# 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 ( $\delta^{18}$ O,  $\delta^{2}$ H, Cl<sup>-</sup> & SO<sub>4</sub><sup>2-</sup>), line condition (Ic)-excess, complemented by soil analysis and physical measurements from piezometers. The depth profiles show a steady increase in both  $\delta^{18}$ O,  $\delta^{2}$ H tracers and lc -excess below depth, from the ground surface to >2m in lowlands and >5m in both uplands and piezometers. The Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> also showed leaching to similar depths. The change in  $\delta^{18}$ O,  $\delta^{2}$ 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 aguitards 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 ( $\delta^{18}O_{water'}$ ,  $\delta^{34}S_{sulfate}$ , and  $\delta^{33}S_{sulfate}$ ). 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 Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> concentration ratio showed the value near 1. (2) Hot springs which showed large time variations of Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> concentration ratios because of decrease of Cl<sup>-</sup> concentration. The isotopic ratios of water were plotted between MV and local meteoric water (LMW). (3) Hot springs which were mainly composed of SO<sub>4</sub><sup>2-</sup> without Cl<sup>-</sup> and showed low anion concentrations and the low isotopic ratios near LMW.

We also measured the  $\delta^{34}$ S value of sulfate in the hot-spring waters. Generally, primary sulfates (derived from SO<sub>2</sub> disproportionation) in hot springs show higher  $\delta^{34}$ S values than secondary sulfates (formed by the H<sub>2</sub>S oxidation). The  $\delta^{34}$ 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<sub>2</sub>S because  $\delta^{34}$ S showed low values. On the other hand,  $\delta^{34}$ 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  $\delta^{33}$ S and  $\delta^{33}$ 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  $\Delta^{33}$ S) of samples in the JV was not zero, which is considered to be affected by kinetic isotope effects. The intersection point ( $\delta^{34}$ S ~ 9‰) between the regression line of samples and the  $\Delta^{33}$ 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  $\delta^{18}$ O value of the groundwater in the Katakai River fan in 2002 was similar to the  $\delta^{18}$ 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<sub>3</sub>. 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 Na  $\cdot$  Ca-Cl, it may take a long time for water recharging from Katakai River. This seems to suggest t the vulnerability of deep confined groundwater should be considered for sustainable groundwater management in the future.

Keywords: ground water, Katakai River alluvial fan, Uoze 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 d180 (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 d180 (or d2H) value in net rainfall was higher than that in gross rainfall because of fractionation by EW. Calculated EW by the values of d180 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 d180 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.

This work was supported by JSPS KAKENHI Grant Number JP15H40250.

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 exploit not only for climate proxy (e.g. Dansgaard, 1993) but for studying precipitation systems.

The Baiu Front (BF) is stationary front during the late spring and early summer near Japan, which is the

"boundary" between tropical and extratropical airmass. BF is characterized by 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 water cycle associated the front.

From observational study by Kurita et al. (2015), highest isotope ratio in water vapor near surface correspond to the warm airmass advection by southerly flow, while abrupt isotopic depleting 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 (airmass) advection and depletion by rainout on isotopic variability associated with the BF.

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

To check validity of our isotope-incorporated model, simulated values in our model are compered with observation at 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 to precipitation intensity by BF, dD contrast between north and south of BF reflects airmass difference in the case with weak precipitation, which consistent with Kurita et al. (2015). On the other hand, heavy precipitation case is almost same with weak precipitation case except for "V-shape" depletion near BF region. this result is consistent with 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 $\delta^{13}$ 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<sub>2</sub> degassing after flowing out of the springs. In this talk, we present results of the  $\delta^{13}$ C and  $\delta^{18}$ O in R. Nogori and the tufa deposits, and then discuss the possibility of tufa  $\delta^{13}$ C record as a reflection of volcanic activity.

Keywords: Tufa,  $\delta$  13C,  $\delta$  18O

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

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The oxygen isotope composition ( $\delta^{18}$ O) of speleothem is widely used as paleoclimate proxy. Interpretation of the  $\delta^{18}$ O value is not straightforward because it is controlled by two factors;  $\delta^{18}$ O of dripwater and temperature at calcite formation. The  $\delta^{18}$ 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 inclusioon

### 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 km<sup>2</sup>), Sierra Nevada, California. Mean isotopic values in small tributaries (basin area < 122  $km^{2}$ ), rock glacier outflows and groundwater were correlated with mean basin elevation (n = 16, p < 1000.001), suggesting an isotopic lapse rate of -1.9‰/100 m for  $\delta$  <sup>2</sup>H and -0.22‰/100 m for  $\delta$  <sup>18</sup>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 (<u>isotope-incorporated regional spectrum model</u>) 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 <sup>35</sup>S in water/snow samples and its applications to snow and glacier hydrology

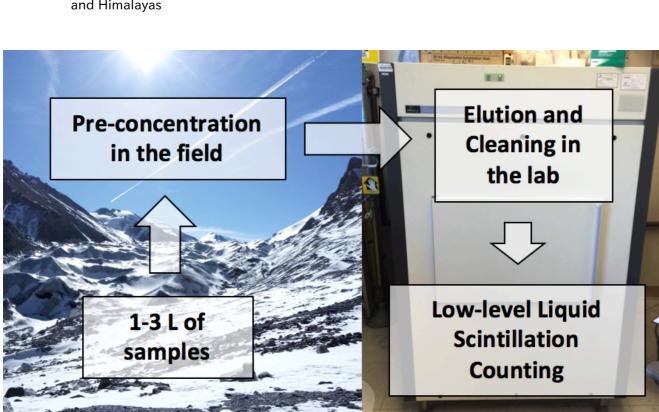
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Cosmogenic <sup>35</sup>S is useful in understanding a wide variety of chemical and physical processes in the atmosphere, the hydrosphere and the cryosphere. The 87.4-day half-life and the ubiquity of sulfur in natural environments renders it an ideal tracer of many phenomena. For example, recent <sup>35</sup>S measurements in aerosol samples provided new insights into the vertical and horizontal transport processes in the atmosphere [1-2]. However, measurements of <sup>35</sup>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 <sup>35</sup>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 <sup>35</sup>S standards (with activities of <5 disintegrations per minute) showed a <sup>35</sup>S recovery percentage of ~95%, demonstrating a relatively small deviation from the true value. This new method will provide a powerful tool in studying <sup>35</sup>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 <sup>35</sup>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 <sup>35</sup>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<sup>18</sup>O), our <sup>35</sup>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