

Seasonal and spatial variation of dissolved iron transformation kinetics in the Shizugawa bay and its adjacent rivers

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Importance of Fe as an essential nutrient for microorganisms is well recognized such as cellular respiration, photosynthesis and nitrogen fixation. However, the extremely low solubility of thermodynamically stable Fe(III) in oxygenated and circumneutral pH natural waters resulted in low concentration of dissolved Fe in some coastal and oceanic seawaters. The bioavailability of Fe in natural waters can be affected by concentration of dissolved Fe and its redox kinetics, given that Fe(II) has much higher solubility and thus higher bioavailability than Fe(III) does. In the river-coastal dynamic system, changes in land cover, salinity gradients, types of riverine input or organic matter, and seasonal changes may affect to the Fe oxidation kinetics as the Fe(II) oxidation is affected by water qualities such as pH and organic matter. In this study, we mainly focus on the Fe(II) oxidation kinetics in the river-coastal system in order to grasp the seasonal and spatial scales of Fe bioavailability between two different aquatic environments.

The study area was located in Shizugawa bay, Miyagi prefecture (N38° E141°) and totally 6 stations from near to offshore (SB-1 to SB-6) were selected as sampling stations. Also, this study included upstream and downstream of three rivers: Hachiman upstream (HR Up) and downstream (HR Down), Oritate upstream (OR Up) and downstream (OR Down), and Mizushiri upstream (MR Up) and downstream (MR Down). All the surface water samples were collected manually with acid-wash 1 L Nalgene bottles for three consecutive seasons starting from summer year 2014. All water samples were filtered through 0.45 micrometer Milipore membrane and stored in the dark at 4 °C for further analysis.

Fe(II) oxidation rates were determined by measuring time course of Fe(II) concentration using a flow injection analysis (FIA) system with a luminal chemiluminescence detection. Water sample and luminol reagent were both simultaneously pumped into the system using a peristaltic pump with flow rate at 2.4 mL per min. Water sample and luminol mixing was conducted in the flow cell situated at the front of a photomultiplier tube (PMT, Hamamatsu) and the PMT signal was recorded by WA control v91 software. Calibration was conducted for each water sample from three standards addition of Fe(II) (varied between 0.5 and 40 nM depending on signal response of each water sample). The initial signal (i.e., signal when Fe(II) was added) was obtained by extrapolation of signal data collected after 50 seconds back to time zero using a regression line which was obtained from time versus log-transformed signal data. The linear response of initial signal to the nominal initial Fe(II) concentration was found. Thus, the signal value was converted to the Fe(II) concentration by using the linear regression equation. The Fe(II) oxidation rate constant ($M^{-1} s^{-1}$) for each standard Fe addition was derived by assuming a pseudo-first order reaction.

Fe(II) oxidation rates in Shizugawa for three consecutive seasons from summer to winter were shown in Figure 1. The Fe(II) oxidation rates shown here are the average of three standards addition of Fe(II). A distinct seasonal trend of Fe(II) oxidation was observed particularly in autumn season with higher Fe(II) oxidation rates. Generally, Fe(II) oxidation is a pH-dependent reaction. Supposedly, the oxidation rate at seawater pH (>7.9) should be higher than that for typical freshwater pH (e.g. pH ranges between 6.8 and 7.9 in the river investigated). In our study, however, the oxidation rates in coastal seawater tended to be slower compared to those in freshwater. The results of Fe(II) oxidation in freshwater indicated that water quality variables other than pH affect the oxidation process. These factors may include dissolved organic matter concentration and its chemical properties (binding strength) and/or interaction between Fe and other trace metals which will be investigated further.

Keywords: dissolved iron, oxidation, river, coastal

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