in the aqueous phase at salinity of seawater level.

Fig. 2 shows the removal kinetic curves of iron and HSs during the mixing with artificial seawater. The kinetic curves were different from each other. The slightly amount of HSs was rapidly removed from the mixture to reach the plateau after 5 min, while the dissolved iron was more slowly removed to reach the plateau after 30 min. This discrepancy means that the dissolved iron and HSs are independently removed during the mixing with the artificial seawater. Thus, these results suggest that the fractionation between the suspended particles of iron and the complexes with HSs can occur in the estuary.

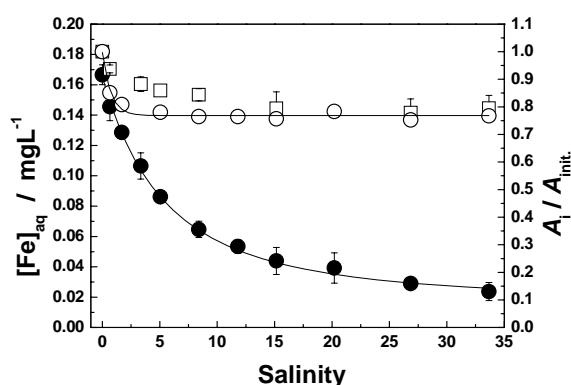


Fig. 1 The concentration of Fe (●) and residual ratio of HSs in the Bekanbeushi River water as a function of salinity. Residual ratio: absorbance at 280 nm (○), peak area in SEC (□).

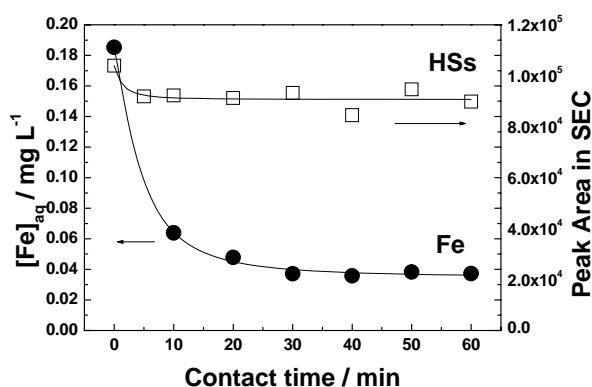


Fig. 2 Removal kinetics of dissolved Fe and HSs in the Bekanbeushi River water.

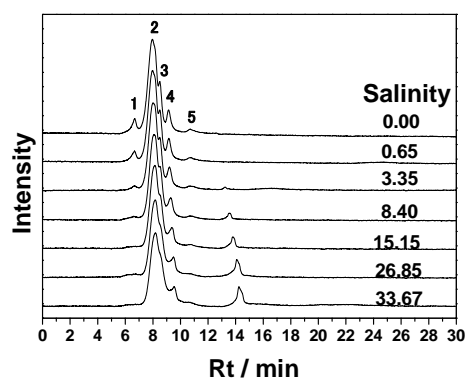


Fig. 3 SEC chromatograms of HSs in the Bekanbeushi River water at each saline conditions.

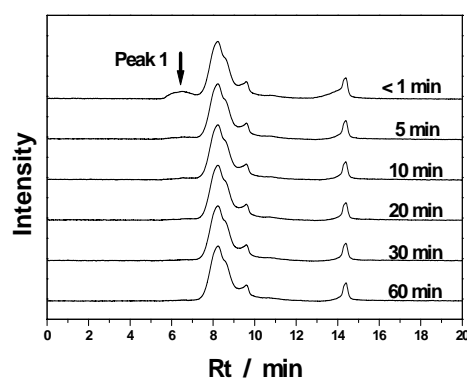


Fig. 4 SEC chromatograms of HSs at a variety of contact time. Salinity: 33.7.

The SEC chromatograms of HSs in the river water sample at each salinity level are shown in Fig. 3. In the river water sample mixed with pure water (i.e. salinity 0.0), the major peaks from 2 to 5 corresponded to that of FA, which was isolated from the river water. The peak 1 was observed in the chromatograms of humic acid (HA) isolated from the river water. The peak 6 was a system peak due to the change of density in the sample solution. Thus, the SEC chromatogram obtained is attributed to the dissolved HSs in the river water. When the salinity increased, the peak 1 disappeared at the salinity of 3.35. In addition, the peak 1 also disappeared after 5 min, as shown in Fig. 4. Thus, these suggest that one of portion in HA is removed, while the FA remains in the aqueous phase at salinity of seawater level.

As shown in Fig. 2, the fractionation between the complexes with HSs and suspended particles of iron could occur during the mixing with artificial seawater. This fractionation may be explained on the basis of the difference in the size distribution character, as described above. Thus, we examined the size fractionation by using eight types of filters with different pore size (e.i. 5 KDa – 400 nm). Fig. 5 shows the size distributions of iron and HSs in the river water sample. The size distributions were significantly different from each other. Approximately 94% of the dissolved iron was enriched in the size range from 20 to 400 nm, while only 6% of the dissolved iron was distributed below 20 nm. On the other hand, the majority of HSs (i.e. 89%) were enriched in the fractions below 20 nm. In the comparison between the distribution and removal ratios of iron or HSs, the distribution ratios in the range from 20 to 400 nm were approximated to the removal ratios in Fig. 1. In addition, the peak 1 in the difference SEC chromatograms (Fig. 6) was detected in the size fractions from 20 to 400 nm. These results indicate that the iron fractions from 20 to 400 nm are removed from the aqueous phase as a result of the mixing with seawater. As the result followed by this, the distribution ratios of iron and HSs below 20 nm were approximated to the residual ratios of iron and HSs (Fig. 1). Therefore, the dissolved irons below 20 nm are identified as the remaining fractions in the estuarine mixing zone. Also, this result suggests that the fractions distributed below 20 nm are due to the complexes of iron with HSs.

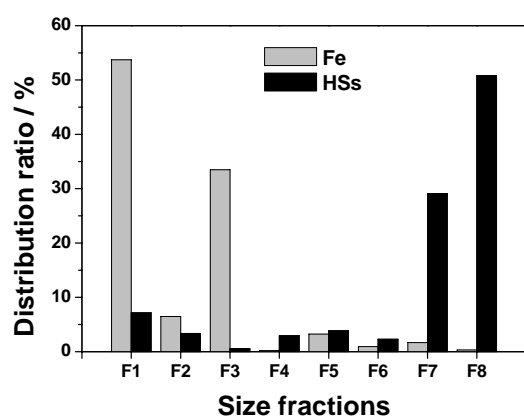


Fig. 5 Size distributions of dissolved Fe and HSs in the Bekanbeushi River water. F1 200 – 400 nm, F2 100 – 200 nm, F3 20 – 100 nm, F4 300KDa – 20 nm, F5 100KDa – 300KDa, F6 30KDa – 100KDa, F7 5KDa – 30KDa, F8 <5KDa.

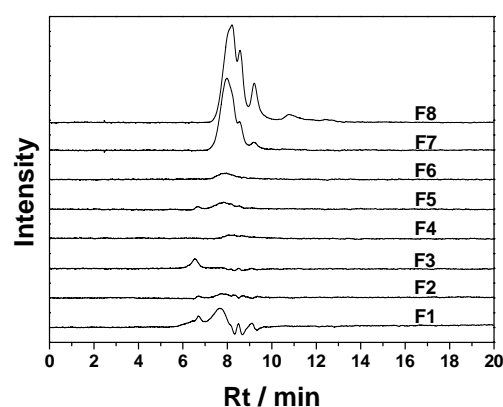


Fig. 6 Difference SEC chromatograms of HSs at each size fraction. F1 200 – 400 nm, F2 100 – 200 nm, F3 20 – 100 nm, F4 300KDa – 20 nm, F5 100KDa – 300KDa, F6 30KDa – 100KDa, F7 5KDa – 30KDa, F8 <5KDa.

### 3. REMOVAL CHARACTERISTICS OF FE AND HSS IN ARTIFICIAL RIVER WATER

To clarify the size distribution and removal characteristics of iron complex with HSs, the artificial river water was prepared by mixing  $\text{FeCl}_3$  with FA in the aqueous solution including the major cations in the Bekanbeushi River water (i.e.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ). Here, FA was chosen as a typical example of aquatic HSs, because the FA comprises the major fraction of HSs in the river water system. Fig. 7 shows the size distributions of iron and FA in the artificial river water. Approximately 82% of the dissolved iron was enriched in the fractions from 20 to 400 nm, while 94% of the total FA was distributed below 20 nm. The size distribution of FA in the absence of iron showed the same pattern as that in the presence of iron (data not shown). Moreover, 95% of the total iron in the absence of FA was enriched in the fractions above 200 nm (data not shown). Furthermore, the distribution ratio of dissolved iron below 20 nm in the presence of FA increased with decrease in pH from 7.2 to 4.0 (data not shown). Thus, these results reveal that the complexes of iron with FA are assigned to the fractions below 20 nm, while the flocks such as iron hydroxide are distributed into the fractions above 20 nm. The residual ratios of iron and FA as a function of salinity are shown in Fig. 8. The dissolved iron was gradually removed by an increase in salinity, while the FA was slightly removed from the aqueous phase. At the salinity of 33.7, the residual ratios were evaluated to be 0.57 for iron and 0.94 for FA, respectively. In the comparison between the residual and distribution ratios of iron or FA, the residual ratios were good agreements with the distribution ratios below 100 nm:  $[\text{Fe}]_{\text{aq}}/[\text{Fe}]_{\text{tot.}} \approx [\text{Fe}]_{<100\text{nm}}/[\text{Fe}]_{\text{tot.}}$ , and  $[\text{FA}]_{\text{aq}}/[\text{FA}]_{\text{tot.}} \approx [\text{FA}]_{<100\text{nm}}/[\text{FA}]_{\text{tot.}}$ . Based on this result, the iron fractions below 20 nm remain in the aqueous phase at salinity of seawater level. Thus, these results demonstrate that the iron complexes with FA in the river water sample preferentially remain in the aqueous phase after the mixing with seawater.

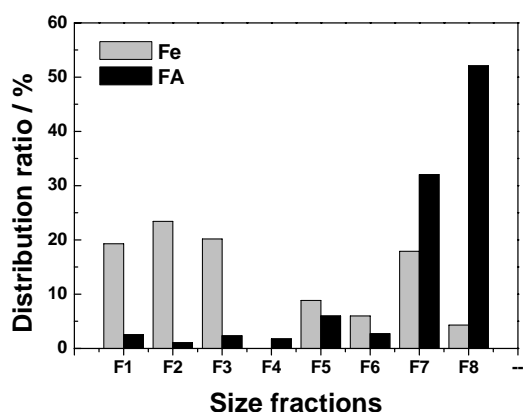


Fig. 7 Size distribution of Fe and FA in the artificial river water. Initial concentrations:  $0.1 \text{ mg L}^{-1}$  for Fe,  $10 \text{ mg L}^{-1}$  for FA. pH: 7.2. F1 200 – 400 nm, F2 100 – 200 nm, F3 20 – 100 nm, F4 300KDa – 20 nm, F5 100KDa – 300KDa, F6 30KDa – 100KDa, F7 5KDa – 30KDa, F8 <5KDa.

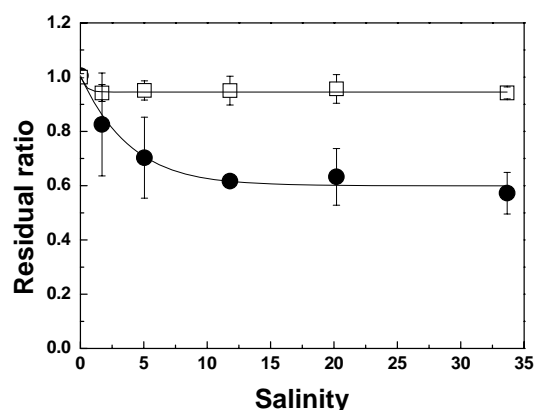


Fig. 8 Residual ratios of Fe (●) and FA (□) as a function of salinity. Initial concentrations:  $0.1 \text{ mg L}^{-1}$  for Fe,  $10 \text{ mg L}^{-1}$  for FA.

#### 4. CONCLUSION

The iron fractions distributed below 20 nm in the Bekanbeushi River water sample remained in the aqueous phase at salinity of seawater level. The iron fractions would be due to the complexes with FA. These results demonstrate that the iron complexes with FA in the river water sample preferentially remain in the estuarine mixing zone, but not be removed. Thus, our findings will be useful for understanding the impact of dissolved iron in river waters on the bio-productivity in marine environments.

#### REFERENCES

- Baalousha, M., Kammer, F. V. D., M.-Heino, M., Baborowski, M., Hofmeister, C., Le Coustumer, P., Size-based speciation of natural colloidal particles by flow field flow fraction, inductively coupled plasma-mass spectroscopy, and transmission electron spectroscopy/X-ray energy dispersive spectroscopy: colloids-trace element interaction. *Environ. Sci. Technol.* **2006**, *40*, 2156 – 2162.
- Benedetti, M. F., Ranville, J. F., Allard, T., Bednar, A. J., Menguy, N., The iron status in colloidal matter from the Rio Negro, Brazil. *Colloids Surf. A* **2003**, *217*, 1 – 9.
- da Silva, J. C. G. E., Machado, A. A. S. C., and Oliveira, C. J. S., Effect of pH on complexation of Fe(III) with fulvic acids. *Environ. Toxicol. Chem.* **1998**, *17*, 1268 – 1273.
- Hunter, R. J., Foundations of Colloid Science, Oxford Univ Pr (Sd), **2001**.
- Lead, J., Wilkinson, K. J., Starchev, K., Canonica, S., and Buffle, J., Determination of diffusion coefficients of humic substances by fluorescence correlation spectroscopy: role of solution conditions. *Environ. Sci. Technol.* **2000**, *34*, 1365 – 1369.
- Nagao, S., Matsunaga T., Suzuki Y., and Hiraki, K., Convenient method of UV absorbing organic materials in river waters by high-performance gel permeation chromatography. *Chikyukagaku (Geochemistry)* **2001**, *35*, 107 – 120.
- Ngo Manh, Th., Geckeis, H., Kim, J. I., Beck, H. P., Application of the flow field flow fractionation (FFFF) to the characterization of aquatic humic colloids: evaluation and optimization of the method. *Colloids Surf. A* **2001**, *181*, 289 – 301.
- Nomizu, T., Goto, K., and Mizuike, A., Electron microscopy of nanometer particles in freshwater. *Anal. Chem.* **1988**, *60*, 2653 – 2656.
- Pranzas, P. K., Willumeit, R., Gehrke, R., Thieme, J. and Knöchel, A., Characterisation of structure and aggregation processes of aquatic humic substances using small-angle scattering and X-ray microscopy. *Anal. Bioanal. Chem.* **2003**, *376*, 618 – 625.
- Sholkovitz, E. R., Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta* **1976**, *40*, 831 – 845.
- Sholkovitz, E. R., Boyle, E. A., and Price, N. B., The removal of dissolved humic acids and iron during estuarine mixing. *Earth and Planetary Science Letters* **1978**, *40*, 130 – 136.

- Sholkovitz, E. R., and Copland, D., The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochim. Cosmochim. Acta* **1981**, *45*, 181 – 189.
- Thurman, E. M., *Organic geochemistry of natural waters*, Martinus Nijhoff / Dr W. Junk Publishers, Dordrecht, **1985**, pp. 103 – 110.
- Tipping, E., The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* **1981**, *45*, 191 – 199.
- Tipping, E., Rey-Castro, C., Bryan, S., and Hamilton-Taylor, J., Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochim. Cosmochim. Acta* **2002**, *66*, 3211 – 3224.
- Waite, T. D., and Morel, F. M. M., Ligand exchange and fluorescence quenching studies of the fulvic acid – iron interaction, Effects of pH and Light. *Anal. Chim. Acta* **1984**, *162*, 263 – 274.