

## GC/C/IRMS as a tool to evaluate the degradation of chlorinated organic compounds in groundwater

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The in-situ remediation techniques by microbial activity are used for reduction of chlorinated organic compounds in polluted groundwater. However, the evaluation of microbial activity for decomposition of chlorinated organic compounds is not clear by only the concentration analysis. So, we focus on the usage of the stable carbon isotope analysis of chlorinated organic compounds such as trichloroethylene (TCE), and its daughter products; cis-dichloroethylene (cis-DCE) and vinyl chloride (VC).

The stable carbon isotope ratio ( $\delta^{13}\text{C}$ ) of these organic compounds were analyzed by a GC (Agilent : 7890A) coupled to an isotope ratio mass spectrometer (SerCon : 20-22) with combustion interface (SerCon : GC-CP) (GC/C/IRMS). The system was equipped with a purge-and-trap concentrator (GL science : AQUA PT 5000J PLUS) connected to the GC. In the  $\delta^{13}\text{C}$  value measurement, the measurement limit was usually 200ng-C, and standard deviation in TCE, cis-DCE and VC were  $\pm 0.08$ ,  $\pm 0.37$ ,  $\pm 0.11$  permil, respectively.

Groundwater samples were collected at polluted site with and without bioremediation treatment.

In samples from without treatment site, even the concentration decreasing were detected, the  $\delta^{13}\text{C}$  values of TCE are almost same as original one. On the other hands,  $\delta^{13}\text{C}$  values of not only TCE but also the daughter products increase with a decrease in concentration of TCE. These results show the usefulness of GC/C/IRMS for distinguishing the reason of concentration reduction by in-situ microbial activity of decomposition of these organic pollutants from physical factors such as dilution, diffusion, and adsorption.

Keywords: GC/C/IRMS, chlorinated organic compounds, biodegradation

## Isotope characteristic of rain water and atmospheric vapor in Hiratsuka, Japan

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### Introduction

The stable isotope ratios of hydrogen and oxygen in meteoric water ( $\delta D$  and  $\delta^{18}O$ ) are affected by geological and climatic conditions. Global meteoric water line (GMWL) describes the average isotopic compositions in the world. According to Craig (1961), the relationship between  $\delta D$  and  $\delta^{18}O$  was expressed as

$$\delta D = 8\delta^{18}O + 10 \quad (1)$$

However those intercept are not always 10 in each area. In Japan, the meteoric water originates in both Pacific Ocean and Japan Sea. The effects of two seas vary due seasonally. The isotope ratio of atmospheric vapor is important for study of atmospheric circulation, however, the number of published paper is not so much. In this study, we investigate the d-excess ( $d = \delta D - 8\delta^{18}O$ ) of rain water and atmospheric vapor in Hiratsuka, Japan.

### Sampling methods

Samples were collected on the roof of a No.17 building at Shonan campus, Tokai University from May to December 2013. Rain water samples were collected based on a method described by Negrel et al. (2011) and Yoshimura (2002). The collection duration was days or hours in scale. Rain water samples were percolated through 0.2  $\mu m$  filter, and kept into a 100 ml low-density polyethylene bottle. Atmospheric vapor samples were collected through a trap cooled with ethanol and dry ice mixture. Samples were 42 of rain water and 11 of atmospheric vapor.  $\delta D$  and  $\delta^{18}O$  of samples were measured by a Cavity Ring-Down Spectrometer analyzer (model L2120-I from PICARRO). Some data of rain water, which were sampled several times in a day, were processed to be the average value.

### Results and discussion

Rain water shows a wide variation in  $\delta D$  and  $\delta^{18}O$  from -86.4 to +6.2 ‰ and -12.6 to -2.6 ‰, respectively. Atmospheric vapor shows a variation from -223.5 to -98.6 ‰ and -31.2 to -14.7 ‰, respectively. The  $\delta D$ - $\delta^{18}O$  relationship of rain water gives a regression line:  $\delta D = 9.2\delta^{18}O + 24.0$  ( $R^2 = 0.95$ ) and that of atmospheric vapor gives a regression line:  $\delta D = 7.3\delta^{18}O + 7.9$  ( $R^2 = 0.96$ ). The d-excess values show a variation from 4.4 ‰ to 33.2 ‰. In Japan, origin of meteoric water affects to d-excess (Waseda and Nakai, 1983). In case of Pacific Ocean, d-excess is low ( $10 \geq d$ ). In case of Japan Sea, d-excess is high ( $20 \leq d$ ). In this study, the d-excess was low in summer when southern winds were blown from Pacific Ocean as the seasonal wind, and that value was high in winter when northern winds were blown from Japan Sea. Samples of atmospheric vapor show also this trend. Suggesting that atmospheric vapor is influenced by the same effect of meteoric water. The meteoric water line of rain samples was affected by d-excess which reflects variations of moisture sources, which is the reason why the slope of this line would be bigger than GMWL.

Keywords: rain water, isotope

## Exploring the sources of sulfur ion deposition and runoff in forest watersheds on the northern side of Lake Biwa

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To clarify the sources of sulfur ions in precipitation and runoff from forest watersheds, bulk deposition and stream water samples were collected within the small Kutsuki and Surumi forest watersheds on the northern side of the Lake Biwa basin, central Japan. Samples were analyzed for major ions and  $\delta^{34}\text{S}$ . Continuous monitoring from 1990 to 2010 showed that the average  $\text{SO}_4^{2-}$  concentration in stream water samples was  $1.62 \pm 0.31$  (0.76, 3.58)  $\text{mg l}^{-1}$  at Kutsuki and  $6.59 \pm 1.54$  (3.68, 16.1)  $\text{mg l}^{-1}$  at Surumi (t-test,  $p < 0.01$ ). However, the average  $\text{SO}_4^{2-}$  concentration in bulk deposition samples was similar in both watersheds:  $2.15 \pm 1.31$  (SD)  $\text{mg l}^{-1}$  (range, 0.202-10.2  $\text{mg l}^{-1}$ ) at Kutsuki and  $2.24 \pm 1.29$   $\text{mg l}^{-1}$  (0.350-6.07  $\text{mg l}^{-1}$  at Surumi (t-test,  $p > 0.05$ ). The  $\delta^{34}\text{S}$  values in bulk deposition samples fluctuated from +8.86 to +9.14 ‰ at Kutsuki and from +9.87 to +11.1 ‰ at Surumi, whereas non-sea salt (nss-)  $\delta^{34}\text{S}$  in stream water samples varied from +6.89 to +12.0 ‰ and from +4.64 to +5.11 ‰, respectively (t-test,  $p < 0.01$ ). It is said that the  $\delta^{34}\text{S}$  values in coal products from northern China varied from -3 to -1 ‰ and Japanese oil varied from +5 to +18 ‰.

Our findings suggest that the difference in the ability of canopies in the watersheds to catch  $\text{SO}_4^{2-}$  dry deposition is the reason for the significant difference in nss-  $\delta^{34}\text{S}$  values in stream water samples. The more open canopy in the Kutsuki watershed consists of young conifers and deciduous broadleaf trees, whereas the canopy in the Surumi watershed consists of mature conifer trees at a high density. Therefore, it appears that the Kutsuki watershed was only affected by  $\text{SO}_4^{2-}$  deposition from the Asian continent. There were not any domestic air pollution sources on the north side of Kutsuki. In contrast, the dense canopy of the Surumi watershed was affected by local  $\text{SO}_4^{2-}$  pollution sources of national roads which were located 1 km northwest from Kutsuki, rather than continental sources. Overall, this investigation suggests that the difference in stream water  $\text{SO}_4^{2-}$  concentrations in both watersheds is caused by the canopy differences.

## Geochemical and isotope systematics of Asahi and Yoshii rivers

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We have undertaken a detailed geochemical and isotopic analysis of water samples collected from the Asahi and Yoshii rivers of the Okayama Prefecture, Japan. More than 300 samples were collected from the rivers and their tributaries during March 2011 to January 2014. In several locations, samples were collected periodically in order to monitor the long-term fluctuation of the geochemical properties. All samples were filtered with 0.2  $\mu\text{m}$  filter prior to the analyses for major dissolved constituents (F, Cl,  $\text{NO}_3$ ,  $\text{SO}_4$ , Br,  $\text{PO}_4$ , Ca, Mg, Na, K), trace elements and O-H-Sr-S isotopes.

Based on the results obtained so far, we have constructed a high-resolution geochemical map of the rivers covering central to eastern Okayama Prefecture. The map shows that the concentrations of most major dissolved constituents, as well as the O-H-Sr isotope ratios changes systematically from the upstream towards the downstream. For example, the deuterium excess (DE) is generally high in the upstream ( $>20$ ) and gradually decreases towards the downstream ( $<12$ ). This difference in the DE exceeds the seasonal variation observed in locations where the long-term monitoring was conducted. Thus, the regional change in the DE is interpreted to be the result of different air mass contributing to the meteoric water of different locations.

The Ca, Sr, and Ba concentrations are generally low in the upstream and gradually increase towards the downstream. The  $^{87}\text{Sr}/^{86}\text{Sr}$  also changes from approximately  $\sim 0.705$  and  $\sim 0.706$  in the headwaters of the Asahi and Yoshii rivers, respectively, to  $\sim 0.708$  in the areas close to the Seto inland sea. The shift in the Sr isotope ratio seems to correlate well with the change in the ages of the rocks exposed in the river basin. This implies that these variations are likely related to the water-rock interactions.

The concentrations of other important dissolved constituents such as the  $\text{NO}_3$  and  $\text{SO}_4$  tend to increase abruptly in the densely populated regions. This is also accompanied by a shift in the S isotopic composition. These variations may reflect a change in the degree of human influence such as breakdown of fertilizers used for agricultural activities.

Keywords: Geochemical map, Asahi River, Yoshii River

## Characteristics of groundwater discharge around western foot of Mt.Chokai

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To clarify the total discharge rate of the submarine spring from Mt. Chokai, base-flow observation was conducted on 15 streams around western foot of Mt. Chokai at the end of January 2014. In this presentation, based on the distribution of specific discharge rate, we discuss the characteristics of the groundwater discharge and the hydrological balance in this area.

Keywords: Mt.Chokai, submarine spring, base-flow, hydrological balance, groundwater age

## Estimation of groundwater recharge area at the south foot of Mt. Bandai using the observation data in 2013

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The Mt. Bandai (1,816 m a.s.l.) which is an active volcano of the Quaternary period is located at Fukushima prefecture. Because of the geological characteristics in the volcanic area, it is estimated the groundwater recharge is large around Mt. Bandai. The groundwater and spring water around Mt. Bandai is used as the source of the public tap water, so it is important to comprehend the groundwater flow and groundwater recharge ratio at Mt. Bandai. To make clear the groundwater flow systems at Mt. Bandai, the investigation was carried out.

The EC value is under 10 mS/m and water quality indicates the Ca-HCO<sub>3</sub> type at most points in the south slope of Mt. Bandai. The oxygen isotopic ratios ( $\delta^{18}\text{O}$ ) are -11.1 to -10.8 ‰ (Site 1) and -11.2 to -11.1 ‰ (Site 2), and hydrogen isotopic ratios ( $\delta\text{D}$ ) are -67 to -65 ‰ (Site 1) and -68 to -67 ‰ (Site 2). The altitude effect is recognized in these areas. The average recharge area (altitude) in the south slope at Mt. Bandai is estimated from 1,150 to 1,270 m (Site 1) and from 1,360 to 1,420 m (Site 2). These recharge area (altitude) in the south slope is lower rather than the north and west slopes. In future, the investigation at more low altitude area (about 520 to 550 m) will be carried out, and estimate the groundwater flow in the south slope at Mt. Bandai.

Keywords: Mt. Bandai, recharge area, spring water, water quality, stable isotopes