

# Division of Environmental Chemistry – Hydrospheric Environment Analytical Chemistry –

[http://inter3.kuicr.kyoto-u.ac.jp/scope\\_E.html](http://inter3.kuicr.kyoto-u.ac.jp/scope_E.html)



Prof  
SOHRIN, Yoshiki  
(D Sc)



Assoc Prof  
UMETANI, Shigeo  
(D Sc)



Assist Prof  
TAKANO, Shotaro  
(D Sc)



Techn Staff  
MINAMI, Tomoharu  
(D Eng)

## Students

ZHENG, Linjie (D1)  
MURATA, Rena (M2)

SASAKI, Masanobu (M2)  
TSUJISAKA, Makoto (M1)

UEHARA, Wataru (M1)

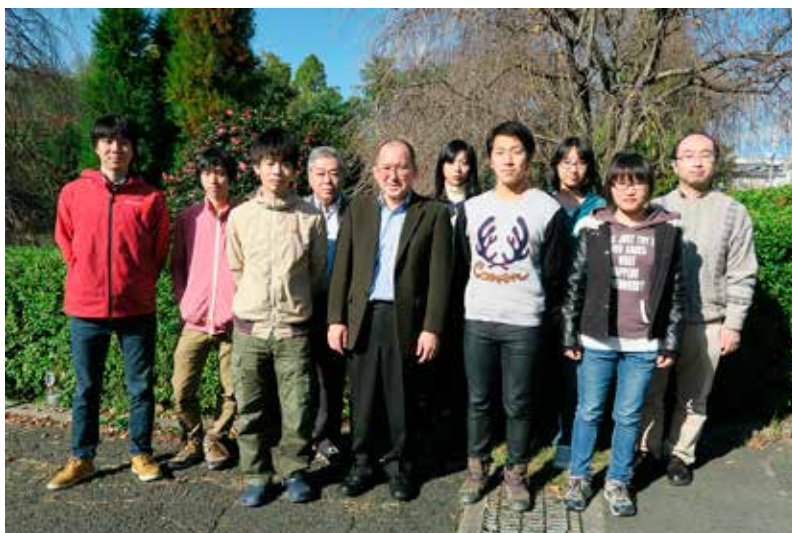
## Scope of Research

(i) Biogeochemistry of trace elements in the hydrosphere: Novel analytical methods are developed for trace metals and their isotopes. Distribution of trace elements in the hydrosphere and their effects on the ecosystem are investigated. The study also covers hydrothermal activity, deep biosphere, and paleocean.

(ii) Ion recognition: Novel ligands and ion recognition system are designed, synthesized, and characterized.

### KEYWORDS

Marine Chemistry  
Analytical Chemistry  
Trace Elements  
Stable Isotopes  
Metal Ion Recognition



## Selected Publications

Minami, T.; Konagaya, W.; Zheng, L.; Takano, S.; Sasaki, M.; Murata, R.; Nakaguchi, Y.; Sohrin, Y., An Off-line Automated Preconcentration System with Ethylenediaminetriacetate Chelating Resin for the Determination of Trace Metals in Seawater by High-resolution Inductively Coupled Plasma Mass Spectrometry, *Anal. Chim. Acta*, **854**, 183-190 (2015).

Takano, S.; Tanimizu, M.; Hirata, T.; Sohrin, Y., Isotopic Constraints on Biogeochemical Cycling of Copper in the Ocean, *Nat. Commun.*, **5**, [5663-1]-[5663-7] (2014).

Nägler, T. F.; Anbar, A. D.; Archer, C.; Goldberg, T.; Gordon, G. W.; Greber, N. D.; Siebert, C.; Sohrin, Y.; Vance, D., Proposal for an International Molybdenum Isotope Measurement Standard and Data Representation, *Geostand. Geoanal. Res.*, **38**, 149-151 (2014).

Takano, S.; Tanimizu, M.; Hirata, T.; Sohrin, Y., Determination of Isotopic Composition of Dissolved Copper in Seawater by Multi-collector Inductively Coupled Plasma Mass Spectrometry after Pre-concentration Using an Ethylenediaminetriacetic Acid Chelating Resin, *Anal. Chim. Acta*, **784**, 33-41 (2013).

Vu, H. T. D.; Sohrin, Y., Diverse Stoichiometry of Dissolved Trace Metals in the Indian Ocean, *Sci. Rep.*, **3**, [1745-1]-[1745-5] (2013).

Firdaus, M. L.; Minami, T.; Norisuye, K.; Sohrin, Y., Strong Elemental Fractionation of Zr-Hf and Nb-Ta across the Pacific Ocean, *Nature Geosci.*, **4**, 227-230 (2011).

## Trace Elements Influenced by Environmental Changes in Lake Biwa: (I) Seasonal Variations under Suboxic Hypolimnion Conditions during 2007 and 2009

Dissolved oxygen (DO) in the Lake Biwa hypolimnion reached its lowest level of  $< 1 \text{ mg kg}^{-1}$  in 2007. Here we report the variations of total dissolvable (TD), dissolved (D), and labile particulate (LP) fractions of Al, Si, P, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo, W, and U in Lake Biwa between 2007 and 2009. Al and Fe species were predominantly in the form of LP-Al and LP-Fe, with a strong correlation with one another ( $r = 0.99$ ), suggesting that weathering of aluminous minerals and supply of clay mineral particles mainly control the distribution of Al and Fe. Although D-Al increased in the summer epilimnion, D-Fe was relatively low, probably as a result of uptake by plants. Reductive release of Fe from the bottom was not seen. Mn was also dominated by LP-Mn, but this fraction showed a different distribution than LP-Al and LP-Fe. The D-Mn and LP-Mn concentrations varied by factors of 700–1000, showing marked increases in bottom water during stratification in 2007. We expect  $\text{Mn}^{2+}$  to have been released from the sediments and oxidized by DO in bottom water. Ni, Cu, Zn, and Cr, which exist as cationic species, had LP/TD ratios of 0.1–0.7 and relatively uniform distributions. Si, P, V, As, Mo, W, and U, which form oxoacid species, had LP/TD ratios of 0–0.8. Si, P, and As were characterized by a nutrient-like profile; V, W, and U showed summer maxima in the epilimnion; and Mo had a uniform distribution. TD-Mo increased in bottom water in company with TD-Mn, while TD-V and TD-W showed significant decreases. The results are likely attributed to differences in adsorption of these elements onto manganese oxides and iron hydroxides.

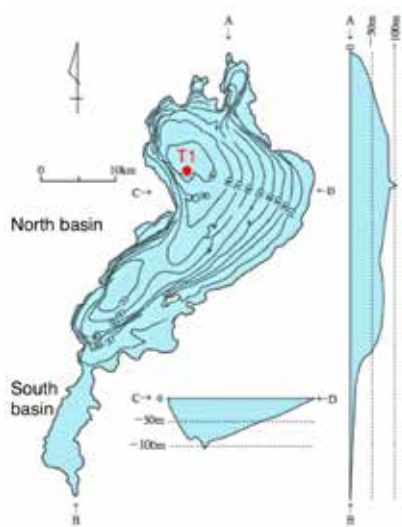


Figure 1. Location of the sampling station T1.

## Trace Elements Influenced by Environmental Changes in Lake Biwa: (II) A Regime Shift in the Hypolimnion over the Last Half-century

The history of the deep north basin of Lake Biwa extends over 430,000 years. Although it has probably been oxic and oligotrophic since its formation, human impact has been changing lake conditions. In this paper, we discuss long-term changes in the chemistry of bottom water by compiling literature and through our own data over the last half-century. Long-term records show an increase in temperature, a decrease in DO, and an increase in nutrients in bottom water. The stoichiometry between oxygen and nutrients indicates that changes are basically consistent with aerobic decomposition of organic matter. These changes are most likely the result of global warming and local eutrophication. Of particular note, yearly minimum DO concentrations of less than  $50 \mu\text{mol kg}^{-1}$  have started to occur frequently at  $\sim 90 \text{ m}$  depth since 1999. Manganese concentrations in bottom water are at their minimum during the turnover period and at a maximum during the late stratification period each year. Yearly minimum Mn concentration has been within a narrow range over the last 30 years ( $0.25 \pm 0.07 \mu\text{mol kg}^{-1}$ ,  $n = 12$ ). However, abnormally high Mn concentrations (up to  $9.3 \mu\text{mol kg}^{-1}$ ) were observed in 2007, caused by reductive release of a substantial amount of Mn from suboxic sediments and subsequent oxidation in bottom water. The concentration of arsenic has gradually increased over the last 20 years in a similar manner with a homologous element of phosphorus, resulting in an observed range of  $17\text{--}29 \text{ nmol kg}^{-1}$  in 2010. The accumulation rate was  $\sim 0.8 \text{ nmol kg}^{-1} \text{ yr}^{-1}$  for As and  $\sim 6 \text{ nmol kg}^{-1} \text{ yr}^{-1}$  for P.



Figure 2. Mr. Nakajima and a water sampling bottle on board the training investigation ship Hassaka, belonging to the University of Shiga Prefecture.