

HIGH RESOLUTION MULTI-TRACER STUDY OF WATER FLOW AND SOLUTE TRANSPORT IN THE GLACIAL TILL

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The aim of this study was to explore water flow and solute transport mechanisms in the unsaturated and saturated zone (aquitards) and how the mechanisms differ between uplands and lowlands in the Canadian Prairie glacial till. Past and recent studies on surface water-groundwater interaction involving physical measurements and stable isotope tracers show that prairie wetland ponds have distinctive isotope signatures from till aquitards and aquifers and that they may not play significant roles in groundwater recharge. Tritium data from aquitards and aquifers also suggest that aquifers are recharged with modern water. The observations suggests that uplands may play an important role in prairies groundwater recharge and possibly contribute more recharge water to aquitards and aquifers. We studied three soil profiles depths (0.2- 8 m, 0.2-10 m, and 0.2 -14 m) obtained from uplands and lowlands to identify the extent of deep percolation in the uplands and the lowlands and to test the established hypothesis of depression focused recharge, and critique it. We employed sets of tracers ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Cl^- & SO_4^{2-}), line condition (lc)-excess, complemented by soil analysis and physical measurements from piezometers. The depth profiles show a steady increase in both $\delta^{18}\text{O}$, $\delta^2\text{H}$ tracers and lc -excess below depth, from the ground surface to >2m in lowlands and >5m in both uplands and piezometers. The Cl^- and SO_4^{2-} also showed leaching to similar depths. The change in $\delta^{18}\text{O}$, $\delta^2\text{H}$ and lc-excess values below 7 m depth is muted and no significant evaporated water signals was found in the aquitards. It is suggested that the major process responsible for enhancing deep water flow and solutetransport into aquitards and intertill aquifers is not soil infiltrability beneath permanent recharge wetlands (i.e., depression focused) but rather preferential flow; since the former will lead to greater degree of evaporation before recharge.

Keywords: Glacial till, stable isotopes, lc-excess, chemical ions, water flow and solte transport, mechanisms

The isotopic ratios of the hot springs in the Jigokudani Valley, Tateyama Volcano

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Tateyama Volcano in the Hida Mountains has an active solfatara field called Jigokudani Valley (JV). The JV is formed by repeated phreatic eruptions about 40,000 years ago. These situations are suggestive of the presence of a well-developed hydrothermal system beneath the JV because phreatic eruptions mostly occur within the hydrothermal system. Recently, the JV showed the increased volcanic activity such as the sulfur outflow and the changes in the composition of fumarolic gases. We conducted resistivity surveys and geochemical analyses of the hot-spring water in order to reveal the hydrothermal system beneath the JV.

Hot-spring waters were sampled from 2014 to 2016, and we measured anion concentrations and isotopic ratios of them ($\delta^{18}\text{O}_{\text{water}}$, $\delta\text{D}_{\text{water}}$, $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{33}\text{S}_{\text{sulfate}}$). The results of the isotopic ratio of water and the anion concentration suggested that the hot springs of the JV were classified into the following three groups. (1) Hot springs characterized by high anion concentration and the isotopic ratio of water close to the magmatic vapor (MV). In addition, the $\text{Cl}^-/\text{SO}_4^{2-}$ concentration ratio showed the value near 1. (2) Hot springs which showed large time variations of $\text{Cl}^-/\text{SO}_4^{2-}$ concentration ratios because of decrease of Cl^- concentration. The isotopic ratios of water were plotted between MV and local meteoric water (LMW). (3) Hot springs which were mainly composed of SO_4^{2-} without Cl^- and showed low anion concentrations and the low isotopic ratios near LMW.

We also measured the $\delta^{34}\text{S}$ value of sulfate in the hot-spring waters. Generally, primary sulfates (derived from SO_2 disproportionation) in hot springs show higher $\delta^{34}\text{S}$ values than secondary sulfates (formed by the H_2S oxidation). The $\delta^{34}\text{S}$ of hot springs in the JV showed the values from -0.81‰ to 19.93‰. The sulfate of (3) is considered to be derived from the oxidation of H_2S because $\delta^{34}\text{S}$ showed low values. On the other hand, $\delta^{34}\text{S}$ values of (1) and (2) were distributed over a wide range regardless of the ion concentration and the isotopic ratio of water. A linear relationship between $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ is known because isotopic fractionation depends on the mass difference, which is called the mass dependent fractionation (MDF). The deviation from MDF (defined as $\Delta^{33}\text{S}$) of samples in the JV was not zero, which is considered to be affected by kinetic isotope effects. The intersection point ($\delta^{34}\text{S} \sim 9\text{‰}$) between the regression line of samples and the $\Delta^{33}\text{S} = 0$ line might indicate the sulfate value of the primitive magmatic gases.

These results indicate the following formation processes of hot springs of JV; (1) Hot springs derived from the condensation of volcanic gases. (2) Hot springs formed by the mixing of the vapor phase of two-phase fluid and meteoric water at shallow depth. (3) Hot springs formed by the surface water in which H_2S in volcanic gases were dissolved.

We compared the results of the geochemical analysis with the resistivity structure (Seki et al., 2016), which indicates that all hot springs of the JV are formed within the depth of 500 m. In particular, we found that the hot-spring water of (2) was formed directly beneath the cap rock that is a key structure of the occurrence of phreatic eruptions. It is important to monitor the chemical and isotopic compositions of the hot-spring water in order to detect the changes in the volcanic activity because the hot spring of JV is formed in the shallow depth and affected by the conditions of temperature and pressure.

Keywords: Hydrothermal system, Hot spring, Water isotopic ratio, Sulfur isotopic ratio

A study of water quality and groundwater recharge in Katakai River alluvial fan over the past 15 years based on isotopic composition and chemical concentration

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In the Katakai River alluvial fan located in Uozu City, Toyama Prefecture, groundwater is used extensively for tap water, agricultural and industrial purposes, etc. However, the quality of the groundwater has been, as it were, taken for granted, and monitored only partially and irregularly in the recent past. The aim of this study was to reanalyze the data from two previous studies in order to evaluate the groundwater quality in the area, based on the stable isotopes of hydrogen and oxygen and chemical composition.

Suzuki, who studied the groundwater from wells throughout the area and its relation to water from Katakai River, suggested that there are at least two layers of aquifers in the Katakai River alluvial fan –one shallower than 70 m from the ground surface and the other deeper than 80 m. By measuring tritium concentration, he also found that the residence time of groundwater is 10 to 20 years (Suzuki, 2002). Also in 2002, Uozu City conducted a groundwater research throughout the area, and has been conducting an annual monitoring of groundwater quality in the northern part of the river fan since 2004.

The $\delta^{18}\text{O}$ value of the groundwater in the Katakai River fan in 2002 was similar to the $\delta^{18}\text{O}$ value of the river water from the Katakai River along the coast. Furthermore, the contribution ratio of river water to groundwater was about 80 %. The similar isotopic composition of river water and groundwater, indicates that the Katakai River discharged to groundwater through the ancient river course without being affected by precipitation.

Both the hexa-diagram of unconfined groundwater described in Suzuki (2002) and that obtained in my own study in 2016 were the type of Ca-HCO_3 . Therefore, it seems that water quality has not changed over these years. In addition, from the annual monitoring data of self-discharge quantity of confined groundwater in 2004-2016, it was found that the volume of water increased in summer and decreased in winter. The exploitation of groundwater for the snow melting on the roads may be causing the decrease of confined groundwater flux in winter. At one well with the depth of 100 m, a decrease was observed in the volume of confined water. Since this groundwater is the type of $\text{Na} \cdot \text{Ca-Cl}$, it may take a long time for water recharging from Katakai River. This seems to suggest the vulnerability of deep confined groundwater. Consequently, the reasonable utilization and conservation of deep groundwater should be considered for sustainable groundwater management in the future.

Keywords: ground water, Katakai River alluvial fan, Uozu city

A new approach to estimate evaporation of canopy interception using stable isotope of water

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Evaporation of canopy interception CI, accounts for around 20% of gross rainfall PG. However, it is strange that CI is proportional to PG on an hourly basis during rainfall (e.g. Murakami, 2006, J. Hydrol.; Saito et al., 2013, J. Hydrol.). To understand the mechanism of canopy interception we estimated evaporation of wet canopy surface EW using stable isotope of water.

Murakami and Toba (2013, Hydrol. Res. Lett.) measured CI in a plastic Christmas tree stand placed on a 180-cm square tray that was set outside under natural rainfall. We used the same system to measure PG and net rainfall PN to calculate CI ($= PG - PN$) using water balance. Manual sampling of gross and net rainwater was also conducted on an hourly basis. EW was estimated based on the difference of d18O (or d2H) values in gross and net rainwater using fractionation factor, and the results were compared with CI. In a rain event we focused on, PG and PN (runoff from the tray) were 28.0 mm and 22.7 mm, respectively, with CI of 5.3 mm (18.9% of PG). The d18O (or d2H) value in net rainfall was higher than that in gross rainfall because of fractionation by EW. Calculated EW by the values of d18O was 5.2% of PG on average. We tried to reproduce the results using a tank model (Yoshida et al., 1993, J. Japan Soc. Hydrol & Water Resour.). Firstly, evaporation rate is assumed to be constant, 20% of PG and the calculated PN was 23.1 mm, i.e. CI was 4.9 mm (17.5% of PG). Secondly, retaining the parameter of the model, we calculated PN based on hourly surface evaporation derived from the d18O values. The simulated PN was 25.6 mm that means CI was only 2.4 mm (8.6% of PG).

The difference between the two methods can be explained by rapid evaporation of micro-droplets produced by splash after rain impacts the canopy (Murakami, 2006). We will present the results using d2H data at the session.

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Keywords: Canopy interception, Splash, Stable isotope of water

Stable water isotope behavior associated with the Baiu front simulated by NICAM-isotope

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Stable water isotopes (SWI) are an observable water tracer that reflects integrated history of phase change and mixing. SWI are exploited not only for climate proxy (e.g. Dansgaard, 1993) but for studying precipitation systems.

The Baiu Front (BF) is a stationary front during the late spring and early summer near Japan, which is the “boundary” between tropical and extratropical air mass. BF is characterized by a large gradient of SWI as well as equivalent potential temperature. To study BF from the viewpoint of SWI, it is expected to improve our understanding about the water cycle associated with the front.

From an observational study by Kurita et al. (2015), the highest isotope ratio in water vapor near the surface corresponds to the warm air mass advection by southerly flow, while abrupt isotopic depletion corresponds to cold air advection associated with southward migration of BF. Rainfall results in isotopic depletion of water vapor since heavy isotopologues (HDO) preferentially condensate and are taken away from water vapor by rainout. In this study, we attempt to quantify the effect of water vapor (air mass) advection and depletion by rainout on isotopic variability associated with the BF.

We developed an isotope-incorporated microphysics scheme based on NSW6 (Tomita, 2008), which is a version of the microphysics scheme by Lin et al. (1983). We simulate the isotopic behavior associated with BF using this scheme on a global cloud-resolving model NICAM (Satoh et al. 2008; 2014).

To check the validity of our isotope-incorporated model, simulated values in our model are compared with observation at a paddy field in Tsukuba, Japan (Wei et al. 2015; 2016). Although there is some discrepancy between the observation and our simulation, our model successfully reproduced ascending/descending timing of dD.

From composite analysis against precipitation intensity by BF, the dD contrast between north and south of BF reflects air mass difference in the case with weak precipitation, which is consistent with Kurita et al. (2015). On the other hand, the heavy precipitation case is almost the same with the weak precipitation case except for “V-shape” depletion near the BF region. This result is consistent with the temporal V-shape change in isotope ratio of precipitation associated with front passing (e.g. Celle-Jeanton et al. 2004).

Keywords: Baiu front, stable water isotopes, cloud resolving model

A possibility of annually-laminated tufa $\delta^{13}\text{C}$ record as a reflection of volcanic activity

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Mt. Asama, central Japan, is one of the most active volcano in the Japanese Archipelago, and many springs are distributed in the mountain body and its surrounding areas. The river from Nogori springs (R. Nigori) studied in this work is located in the southern part of the mountain, the spring water of which contains the high concentrations of carbonic acid and iron with 5.7 of pH. From the riverbed and the terrace, we found the carbonate-rich deposits with the annually-lamination (thereafter called tufa) which are formed during the CO_2 degassing after flowing out of the springs. In this talk, we present results of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in R. Nogori and the tufa deposits, and then discuss the possibility of tufa $\delta^{13}\text{C}$ record as a reflection of volcanic activity.

Keywords: Tufa, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$

Isotope analysis of past drip water preserved as fluid-inclusions in stalagmites

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The oxygen isotope composition ($\delta^{18}\text{O}$) of speleothem is widely used as paleoclimate proxy. Interpretation of the $\delta^{18}\text{O}$ value is not straightforward because it is controlled by two factors; $\delta^{18}\text{O}$ of dripwater and temperature at calcite formation. The $\delta^{18}\text{O}$ of speleothem fluid-inclusions, paleo-dripwaters in cave (i.e., paleo ground water), will provide an important constraint for the unknown quantity. Its paleoclimatic applications, however, have been hampered by technical difficulties for isotope measurements of fluid inclusions, recent developments of a new laser-based isotope ratio mass spectrometer have opened a new door of fluid inclusions analysis (e.g., Affolter et al., 2014; Arienzo et al., 2013). We also have developed a precise isotopic technique based on cavity ring-down spectroscopy with a low sample-amount requirement of 20-300 nL of inclusion water from stalagmites (Uemura et al., 2016). I will show detailed comparison with modern observation and recent results.

Keywords: stable isotope, speleothem, fluid inclusion

Controls on the isotopic composition of surface water and groundwater and hydrologic implications in the mid Merced River basin, Sierra Nevada, California, USA

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Isotopic composition in stream water, springs, groundwater, and precipitation was examined to understand the controls on the spatiotemporal variability from 2006 to 2008 in the mid Merced River basin (1,873 km²), Sierra Nevada, California. Mean isotopic values in small tributaries (basin area < 122 km²), rock glacier outflows and groundwater were correlated with mean basin elevation ($n = 16$, $p < 0.001$), suggesting an isotopic lapse rate of -1.9‰/100 m for $\delta^2\text{H}$ and -0.22‰/100 m for $\delta^{18}\text{O}$ in meteoric water. Evaporation had little effect on the isotopic signature of precipitation, springs, and groundwater, but affected stream water during low flows in summer and fall. The isotopic composition in stream water in the Merced River was most depleted during snowmelt. However, the isotopic composition-elevation relationship in tributaries and the Merced River did not vary much over seasons. A basin-characteristic isotopic value was established for each basin based on the relation between isotopic composition and the mean basin elevation to elucidate hydrometeorologic processes over seasons. It is suggested that flow and flow duration of Yosemite Creek are most sensitive to temperature increase due to its strong evaporation. Based on the isotope-elevation relation, groundwater in Yosemite Valley was recharge from the upper snow-rain transition zone (2,000-2,500 m), suggesting its strong vulnerability to temperature increase, shift in snow-rain ratio and the earlier onset of snowmelt. The information helps advance our understanding of hydrologic responses to climate change in snowmelt-fed river systems in the U.S. West.

Keywords: Stable isotopes, Isotopic lapse rate, Snow-rain transition, Merced River

Reanalysis, Stable Isotopes and the Age of Water: Improving Constraints for Model Identification at a Critical Zone Observatory

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This paper presents a hydrologic model for an upland catchment constrained by climate observations and stable isotopes of oxygen and hydrogen at the Susquehanna/Shale Hills Critical Zone Observatory (SSH_CZO).

Model forcing uses NLDAS-2 reanalysis time series for daily weather forcing and IsoRSM regional atmospheric model (isotope-incorporated regional spectrum model) for simulating stable isotopes in precipitation and water vapor at 10 km x 10 km spatial resolution. The regional model is developed through a dynamical downscaling technique that applies the results of the global simulation and a spectral nudging technique to produce the higher resolution data (Kei Yoshimura & Kanamitsu, 2008). The regional model results were compared to 4 years of daily sampled stable isotope data in precipitation at the SSH/CZO and good agreement is found, extending the precipitation isotope data to the full reanalysis period (1979-2014).

The paper next develops the theoretical basis for simulation of flow, isotope ratios and “age” as water moves through the canopy, to the unsaturated and saturated zones and finally to an intermittent stream. The model formulation demonstrates that the residence time and age of environmental tracers can be directly simulated without knowledge of the form of the underlying residence time distribution function and without the addition of any new physical parameters.

The model is then used to explore the rapid attenuation of event and seasonal isotopic ratios in precipitation over the depth of the soil, and the impact on streamflow and stream isotope ratios. The results suggest the importance of mobile macropore flow on recharge to groundwater during the non-growing cold-wet season. The soil matrix is also recharged during this season with a cold-season isotope signature on recharge and baseflow. During the growing (dry) season, root uptake and evaporation from the soil matrix along with a declining water table determines the growing season isotope signature.

The paper concludes by illustrating how system memory, age and residence time estimation can be used to constrain the model through sensitivity analysis of parameters as a function of mean isotopic age.

Keywords: catchment hydrology, stable isotopes, dynamical model, isotopic age of water

An improved analytical method for determining radioactive ^{35}S in water/snow samples and its applications to snow and glacier hydrology

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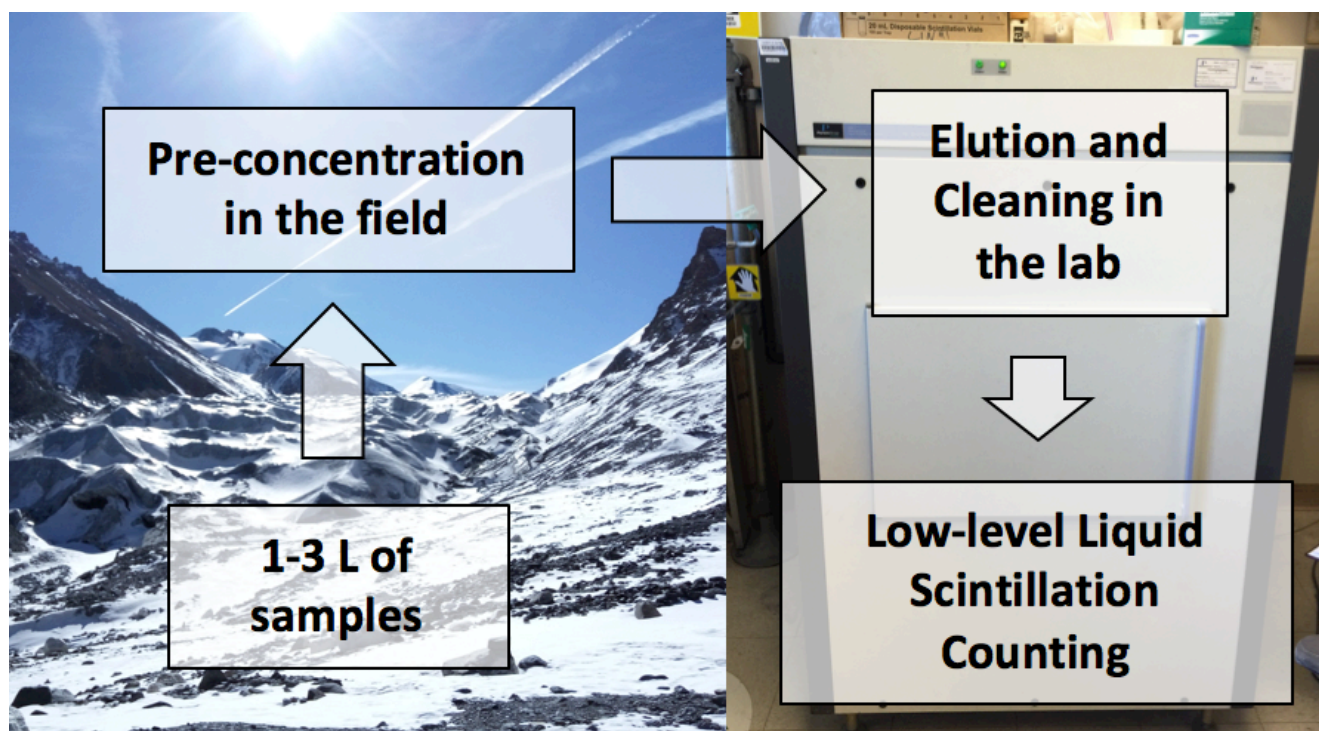
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Cosmogenic ^{35}S is useful in understanding a wide variety of chemical and physical processes in the atmosphere, the hydrosphere and the cryosphere. The 87.4-day half-life and the ubiquity of sulfur in natural environments renders it an ideal tracer of many phenomena. For example, recent ^{35}S measurements in aerosol samples provided new insights into the vertical and horizontal transport processes in the atmosphere [1-2]. However, measurements of ^{35}S in snow and water samples remained scarce as existing analytical methods required a large volume of sample (>20 L) due to their high analytical activity background and low counting efficiency [3-4]. Here, we present a new set of snow/water sample collecting and handling procedures for high-sensitivity determination of cosmogenic ^{35}S using an optimized low-level liquid scintillation spectrometer technique [5]. The counting background and efficiency of this technique were ~0.9 counts per minute and ~78%, respectively, and therefore we can easily analyze water samples as small as ~2 L, ~10 times smaller than previous methods. Laboratory experiments using diluted ^{35}S standards (with activities of <5 disintegrations per minute) showed a ^{35}S recovery percentage of ~95%, demonstrating a relatively small deviation from the true value. This new method will provide a powerful tool in studying ^{35}S in small volumes of snow and water samples, especially those from remote but climatically important regions such as the polar regions and the Tibetan Plateau and Himalayas (also known as the Third Pole). The measurements are particularly important as the radioactive sulfur provides an actual clock of glacial melting processes. With the growing rate of glacial loss, the need for measurements from remote locations becomes all the more important. Using this method, we successfully measured ^{35}S in ~1 L of fresh snow sample collected from a glacier on the Tibetan Plateau (Laohugou Glacier No.12; 39°05' -40' N, 96°07' -97°04' E; 4260–5481 m above sea level) to be 47 ± 7 mBq/L. We point out that the precision can be easily improved by collecting relatively larger amounts of samples (e.g. ~3 L) and measuring samples as soon as possible. Based on ^{35}S activities in 9 natural samples (fresh and aged snow, ice, runoff) made in this pilot study, a first proof-of-concept approximation for age determinations and source attributions will be presented. Along with water stable isotope measurements (dD and d ^{18}O), our ^{35}S measurements may assist in quantifying snow melting rates. More samples (n>100) collected from Laohugou Glacier No.12 and other three glaciers across the Tibetan Plateau and Himalayas (East Rongbuk Glacier at Mount Everest, Xiao Dongkemadi Glacier at Tanggula Range and Baishui Glacier No.1 at Mount Yulong) during 2015-2016 are being measured and will be reported. We anticipate that these results will provide deeper insight into snow/glacier melting processes over the Tibetan Plateau and Himalayas.

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Keywords: Sulfur isotopes, Cosmogenic nuclides, Snow melt, Glacier retreat, Cryosphere, Tibetan Plateau and Himalayas



Continuous isotopic Water Sampling Cavity Ring-Down Spectroscopy (CWS-CRDS) for real-time measurements of water isotopes

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Stable isotopes of water (d^2H , $d^{18}O$) are unique tracers of many hydrological processes including evaporation, precipitation, reservoir mixing and residence time. Historically, discrete water samples have been collected and analyzed via either Isotope Ratio Mass Spectrometry, or more recently laser-based spectroscopic methods, such as Cavity Ring-Down Spectroscopy (CRDS). However, the analysis of discrete samples precludes the ability to construct high resolution water isotopes data sets through time and space. Previously, research groups have developed laboratory-built diffusive samplers for extracting water vapor from liquid [1,2] and then analyzed that vapor via CRDS instruments, whose continuous flow design and high frequency measurement interval (< 1 Hz) makes them uniquely suited to real-time, high throughput measurements. Here we present details of the first commercially-available and field-deployable Continuous isotopic Water Sampler (CiWS) coupled to a Picarro L2130-*i* for isotopic water analysis. The CiWS device utilizes an expanded polytetrafluoroethylene (ePTFE) membrane to extract water vapor into a dry air stream. The resultant water vapor is analyzed by a Picarro L2130-*i* for d^2H and $d^{18}O$. An automated software program provides user-specified time-averaged data and switches between four ports to enable easy calibration. Tight temperature and flow rate control regulates fractionation across the membrane. In-lab testing demonstrates that the system can achieve a raw precision (1s of 3 minute average) better than 0.05/0.15 ‰($d^{18}O/d^2H$), respectively, and a reproducibility of 0.15/0.5 ‰($d^{18}O/d^2H$) over seven days, even under variable ambient air and water temperature conditions.

Keywords: cavity ring-down spectroscopy, water stable isotope

Seasonal variation of ^{17}O -excess of precipitation in East Asian Monsoon region, Okinawa, Japan

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A high-precision analysis of the $\delta^{17}\text{O}$ of water has provided a promising new tracer ^{17}O -excess (Barkan and Luz, 2005). The changes in ^{17}O -excess is caused by molecular diffusion process during evaporation, which is basically similar to d-excess ($= \delta\text{D} - 8 \times \delta^{18}\text{O}$). In fact, a positive correlation between ^{17}O -excess and d-excess of water vapor was observed in the ocean (Uemura et al., 2010). However, much lower correlations were found in Antarctica (Landais et al., 2008; Touzeau et al., 2016) and in the United States (Li et al., 2012), probably because of kinetic fractionations. Here, we measured the isotopic composition in precipitation on Okinawa jima (Japan) to reveal seasonal ^{17}O -excess variation in East Asian monsoon region. Precipitation samples were collected every week over 2 years in Okinawa, Japan. The $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and δD of water were measured using a cavity ring-down spectroscopy (L2140-i, Picarro). The ^{17}O -excess in precipitation shows lower values in summer and higher values in winter. The seasonal variation is similar to that of d-excess, which was interpreted as changes in relative humidity in the moisture source ocean (Uemura et al., 2012). The results suggest that the precipitation in Okinawa is mainly controlled by isotope fractionation during the evaporation in the ocean.

Keywords: ^{17}O -excess, the triple isotopic composition, precipitation

Alternative to toxic substance for water sample preservation to measure stable carbon isotopic composition of DIC: preliminary result

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Carbon isotopic composition of dissolved inorganic carbon (DIC) of natural waters plays an important role in understanding of the carbon behaviors in the fields of oceanography and hydrology. It is indisputable that the isotopic change after sampling to measurement should be prevented. The employment of a toxic substance, e.g., mercuric chloride (HgCl_2) or sodium azide (NaN_3), to suppress biological (microbial) activities has established as a means of analyzing seawater samples. However, we cannot use the toxic substance without permission in the field campaign. Moreover, the use of toxic substance causes high ecological risks, e.g., human or organisms heaths. It requires the cost and time for disposal of wastewater. We suggested the possibility of salt (NaCl) to inhibit microbial activities at the Goldschmidt Conference 2016. The additional examinations using salt was carried out. As the result, salt cannot be used for low DIC concentration samples to measure carbon isotopes. The carbon isotopic ratios of those samples were shown slightly lower values than those of salt-free ones. However, the carbon isotopic ratio change is negligible in high DIC concentration samples by salt addition. DIC concentration was measured lower for the salt added samples, especially high DIC concentration samples. These changes may be caused by solubility change of gas species.

Kuo (1998) utilized benzalkonium chloride (BAC: cationic surfactant) as a less hazardous alternative to HgCl_2 for drinking water analysis. Gloël et al. (2015) represented that BAC could be an effective tool for short-term preservation of seawater samples, but is ineligible for sample storage over weeks to months. However, we consider that BAC has a potential for sample sterilization for DIC analysis, because BAC permeates the cytoplasmic membrane causing cell death. We examined the effect of BAC for carbon isotopic analysis of DIC samples, in order to establish procedure without using the toxic substance. Water samples were preserved into 10mL or 30mL glass vials after dissolving sugar, and BAC was added to half of those vials.

The preliminary results by groundwater, pond water and river water suggested that the BAC could be used to sample sterilization for carbon isotopic analysis of groundwater samples. DIC concentration was increased and carbon isotopic ratio was decreased during 4 weeks preservation for the no sterilized samples (BAC-free), but they were shown to be constant for the sterilized ones (BAC added). For the next step, we will examine the effectiveness of BAC to inhibit microbial activities in water using other natural water samples.

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Keywords: DIC, carbon isotope, benzalkonium chloride

Estimation of DIC escape from a mangrove forest in Ishigaki Island inferred from using stable carbon isotopic analysis.

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It has been considered that mangrove forests have a largest carbon reservoir in terrestrial ecosystem and most carbon-rich tropical forests and substantial amount of carbon sink. However, the majority of the mangrove net primary production remains unaccounted for by current carbon budgets. Previous observation of mangrove carbon budgets has neglected the exchange of both ecosystem gross primary production and respiration. In addition, neglecting the escape of DIC derived from heterotrophic respiration leads to an overestimation of ecosystem net productivity estimates based on eddy covariance techniques. Here, we measured DIC concentrations and carbon isotopes over complete tidal and diel cycles in the mangrove tidal creek in Ishigaki island, SW Japan. The DIC escape calculated from the mangrove forest was computed using isotopic mass balance model. DIC concentrations and carbon isotopic values showed consistent tidal variation in August, with DIC ranging from 2017 to 3061 $\mu\text{mol/L}$, and 0.37 to 10.33 ‰, respectively. The carbon isotopic values were lower than expected for the mixing of the river water and seawater DIC during low tide, due to the ^{13}C -depleted DIC inputs from the mangroves. An isotopic mass balance model was used to determine the DIC concentration derived from mangrove in the estuarine waters. The contribution to DIC escape from the mangrove in estuarine water was risen sharply in tandem with low tide ranging from 55 to 836 $\mu\text{mol C/L}$.

Keywords: Carbon cycle, Mangrove forest, DIC, ^{13}C

Preliminary study of volatile flux from magma of Aso volcano through shallow groundwater layer, Kumamoto Prefecture, Southwest Japan

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Volatile flux of magma of Aso volcano through shallow ground water layer is preliminary studied by groundwater and river (Shirakawa, Kurokawa and Midorikawa) surveys in Aso caldera and adjacent areas. Flow rates of S and Cl of Kurokawa river (Ofuchi Bridge, Aso-dani, Akamizu) are 53.7ton/day and 25ton/day, and of Shirakawa river (Myoken Bridge, Nango-dani, Kain) are 12.3ton/day and 5.4ton/day, respectively.

It is necessary to understand volatile flux of magma of Aso volcano through shallow groundwater layer considering the amount of sulfur and chlorine supplied from rainfall or strata, or the influence of hot spring water (deep groundwater) to shallow groundwater layer.

This study was supported by the Secretariat of the Nuclear Regulation Authority, Japan.

Keywords: Aso caldera, groundwater and river survey, volatile flux of magma, hydrogen and oxygen isotopic ratio

Runoff processes of volcano springs in the northeast foot of Mt. Ontake

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Hydrological observation and sampling of the spring were carried out at the northeast foot of Ontake volcano. Stable isotope ratio and concentration of transient tracer (CFCs, SF₆) were measured in Geo-science laboratory. Based on the results, we discuss the runoff-processes of the springs with short residence time less than 10 years.

Keywords: Volcano springs, Mt. Ontake, Runoff-processes

Comparison of stable water isotopes between lake bottom springs and groundwater around Lake Kawaguchi at the northern foot of Mount Fuji

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In Lake Kawaguchi, we previously reported the existence of lake bottom springs at the depth of 8 meters in the east of the Unoshima Island. Lower water isotope values around the springs indicate groundwater inflows from the surrounding mountains, however, the detailed source area of the springs was not determined due to the mixing with lake waters. In this study, we directly obtained spring water by scuba diving, and compared its water isotope ratios with those in groundwater around the lake collected at the same period. Water isotope values of the springs were higher than those in groundwater from the southern side of the lake, and showed more close values to groundwater from the northern side of the lake. This suggests that the source of the lake bottom springs is likely derived from Misaka Mountains.

Keywords: Fuji Five Lakes, springs, stable water isotopes

An isotopic study on origins of water and nitrogen pollution of shallow groundwater in densely populated areas of Kawasaki City, central Japan

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Around 30 water samples in Kawasaki City, the seventh largest city in Japan, was analyzed for water chemistry and isotope ratios of water (δD and $\delta^{18}O$) and nitrate ion ($\delta^{15}N$ and $\delta^{18}O$) to investigate the origins of water and nitrogen pollution of groundwater in the highly urbanized area. All groundwater samples are from either springs or private wells at a depth of less than 15 m. As a result of the δD and $\delta^{18}O$ analysis, it was proved that water leaking from drinking water mains is a major source of shallow groundwater recharge in the study area. The role of drinking water leakage in shallow groundwater recharge was found to be prominent for that in the lowland plains along Tama River, accounting for up to 40 % of the total groundwater recharge. With the help of nitrogen and oxygen isotopes of nitrate ion, we also found the serious effects of sewer leakage on shallow groundwater quality. Distribution of the nitrate ion concentration across the study area was highly heterogeneous, indicating the localized occurrence of denitrification as well as the effects of sewer leakage. Quantifying the effects of sewer leakage to both groundwater recharge and its quality is the subject of our future study.

Keywords: urbanized area, Kawasaki City, shallow groundwater, leakage from water mains, sewage leakage, nitrogen and oxygen isotopes of nitrate ion

Anomalous changes in groundwater and hot spring water after the 2016 Kumamoto earthquake

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We have investigated the groundwater at the 8 springs (A-H in Fig.1) to clarify the changes associated with the 2016 Kumamoto earthquake. We also conducted inquiring survey at the 21 hot springs and investigated spring water newly generated in Aso area (J in Fig.1).

Six of the eight springs (A-D, G, H) were the places where the measurement of flow rate and sampling was done from 6th to 10th March 2016 one month before the earthquake. The same survey was carried out in 2014 for the remaining two springs (E, F) as well. Such pre-earthquake survey revealed the changes in flow rate and major chemical concentration due to the 2016 Kumamoto earthquake.

The flow rate increased more than twice that of before the earthquake at the three springs (A-C) and decreased less than half at the two springs (G, H) (Fig.2). At the other springs (D-F), changes of the flow rate was less than 30 %. The former five springs are located within 7 km from the Futagawa and Hinagu faults that caused the 2016 Kumamoto earthquake.

To compare the flow rate changes and crustal deformation which might occur at the time of earthquake, we calculated the crustal strain changes based on the fault model by Geospatial Information Authority of Japan (2016) using MICAP-G (Okada, 1992, Naito and Yoshikawa, 1999). Spatial distributions of the flow rate changes and the crustal strain changes did not show a clear relationship (Fig.1).

As for the major chemical composition, there were clear changes only in the nitrate ion concentration (Fig.3). The pattern of change was the same for the all springs as follows. The nitrate ion concentration peaked in May 2016 and decreased until September 2016 than before the earthquake.

As the result of our inquiring survey at the hot spring facilities, it became obvious that there were hot spring wells and areas where self-discharge occurred or the amount of self-discharge was markedly increased. A good relationship in the spatial distribution between the changes and the calculated crustal strain changes was found.

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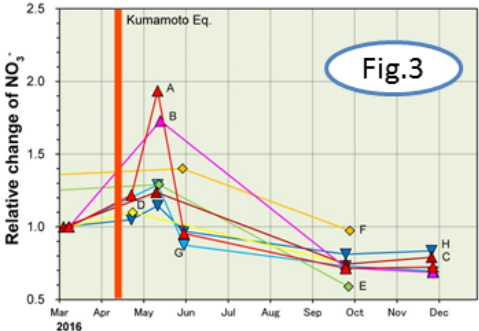
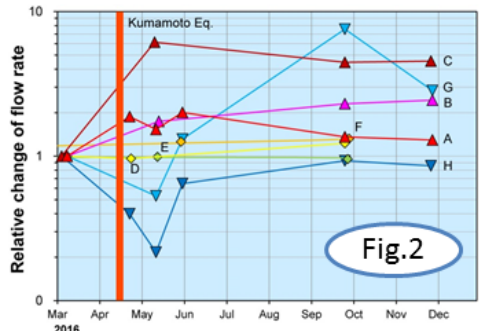
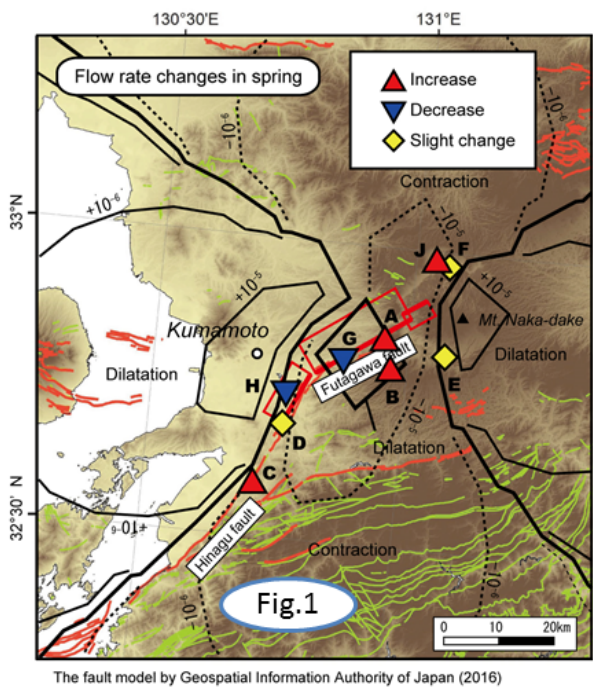
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Fig.1 Spatial distribution of the flow rate changes of the springs in relation to the 2016 Kumamoto earthquake

Fig.2 Relative changes of flow rate of the springs

Fig.3 Relative changes of nitrate ion concentration of the springs

Keywords: The 2016 Kumamoto earthquake, groundwater, flow rate, nitrate ion, crustal strain changes, hot spring



Groundwater flow system in Fukushima Prefecture traced by tritium-³He and ¹²⁹I dating methods

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For developing and effective utilizing of groundwater resources, it is necessary to understand the large circulation of water from precipitation to use by residents (Mahara *et al.*, 1993). In particular, studying the residence time and source (recharge area) of the water is important in evaluating the groundwater flow system. In Fukushima Prefecture, although environmental behaviors of various radionuclides released by the accident of Fukushima Daiichi Nuclear Power Plant have been analyzed, there are few reports on the behavior and contamination status of groundwater by radionuclides, which are necessary to be assessed for safety use of groundwater resources in the future.

In this study, we investigated the groundwater flow system in Fukushima Prefecture and the anthropogenic contamination of groundwater caused by the nuclear accident using ³H-³He dating method, which is possible to acquire not only the age of groundwater but also the information on the water source based on the initial ³H concentration, and ¹²⁹I, one of the radionuclides released by the nuclear accident.

Sampling was conducted in September 2016 and January 2017 mainly on groundwater and spring water at the Hama-dori region, Fukushima Prefecture. The water samples for ³H-³He dating method were collected and sealed in copper tubes with special care to atmospheric contamination and analyzed using a noble gas mass spectrometer at Department of Basic Science, University of Tokyo. After the first extraction of originally dissolved helium, the sample water was sealed in the copper tube again and stored for about a month, and then the amount of ³He produced by the decay of ³H was extracted by the second degassing and analyzed to obtain the initial ³H concentration and the residence time. Water samples for iodine analysis were sampled in 1-L plastic bottles. Iodine in the sample water was extracted and back-extracted to yield silver iodide pellet, and then ¹²⁹I/¹²⁷I ratios and concentration of stable isotope ¹²⁷I was measured using an accelerator mass spectrometer and ICP-MS at Micro Analysis Laboratory, Tandem accelerator, University of Tokyo.

For example, in Minami Soma Sports Park located about 30 km north of the nuclear plant, the concentration of tritium-derived ³He was approximately 2.2×10^{-18} mol/g. The current ³H concentration has been determined by liquid scintillation counter to be 9.3 TU for a sample collected from the same locality (Yabusaki *et al.*, 2015). These values give the initial ³H concentration of 10.1 TU and the residence time of about 1.5 years. This suggests the groundwater system in this region has already been almost completely refreshed since March 2011 due to the short residence time.

For ¹²⁹I/¹²⁷I ratios, most of the samples measured so far showed values below 1.0×10^{-11} , which is the lower limit of the isotope ratio including radioactive iodine of anthropogenic origin (Fehn, 2012). The low ¹²⁹I/¹²⁷I ratio of water from Minami Soma Sports Park is in the range of natural background, which is consistent with the short residence time obtained with the ³H-³He method.

Up to the present, it is not possible to confirm the apparent contamination due to the nuclear accident, but depending on the residence time of the groundwater, the possibility that polluted water will discharge in the future cannot be ruled out. We are planning to carry out further sampling to estimate the residence time and water source by the ³H-³He method and combine it with the ¹²⁹I results to investigate the

environmental impact.

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10-Beryllium-contents of sediments in mountainous catchments topographically constrained by shallow landslides

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Recently, it is being important to understand sediment dynamics in a river basin for a well-balanced sediment management in the entire basin at view points of the national flood control and water resources. However, it is still unclear how much sediment has been produced in a mountainous stream, which is a basic information of the sediment dynamics. In this study, 10-beryllium-contents have been analysed for sediment samples of mountainous catchments in Fukuoka, Japan in order to fundamentally examine the sediment dynamics in the river basin. Since the late 1980s, beryllium isotopes of quartz extracted from rock or river sediment have been analysed to estimate rock- or catchment-scale denudation rates [1].

A lot of slope collapses are observed in the study area, of which the geology mostly consists of Mesozoic granites. Most of those failures were explained as a shallow landslide under around 1m in depth, which accompanied with an infiltration of rains and an increase of a groundwater table in weathering granite [2]. The sediment samples have been collected at four riverbeds and one hillslope in two different sub-catchments (A and B).

The samples that originated from weathering granite are composed of quartz, feldspar, mica and some organic materials. Firstly, they were washed by pure water and sieved over 250 μm to avoid a contamination from aeolian deposits. Then, the quartz was purified with acids and beryllium oxide was produced based on the method of Kohl & Nishiizumi [3]. Finally, beryllium isotopes were analysed with the accelerator mass spectrometer equipped by JAEA (JAEA-AMS-TONO).

As a result, the sample of the catchment B shows a little bit higher value in 10-beryllium-content that is 8.7 ± 1.9 ($\times 10^4$ atoms/g), than those of catchment A that show similar values ranging from 3.1 ± 0.5 to 5.5 ± 0.9 ($\times 10^4$ atoms/g). This result indicates that the river sediment in the catchment B includes quartz grains that have been exposed on a ground surface for a long time compared with the catchment A because topographical settings of these two catchments are similar. It is also possible to think that the river sediment in the catchments A contains more landslide materials because the landslide materials, which have come from a deeper part, might have a lower value in 10-beryllium-content. This result is consistent with distribution of the shallow landslides in 2003.

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Keywords: topography, beryllium isotopes, sediment dynamics

Dynamics of Lake and Groundwater

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Soils and forests are deteriorating; grazing lands are degraded; water points, sources and lakes are drying, and underground water levels are lowered. This could largely be attributed to the employed traditional inappropriate resource management methods; severe soil erosion and degradation reducing infiltration and resulting in sedimentation of water sources and lake basins. Bad cultivation practices, burning and cutting of perennial vegetation, overgrazing and grass fires increase the runoff causing soil erosion and consequently sediment transport to the lake resulting to decrease its storage capacity and quality of stored water.

The present investigations also include the runoff-rainfall studies combined with estimation of sediment transport, pollution of water and rating decrease in storage capacity. The lake discharge has been decreased according to preliminary analysis. The main aim of this research is to quantify the interactions between groundwater and surface water. A multi-disciplinary approach will be used to quantify interactions between groundwater and surface water in the catchment. The methods include modelling, isotopes, hydrochemistry, hydraulic, and temperature approach. These methods will be applied at various spatial and temporal approach. With the help of different GIS/Remote Sensing equipment's, different maps and imageries will be developed and further investigation will be done to evaluate the present mode of land situation and its degradation. Hydrological data and other related data will be collected from the different sources. Analysis of soil samples for different physico-chemical properties and water sample for testing its quality will be done by standard procedures and methods.

The status of land and water surface will be counter checked by ground truth. The results will provide a solid scientific basis on integrated approach of groundwater and surface water. Moreover, depending on the analysis and result, suggestions can be made for adopting some strategies to improve water resource management.

Keywords: lake, groundwater, SWAT & MODFLOW