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Title(English)	Effect of dissolved organic matter properties on iron redox kinetics in natural and effluent waters
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Thesis outline

Effect of dissolved organic matter properties on iron redox kinetics in natural and effluent waters

[Chapter 1] Iron (Fe) is one of the essential trace metals for the growth of microorganisms. Most dissolved Fe is bound to dissolved organic matter (DOM) in natural waters including seawater and coastal waters. However, principal factors of DOM molecular compositions and origins that influence Fe redox transformation kinetics in natural waters remain unclear. The effect of dissolved organic matter properties on Fe transformation kinetics in natural and effluent waters are examined in this thesis.

[Chapter 2] The water quality factors and its effect on Fe redox kinetics in natural waters were extensively reviewed. Dissolved Fe bound to organic ligands and its effect on the Fe redox transformation dynamics in the river and coastal waters is strongly influenced by the DOM properties. A detailed investigation on Fe redox transformation dynamics is required particularly in relating environmental factors and DOM quality and quantity.

[Chapter 3] Fe redox rate constants were determined in well-characterized humic substances (HS) from various origins and the correlations between Fe redox reactions and HS chemical properties were investigated. Results showed that rate of Fe(II) oxidation (by dissolved oxygen) was found to be accelerated in the presence of various types of standard humic and fulvic acids compared with inorganic Fe(II) at circumneutral pH (i.e., pH 8.0). Photo-reduction of organically complexed Fe(III) showed the highest rate at lower pH level (i.e., pH 7.0). Correlation analysis between Fe redox reactions and chemical properties of HS showed that Fe(II) oxidation was strongly negatively correlated with aromaticity.

[Chapter 4] Fe(II) oxidation was further investigated in Sagami River basin samples consisted of river waters impacted to a moderate and minor extent by anthropogenic activities and also treated effluents. Fe(II) oxidation rate was highest for effluents, followed by reservoir and river waters, with less human-impacted tributary waters showed the lowest oxidation rate. At pH 8.0, the addition of MWWTP-derived humic-type DOM to anthropogenically less-influenced tributary water resulted in substantial increase in the oxidation rate. Significant negative correlation observed between the $SUVA_{254}$ and Fe(II) oxidation rate constant (pH 8.0) suggests a potential effect of humic-type DOM with low $SUVA_{254}$ (high aliphatic content) on Fe(II) oxidation in natural and effluent waters.

[Chapter 5] To further investigate Fe(II) oxidation in a more dynamic environment, freshwater (e.g., river water and wastewater effluent) and coastal seawater were collected from Shizugawa Bay watershed. The oxidation rates for freshwater were generally greater than those for coastal seawater at comparable pH values. The substantial decline in oxidation rate constant after the removal of humic-type (allochthonous) DOM suggested that this hydrophobic DOM is a key factor that accelerates the Fe(II) oxidation in the freshwater samples. Observed lower oxidation rates for coastal seawater compared with freshwater and organic ligand-free seawater were likely associated with microbially derived

autochthonous DOM, and the variation of Fe(II) oxidation at a fixed pH was best described by fluorescence index that represents the proportion of autochthonous and allochthonous DOM in natural waters. Fe(II) oxidation was also found to be slower in the presence of cellular exudates from phytoplankton.

In conclusion, the results presented in this thesis highlight the importance of DOM compositions and origins in controlling the transformation kinetics of Fe in a range of aquatic environments.