

# Division of Environmental Chemistry

## – Hydrospheric Environment Analytical Chemistry –

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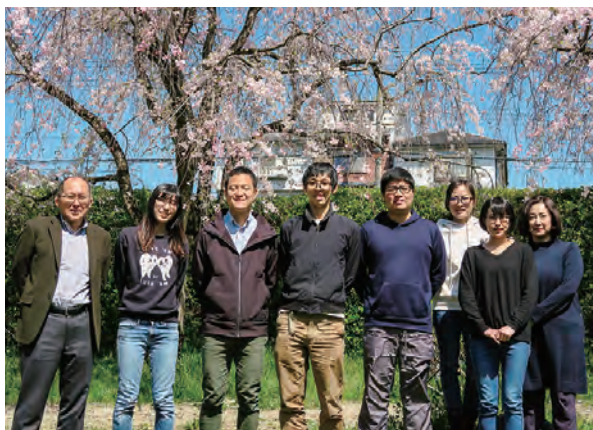
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### Guest Res Assoc

MAHBOOB, Alam    Banaras Hindu University, India, 22 January–20 March

## 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

Tsujsisaka, M.; Takano, S.; Murayama, M.; Sohrin, Y., Precise Analysis of the Concentrations and Isotopic Compositions of Molybdenum and Tungsten in Geochemical Reference Materials, *Anal. Chim. Acta*, **1091**, 146-159 (2019).  
Takano, S.; Liao, W.-H.; Tian, H.-A.; Huang, K.-F.; Ho, T.-Y.; Sohrin, Y., Sources of Particulate Ni and Cu in the Water Column of the Northern South China Sea: Evidence from Elemental and Isotope Ratios in Aerosols and Sinking Particles, *Mar. Chem.*, **219**, 103751 (2020).  
Liao, W.-H.; Takano, S.; Yang, S.-C.; Huang, K.-F.; Sohrin, Y.; Ho, T.-Y., Zn Isotope Composition in the Water Column of the Northwestern Pacific Ocean: The Importance of External Sources, *Global Biogeochem. Cy.*, **34**, e2019GB006379 (2020).  
Fujiwara, Y.; Tsujisaka, M.; Takano, S.; Sohrin, Y., Determination of the Tungsten Isotope Composition in Seawater: The First Vertical Profile from the Western North Pacific Ocean, *Chem. Geol.*, **555**, 119835 (2020).  
Nakaguchi, Y.; Ikeda, Y.; Sakamoto, A.; Zheng, L.; Minami, T.; Sohrin, Y., Distribution and Stoichiometry of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the East China Sea, *Journal of Oceanography*, doi: 10.1007/s10872-020-00577-z (2020).

## Sources of Particulate Ni and Cu in the Water Column of the Northern South China Sea

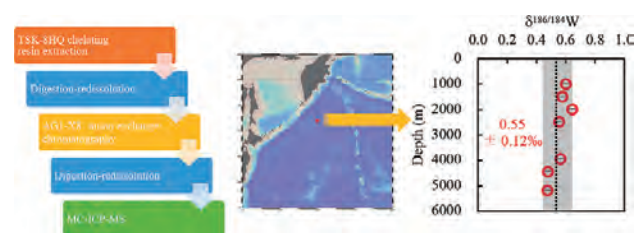
We present isotope ratios of Ni ( $\delta^{60}\text{Ni}$ ) and Cu ( $\delta^{65}\text{Cu}$ ) in sinking particles, aerosols, and seawater collected from the northern South China Sea. In aerosols,  $\delta^{60}\text{Ni}$  values are in the range +0.05‰ to +0.56‰, and  $\delta^{65}\text{Cu}$  values are in the range -0.33‰ to +0.83‰. The isotope ratios are different from those of lithogenic materials, indicating that the aerosols are anthropogenic in origin. In sinking particles collected at depths of 2,000 and 3,500 m,  $\delta^{60}\text{Ni}$  values are in the range +0.01‰ to +0.54‰ at 2,000 m and -0.18‰ to +0.54‰ at 3,500 m, and the values exhibit a similar temporal variation pattern between 2,000 and 3,500 m. Based on the significant correlation between  $\delta^{60}\text{Ni}$  and the ratio of P/Ni or organic-C/Ni, we hypothesize that the main sources of Ni in the sinking particles originate from both resuspended marine sediments off southwest Taiwan, and biogenic organic particles. The  $\delta^{60}\text{Ni}$  in biogenic particles is estimated to be +0.6‰ to +1.0‰, which is 0.3–0.7‰ lighter than that of dissolved Ni in seawater. The isotope ratios of Cu in sinking particles are fairly constant (+0.13‰ to +0.36‰), and the range is between those of marine sediments and labile fractions of marine particles. Thus, Cu in sinking particles is likely to be from marine sediments and biogenic organic particles. Compared with Ni, the correlation between Cu and P or organic-C is weaker, suggesting that the Cu/P and Cu/organic-C ratios are not constant in organic matter or there are additional sources of particulate Cu, such as Fe-Mn oxides and anthropogenic aerosols.



**Figure 1.** Collaboration with Dr. Ho's group, Academia Sinica during the visit of S.T. supported by ICR-iJURC Short-term Exchange Program.

## Determination of the Tungsten Isotope Composition in Seawater

The stable isotope ratio of W is a new tracer in oceanographic studies and a new proxy in paleoceanographic studies; however, precise data for modern seawater have not been reported to date. Because the concentration of W in seawater is as low as  $49 \text{ pmol kg}^{-1}$ , an ~3000-fold pre-concentration is necessary prior to measurement by multi-collector inductivity coupled plasma mass spectrometry (MC-ICP-MS). For the pre-concentration, we investigated solid-phase extraction using chelating resins, namely, NOBIAS Chelate-PA1 with ethylenediaminetriacetic acid groups and TSK-8HQ with 8-hydroxyquinoline groups. We report that TSK-8HQ is useful because the effects of the seawater matrix are minor thermodynamically and kinetically. We present a novel method for analysis of the concentrations and isotope ratios of W and Mo in seawater, consisting of solid phase extraction, chromatographic separation using anion exchange resin AG1 X8, and measurement by MC-ICP-MS. Both W and Mo are quantitatively recovered by this method, which was applied to seawater samples collected from the North Pacific Ocean. The measured concentration of W and the concentration and isotope ratio of Mo are consistent with those in the literature. The isotope ratio of W is found to be uniform throughout the water column in the western North Pacific Ocean;  $\delta^{186/184}\text{W}$  is  $0.55 \pm 0.12\%$  (ave  $\pm 2\text{sd}$ ,  $n = 7$ ) using NIST SRM 3163 as a reference for W. On the basis of this data, we determined that the isotopic difference in  $\delta^{186/184}\text{W}$  is  $\sim 0.49\%$  between seawater and oxic sediments in the modern ocean. This value accords with the reported experimental data for the isotope fractionation of W during adsorption on Mn and Fe (oxyhydr)oxides, suggesting the validity of our data.



**Figure 2.** Schematic of the study.