

On stable isotope ratios of water in the Fuefuki River,
Yamanashi Prefecture, Japan

*Akihiro Sasaoka¹, Takashi Nakamura², Genki Nakanishi³

1.Department of Environment Systems, Faculty of Geo-environmental Science, Rissho University,
2.International Research Center for River Basin Environment, University of YAMANASHI, 3.Special
Master Course Program on International River Basin Environmental Science The University of
Yamanashi

This study is carried out to make clear the changes in stable isotope ratios of water of the Fuefuki River. The Fuefuki River is originating from the Kanto mountainous district located in the northeastern part of Yamanashi Prefecture, and it flows along the south-eastern edge of the Kofu basin.

The results of the analysis are as follows.

At the upper reaches of the Fuefuki River, the values δD are influenced by "the altitude effect of rainfall", and at the down reaches area, the values δD are gradually become larger, i.e. heavier than the water of the upper reaches. δD of the water in the bottom of Kofu basin, downstream area of the Fuefuki River, is more heavier than that of upper reach of the river, However, between St.3 and St.4, and between St.6 and St.7, the values of δD at the downstream points are smaller.

These changes is not possible to explain by altitude effect, and the authors pointed out that there are two type of inflow to the Fuefuki River, one is tributary stream with high mountain basin area, and the other is groundwater discharge to the Fuefuki River near the outlet area of the Kofu basin.

Keywords: Fuefuki River, stable isotopes, rivers recharge

Investigation of the groundwater source estimation in Kofu Basin for hydrological model

*Genki Nakanishi^{1,2}, Nishida Kei², Takashi Nakamura², Kazuyoshi Asai³

1.Special Master Course Program on International River Basin Environmental Science The University of Yamanashi, 2.Interdisciplinary Centre for River Basin Environment, University of Yamanshi, 3.Geo science Laboratory

The end member mixing analysis using hydrological tracers have been applied to identify the groundwater recharge sources in local area, such as scale of alluvial fan. However, it is difficult to apply to large scale, due to the wide values of temporal and special for the hydrological tracers. Objective of this study is investigating the groundwater recharge identification using hydrological tracers to adapt for the hydrological model for basin scale.

Groundwater samples were collected once a year from November 2010 to October 2012. Altogether 12 river water samples were collected in 2003, 2004 and 2006 from main rivers in Kofu basin. Rain water samples were collected once a month since 2008. All groundwater samples (n=50) are classified into three types based on recharge sources. Among them 20% of groundwater are mainly recharged by river water. Other 50% samples are river water mixed with local precipitation and 25% are river water mixed with mountain groundwater.

Keywords: Geoundwater, Kofu Basin, Water Stable Isotopes

Behavior of the age dating tracers in Satoyama-spring

*Kazuyoshi Asai¹, yuji KATO¹, Maki Tsujimura²

1.Geo Science Laboratory, 2.University of Tsukuba

For accumulation of basic data about the age dating tracers, weekly sampling was carried out on Satoyama-spring in Nagoya city for one year. Based on the analysis results (stable isotopes, CFCs, SF₆, dissolved ion), we discuss the factor controlling the temporal variation of age dating tracers.

Keywords: age dating tracer, Satoyama-spring, stable isotope, CFCs, SF6

A study on caldera lake-groundwater system based on a multiple isotope approach

*Masaya Yasuhara¹, Akihiko Inamura², Noritoshi Morikawa², Hiroshi Takahashi², Masaaki Takahashi², Michiko Ohwada², Kohei Kazahaya², Stephen Gingerich⁴, Yoichi Oyama³

1.Rissho Univ., 2.Geological Survey of Japan, AIST, 3.Kushiro Board of Education, 4.USGS

Lake Masyu (212 m deep; 19.6 km² in area; water surface at 352 m a.m.s.l.), eastern Hokkaido, Japan, is a seepage caldera lake with no surface outflow and inflow. The caldera lake-groundwater system was investigated to elucidate the effect of lake-water seepage from Lake Masyu on the hydrology and hydrogeochemistry of Masyu volcano and its adjacent areas. Previous studies on the lake indicated that, on the basis of a conventional water balance method, there is a large amount of seepage of some 65,000 km³/day to the surrounding volcanic aquifers.

The analyses of ²H, ¹⁸O, ¹³C, ³He and water chemistry for samples from rivers, springs, and bores in 2009 and 2010 are reevaluated in detail to quantify the lake-water contribution to river and spring discharges and to the downgradient groundwater field. The water samples from Lake Masyu are markedly enriched in heavy isotopes and fall on a line with a slope of 5.0 in the δD vs. $\delta^{18}O$ diagram, which is characteristic of open-water bodies subject to evaporation. The lake water is also enriched in carbon isotope and in the range between 4 and 5‰ $\delta^{13}C$. The mixing proportion of lake water was calculated on the basis of δD and $\delta^{18}O$ by applying a simple two end-member mixing model. As a result, the lake-water contribution proved to be significant for the huge springs on the southeastern flank (Nishibetsu-Gawa Headwater Springs) and those on the southwestern flank (Biruwa Springs), consisting of 30% of their discharges. Taking into account their total daily discharge of 140,000 m³ measured in July 2009, some 65% of the lake-water seepage from Lake Masyu, that is 42,000 m³/day, is estimated to concentrate in these springs. In contrast, the Kaminoko-Ike Spring on the northern flank with a discharge of some 15,000 m³/day, water of which has long been considered to be of Lake Masyu origin, isotopically showed no evidence of lake water. It is also the case in the other medium-sized springs located on the northern and eastern flanks. The analyses of stable carbon isotope, high isotopic values of -9 to -7‰ $\delta^{13}C$ for Nishibetsu-Gawa Headwater Springs and of -9 to -8‰ $\delta^{13}C$ for Biruwa Springs, and a low value of -21‰ $\delta^{13}C$ for Kaminoko-Ike Spring, are consistent with these estimates. It is also the case with ³He: Nishibetsu-Gawa Headwater Springs and Biruwa Springs had a high content of ³He of magmatic origin, whereas there was no ³He of magmatic origin in Kaminoko-Ike Spring. Rivers that originate in the flanks of Masyu volcano showed little or no isotopic evidence of lake water. An overall estimate, therefore, is that approximately 23,000 m³/day of seepage from Lake Masyu is still unaccounted for. The hydraulic connection of volcanic aquifers to Lake Masyu is likely to account for this. The isotopic analyses show some hot springs and groundwaters from the 100-350m deep bores in the southern and southwestern flanks contain substantial proportions of lake water, indicating seepage water from Lake Masyu plays an important role in forming hydrothermal and groundwater system. A schematic diagram for the caldera lake-groundwater system in and around Masyu volcano is depicted on the basis of these data.

Keywords: groundwater system, caldera lake, lake-water seepage, spring, multiple isotope approach

Origin of mercury in the groundwater in Hirakata City, northeastern Osaka Prefecture

*Yusuke Sakamoto¹, Harue Masuda¹, Akinori Takeuchi², Tsuyoshi Shintani¹

1.Department of Geosciences, Faculty of Science, Osaka City University, 2.National Institute for Environmental studies

Thirty one groundwaters contained excess mercury of standard value (0.5ppb) among the 4513 groundwaters monitored by Osaka Prefecture. Most of those were found in the northeastern part of Osaka (Hirakata and Shijo-nawate cities) and along the active Ikoma Fault system (Osaka Prefecture, 2009). The mercury was plausibly geogenic, however, the source was not clear. This study was planned to reveal the origin of mercury using its stable isotopes.

The groundwater was sampled from 15 shallow dug wells and tube wells <10m depth in July 2015-in November in Hirakata city. The water level was 1~2m from the ground. After analyzing major chemistry and total mercury concentration, the groundwater highly containing mercury were selected to determine the mercury isotope ratios. The total mercury concentration was measured by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), the methyl mercury concentration was measured by Gas Chromatography- Atomic Fluorescence Spectrometry (GC-AFS), and the mercury isotope ratio was measured by Multi-Collector Inductively Coupled Plasma Spectrometry (MC-ICP/MS) attached with hydride generation system.

Major chemistry of the studied groundwaters were Ca^{2+} - HCO_3^- and Na-Cl- SO_4 + NO_3 types. Mercury concentrations were less than the standard value, while the maximum concentration was 133ppt. The mercury concentrations of groundwater from the same wells varied largely, relationship to season and /or precipitation. For one of the case, the groundwaters containing the lower mercury (90ppt) with the higher SO_4^{2-} than that containing higher mercury (133ppt). For the other case, the higher mercury containing groundwater (86ppt) containing higher Ca^{2+} and HCO_3^- than the low-mercury groundwater (59ppt). When the groundwaters taken from two wells, within 20m distance contained 55ppt mercury (well depth >5m) and 2.0ppt (2~3m depth). These observations suggest that the mercury in the groundwater >5m depth is diluted by infiltrating water from the surface around the wells. Therefore, mercury was not contaminated from the source on the ground surface. The most of mercury was in inorganic form, and mono-methyl mercury was less than 1% except one groundwater containing extremely low-mercury. Thus, the mercury does not relate to human activities or bio-chemical reaction.

The mercury isotope ratio is effective to specify origin. The mercury isotope ratio is influenced by bio-chemical fractionation, and many researchs have been done for the bioaccumulation processes (e.g. Blum 2013). While, less studies have reported for the behavior of mercury in the crust using stable isotopes. Although only two groundwaters were analyzed, the present study is the first report on the mercury isotope ratio of shallow groundwaters but not hydrothermal water. $\delta^{202}\text{Hg}$ of groundwater was -0.65‰~-0.85‰. Many mercury mines are known in the Kii Peninsula and Shikoku Island. Takeuchi (2011) reported that $\delta^{202}\text{Hg}$ of cinnabars from Niu-mine was -0.68 ± 0.12 (‰), Yamato mercury mine was -0.19 ± 0.36 (‰), and Mizui mine was -0.51 ± 0.47 (‰). The isotope ratios of studied groundwaters were close to those values, indicating the similar origins of those mercuries. When cinnabar is precipitated from hydrothermal one liquid, isotope fractionation occurs to concentrate heavier mercury in the cinnabar. If so, slightly smaller $\delta^{202}\text{Hg}$ of the studied groundwaters than those of the cinnabars from the Kii Peninsula and Shikoku would suggest a more pristine isotope composition of the fluid from the deep crust. Mercury isotope study will be useful to trace the fluids from the deep in relation to the regional tectonics.

Keywords: mercury, groundwater, isotope

Systematic estimation and correction of Ba induced interference in ICP-MS for direct and quick analysis of REEs in geothermal waters

*Qing CHANG¹, Hitomi Nakamura^{1,2}, Kotona Chiba¹, Hikaru Iwamori^{1,2}

1.Japan Agency for Marine-Earth Science and Technology, 2.Tokyo Institute of Technology

High barium concentration and Ba/REE ratios are commonly observed in geothermal waters such as Arima-type brines, making it difficult to precisely determine REE characteristics, e.g., Eu, Ce anomalies and REE patterns of this kind of high matrix (major solutes) and ultra-low REE waters. We systematically evaluated Ba induced molecular ions in ICP-MS operated at solution mode and established a new correction method for direct determination of REE in high salinity geothermal waters.

Ba has seven isotopes from ¹³⁰Ba to ¹³⁸Ba with natural abundance of 0.1% to 71.7%, each of them will produce molecular ions in forms of oxide, hydroxide, hydride and argide in argon plasma. These molecular ions cover a mass range from 139 (¹³⁸BaH) to 178 (¹³⁸BaAr), theoretically overlapping with most of REE isotopes in complicated combinations. For example, both BaO and BaOH overlap the masses of light to middle REE isotopes, especially Eu. Conventional correction method simply considers that bulk interfering on Eu is contributed by BaO, and may result in large uncertainty or erroneous of REE anomalies and patterns. In this work we separately evaluated production rates of Ba oxide, hydroxide, hydride and argide for each of Ba isotopes in solution mode ICP-MS. Our data show that BaOH and BaO are major interfering species over Nd, Sm, Eu and Gd peaks. BaH and ¹³⁸Ba peak tailing seriously overlap with La and Ce signals. Argides are ignorable. Heavy REEs and Pr are free from a significant overlapping with any of the Ba induced interference. All the interference can be quantitatively estimated and reliably corrected for REE analysis.

We demonstrated the correction strategy by analysis of reference riverine water (SLRS-4) doped with Ba to Ba/Eu=125,000 similar to Arima-type brines. Determined REE data of Ba-doped SLRS-4 agrees very well with certified values. The method was also applied to determine REE compositions of various spring waters including Arima-type brine of the Arima area in southwest Japan (Nakamura et al, 2015). In this case, Ba induced interferences contributed to La, Ce, Nd, Sm, Eu and Gd raw signals for 92%, 24%, 48%, 78%, 96% and 75%, respectively. The intra REE interferences, e.g., PrO, NdO and SmO overlapping over middle and heavy REE signals, were less than 2.7% (mostly <1%), thus ignorable for discussion.

Keywords: Ba-induced interference, REE, geothermal waters, ICP-MS

Characteristics of event-based oxygen isotopic composition in precipitation at western part of Kanagawa prefecture

*Jun SUGIMOTO¹, Hidekazu Suzuki², Yuji Miyashita³

1.Graduate Division of Arts and Sciences, Komazawa Univ., 2.Dep. of Geography, Komazawa Univ., 3.HSRI, Kanagawa Pref.

Stable isotopes in precipitation are useful tool for understanding the hydrological cycle. Precipitation samples for every events have been collected at Hot Springs Research Institute located in the eastern foot of Mt. Hakone, and those oxygen isotopic compositions are analyzed 79 samples collected from Dec. 1, 2012 to Nov. 30, 2013. Annual volume-weighted mean value oxygen isotopic composition in 2013 was -7.62 per mill, and seasonal ones are -11.10 per mill in winter, -5.76 per mill in spring, -8.52 per mill in the Baiu, -6.63 per mill in summer, -7.02 per mill in the Shurin, -5.81 per mill in autumn. Weighted mean value in winter and the Baiu is lower than annual one, while that in other seasons is higher. Thus, a clear seasonal variation is found in 2013. The purpose of this study is to estimate the factor which has lower isotopic composition in winter and the Baiu. Lower isotopic composition in winter resulted from the precipitation by low pressure. When depe southern coast low pressure passed, the tendency which indicates one compared with the very low isotope ratio was seen. The influence of temperature effect is considered as a decline factor in winter. The intensity of rainfall brought by the Baiu front is large. Therefore, it is considered that amount effect was reflected increased. A clear correlation ($R^2=0.83$) was seen between the precipitation and compared with the oxygen isotope, and the phenomenon which represent rain amount effect was confirmed. However, event of precipitation more than 100 mm amount of precipitation 3 times in case of a typhoon in the Shurin, and the low isotopic ratio is high -5.2 per mill, -6.5 per mill and -9.3 per mill of respectively. Though there was a lot of precipitation, the isotope didn't shows low value. Thus the typhoon isotopic ratio is complicated.

Keywords: Mt. Hakone, oxygen isotope, amount effect , precipitation event