

Speciation of iron(II) in oxic inland water

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Introduction

In oxic freshwater, iron(II) is thought to be a minor component in total iron concentration because it is immediately oxidized to iron(III) species in hydrated ionic form. But iron(II) has higher potential bioavailability for primary production than iron(III), because of its high solubility and relatively organic weak complexation compared with that of iron(III) which sometimes forms very stable organic complex unavailable for phytoplankton. In practice, iron(II) was detected in some oxic freshwater. In Lake Biwa (Shiga, Japan), 5 to 20 nmol/L of iron(II) was determined by solid phase extraction as PDTS (Ferrozine) complex and spectrophotometry (Maruo M., Obata H. et al., *Verh. Internat. Verein. Limnol.*, 30, 1379-1383, 2010). Also in Lake Kinneret (Israel), some ten nmol / L of Fe(II) was detected with the same reagent. On the other hand, Iron (II) was detected in the range 0.1 to 0.9 nmol/L by flow injection with chemiluminescence detection (Emmenegger L. et al., *Limnol. Oceanogr.*, 46, 49-61, 2001) in daytime in surface water of Lake Greifen (Switzerland). Iron speciation in freshwater is largely regulated by pH, dissolved oxygen and characteristics of dissolved organic compounds in the water, so the difference in the concentration of Fe(II) between these two methods might be caused by chemical species of iron(II) detected. In this study, iron(II) in freshwater was determined by these two methods simultaneously.

Experimental

In Lake Biwa (av. depth 41.2 m, max. 103.6 m), waters were sampled at station T1 (35°22'N; 136°6'E; maximum depth 90 m) in the north basin of the lake on Feb., 2009 and Sep. 2010 by the research ship Hassaka (Univ. of Shiga Pref.). All water samples were collected in a metal-free Niskin sampling bottle. Collected samples were filtered immediately shipboard by a capsule filter (pore size 0.2 micrometer). Iron (II) measurement by chemiluminescence (King D.W. et al., *Environ. Sci. Technol.*, 29, 818-824, 1995) was performed onboard. For spectrophotometric method (Maruo M. et al., *Bunseki Kagaku*, 59, 1143-1147, 2010), buffer (pH 6.8) and PDTS solution were added to filtered water. Treated samples were ice-cooled to avoid oxidation of iron(II). At the laboratory, samples were passed through the Sep-pak PS-1 column to concentrate iron(II)-PDTS complex. The complex was eluted from the column and eluate was introduced to a long pass flow cell (1000 mm pathlength; LPC-1, Ocean Optics Co.), and absorption at 562 nm was read by a spectrophotometer (USB4000-VIS-NIR, Ocean Optics).

Results and Discussion

Iron(II) concentrations obtained from two methods were clearly different from each other. Chemiluminescence detection gave iron(II) concentrations below 1 nmol/L, while spectrophotometry based on Iron(II)-PDTS complexation showed 10 - 100 times higher values than those from chemiluminescence detection. This difference might be caused by complexation of iron(II) with some ligands in natural water or existence of reactive colloidal iron hydroxides. Without addition of the reagents, iron(II) concentration in Lake Biwa waters showed no significant change within 6 hrs after sampling in a dark condition after filtration (Maruo et al., 2011). This finding also suggests a stability of iron(II) by complexation with natural ligands in the water. Concerning the strong ligands for iron(II), the effect of natural strong ligand like EDTA may retard the ligand exchange of iron(II) into PDTS (Oji B., Yoh M., *Abstracts of 70th Meeting of the Japanese Society of Limnology*, 202, 2005). We also made sure that in iron(II) concentration at 25-100 nmol/L, it took 48hrs to form iron(II)-PDTS complex completely. Even by PDTS method, some portion of iron(II) strongly complexed with organic ligands might be missed.

Keywords: oxic environment, inland water, iron(II), complexation, Lake Biwa, chemical analysis