Multi-Isoscape approach to environmental studies

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Environmental traceability method that is comprised of multi-element and multi-isotope information, which indicate water cycling and material cycling, is applicable to the studies on the movement of living organisms and food web structure. The method is thus applicable to study various environmental issue because human beings live under the cycles. It is both important to perform basic researches on elemental cycling and to make spatio-temporal mapping.

"Environmental Isotope Study", which the Research Institute for Humanity and Nature (RIHN) is operating, proposes co-operative research of the environmental traceability methodology using multi-elemental analysis and multi-isotope analysis. It is possible to understand relationship between local ecosystems if we can show local environmental characteristics using multi-isoscapes. It is only recently considered that research collaboration with local people, local government, and local education is important to solve environmental issue. We propose the importance of research collaboration between universities or institutes.

Keywords: Stable isotopes, Environmental traceability

Study on groundwater flow system at Oshino Village in Yamanashi Prefecture –Report 1. Characteristics of water quality and stable isotopes of shallow and deep groundwater at Oshino Village.

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Oshino Village is located in southern part of Yamanashi Prefecture, Japan. The elevation is 936 m a.s.l. and the area of village is about 8 km from east to west and about 4 km from north to south. The Oshino Hakkai springs that is registered as World Cultural Heritage Site are located in Oshino Village. It is suggested that the Oshino Hakkai springs are recharged at Mt. Fuji as a result of field observation. The objective in this study to clarify the detailed groundwater flow and residence time of springs and groundwater in Oshino Village.

The filed observation in Oshino village were carried out at 18 to 19 in January, 2017. EC, pH, water temperature and depth of water table were measured and spring water and groundwater were sampled for 72 sites. Dissolved inorganic matters, trace elements and stable isotopes of oxygen and hydrogen were analyzed by using the analytical instruments (ICS-3000, Agilent 7500cx, L2130-i). As a result of this observation, followings are revealed.

1) Dissolved inorganic matters and δ^{18} O and δ D of Oshino Hakkai springs (Okamaike, Choshiike, Nigoriike, wakuike, Kagamiike, Shobuike and sokonashiike) are mostly the same. However, the Deguchiike which is one of the Oshino Hakkai springs showsa little different water quality, it is considerate that the groundwater flow of Deguchiike is different from that of other springs of Oshino Hakkai.

2) The water quality of groundwater mostly show the Ca-HCO₃ type, but there are some sites that contain the Na⁺ or Mg²⁺. The amount of dissolved inorganic matter of groundwater are lower at central part than the other area of Oshino Village. It is expected that the different groundwater flow system is existed. 3) There are some sites of shallow groundwater that show a little high nitrate concentration. It is thought that the high concentration of nitrate is due to fertilization to farmland.

4) The deep groundwater that well depth is about 100 m and some sites of shallow groundwater show the high pH (above 8.2), and also show the high concentration of vanadium and phosphorus and relatively low values of δ^{18} O and δ D. There's a high possibility that these sites' groundwater is recharged at Mt. Fuji.

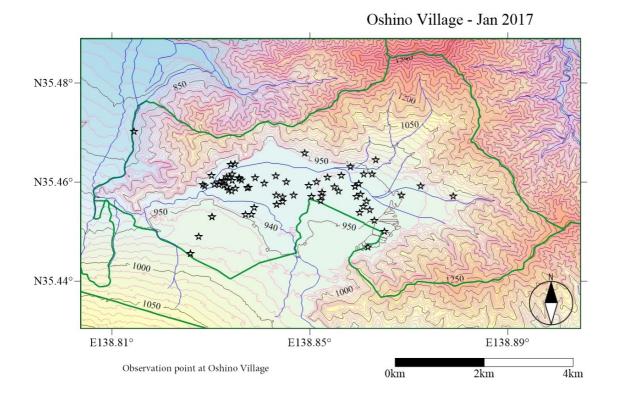
5) It is conceivable that δ^{18} O and δ D values are affected by the difference of recharge area. As a result of correlation chart which showed the EC versus δ^{18} O, observation site was able to divide into three groups. The regression line of δ^{18} O versus δ D is δ D=6.2 δ^{18} O-5.0 (r²=0.969).

6) The artesian well which is located at northwestern part of Oshino village shows Na-SO₄ type. In this site, the water temperature is relatively high and δ^{18} O and δ D is relatively low. These water qualities of the artesian well differ from other sites.

7) From the contour map of water table, the groundwater flow at Oshino Village was divided into two. The groundwater flows from southeast to northwest in eastern part and from south to north in central and western part of Oshino Village.

In future, we are going to carry out the field observation at Spring and Summer in 2017, and to estimate the groundwater flow system and residence time.

Keywords: Oshino Village, Oshino Hakkai, groundwater flow, water quality, stable isotope, trace element



Estimation of the groundwater recharge processes using end-member mixing analysis in a paddy-dominated alluvial fan, Japan

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The Tedori River Alluvial fan in central Japan has abundant groundwater resources, serving as sources of the regional drinking and industrial water. The study area is bounded by the Kakehashi River to the south, the Sai River to the north, the Japan of sea to the west, and the mountains to the east. The rice paddy and crop-rotated paddy fields occupy 45% of its total area (170 km²). The paddy plots are irrigated from the early of May to end of August. Highly turbid water was observed in early of May 2015 and has been continued for a while. This is due to a large-scale landslide occurred at 60 km upper mountainous area from the river outlet. The landslide area has 150 m length 300 m width. Decrements of groundwater level occurred in both 2015 and 2016. The durations with the low groundwater levels were about 6 months in 2015 (from the early of May to the early of November) and 2016 (from the middle of March to the middle of September). Large decrements was observed in the middle section along the Tedori River. From the non-irrigation period, groundwater level raise up to the previous water level before the turbidity accident. Mechanisms of these groundwater fluctuations and the relationship between the groundwater decrements and turbid river water were absolutely not clear. Our study objective is to identify the mechanisms of the changes by the observations of spatial distributions and its temporal changes of groundwater qualities.

We collected 57 water samples including 33 shallow groundwater, 1 deep groundwater, 1 spring water, 11 river water along three rivers, 1 precipitation, and both of paddy irrigation water and standing water at 6 paddy plots during the irrigation period. Water sampling has been conducted with 2 months interval from April 2016. We analyzed stable isotope ratios of hydrogen, oxygen, and strontium and concentrations of major dissolved ions. We had carried out similar water samplings and analysis 4 times from 2008 to 2011. In this area, water samples from the Tedori River show the lowest oxygen and hydrogen isotope ratios and precipitation water samples show the highest. The paddy infiltration water samples show the influence of evaporation. Then, end-member mixing analysis (EMMA) were performed to estimate the contributions of each groundwater source for oxygen and hydrogen isotope ratios of shallow groundwater samples. We compared the EMMA results from the view point of temporal changes in contributions rates.

During the irrigation and non-irrigation period in 2016, groundwater recharge from the Tedori River contributed water balance of the shallow groundwater throughout the alluvial fan. In 3 km buffer area along the river, contributions of the river water ranged from 18% to 97%. Large contributions (over 60%) were calculated around the lower part of the fan. From the comparison between June in 2011 and June in 2016, contributions of river water decreased at the left side of the river, but did not significantly change at the right side. At near the right bank of the Tedori River, contributions of infiltration water from the irrigated paddy fields decreased and contributions of precipitation increased to compensate for it. Turbid water might cause siltation at paddy fields because the irrigation water is derived from the Tedori River. Groundwater recharge from the irrigated paddy fields would be reduced due to the siltation. Future work of this study is quantitative evaluations of groundwater recharge processes by a transient groundwater modeling.

Keywords: shallow groundwater, alluvial river, oxygen and hydrogen isotopes, groundwater level

Spatial variation in chemical soluble ions of the surface ice of the Urumqi No.1 Glacier, Tien Shan Mountains, China

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The chemical soluble ions on the glacier surface are important in order to understand the ecology of the microbes living there and to evaluate the characteristics of melt water and its effect on the ecosystems and local people in the downstream of the glacier. This study aims to describe the spatial variations in chemical soluble ions in the surface ice of the Urumqi No.1 Glacier located in the Tien Shan Mountains, China. We collected surface ices in the ablation area of the glacier in August 2016 and measured the water stable isotopes and the concentrations of major ions (Cl⁻, NO₃⁻, SO₄⁻²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺)of the samples. Based on the results, we created maps of their spatial variation using a GIS software. The results show that the water stable isotopes were relatively higher in the surface of eastern side, while lower in the western side of the glacier. This is probably due to different age of the ice accumulated on the glacier. Since the accumulation area distributed along the ridgeline from south to east of the glacier, the age of ice appears to be older in western side compared with that of eastern side. The chemical soluble ions was also not simply associated with the elevation or glacier flowline, but relatively higher in the area of eastern side of the glacier. This is also likely to be due to age of ice. In contrast, Ca/Mg ratio was generally higher in the lower area of the glacier and had a significant negative correlation with the elevation. This is probably due to additional solutes by chemical weathering of dust deposited on the glacier surface. Results suggest that the spatial variations in chemical soluble ions are mainly determined by the age and flow of the glacial ice and the additional solutes from surface dust on the glacier.

Keywords: mountsin glacier, chemical soluble ion, spatial variation

Geochemical and isotopic analyses of river waters from the Okayama and Tottori Prefectures, Japan

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In order to understand the mechanisms responsible for the geochemical and isotopic variations observed in river waters, we investigated major dissolved components, trace element concentrations, and O-H isotopes of 540 river water samples collected from 379 locations of the Okayama and Tottori prefectures. Some of these samples were also studied for S and Sr isotopes. These data were used to construct high-resolution geochemical and isotopic maps of the two Prefectures.

The O-H isotopes of the studied samples display regional variations that exceed seasonal variations. A clear altitude effect is observed in the O isotopes. The d-excess value is high in the northern Okayama and Tottori Prefectures (>20), and gradually decreases towards the southern Okayama (5~15).

With the exception of a few locations in the northeastern part of the Tottori Prefecture, the SO_4 concentration is low (<5 ppm) in Tottori and northern region of the Okayama Prefecture, and gradually increases towards the southern Okayama (>10ppm). Change in the SO_4 concentration is accompanied by shift in the sulfur isotope ratio, which converges to ~0 in the high SO_4 regions. As proposed by Nakano et al. (2008, Sci. Total Environ., 389, 132), decomposition of fertilizers used in agricultural activities may, at least in part, be responsible for this variation.

The concentrations of major cations such as Ca, Mg, Na, K, as well as trace elements (47 elements) also display regional variations, which can be classified into several groups. By comparing the geochemical maps of these elements with the geological maps, we note that the geochemical variations of some of these elements can be explained by reaction of ground water with rocks exposed in the area. On the other hand, variation of trace elements such as As, Cd, and Zn in some areas requires additional input from sources such as mine drainage.

Keywords: Okayama Prefecture, Tottori Prefecture, River Water

Information visualization for participatory multi-isoscape mapping

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Sustainable environmental monitoring in a region necessarily requires that researchers collaborate with societal actors such as governmental agencies, non-profit organizations, and residents. Such collaboration requires a boundary object as a shared upper-level goal, because different actors may have different motivation, values, beliefs, and incentive.

In water quality monitoring, the co-creation of a map, indicating the location of water sources or springs for instance, can be a boundary object between researchers and civil members. Researchers may input novel scientific knowledge, such as multi-isoscapes to the map and compare the visualized information with the local traditional knowledge, such as characteristics of groundwater in the study area. Mutual learning enables the formation of a community for continuous monitoring by civil members. In our view, researchers can visualize the vocabulary systems using ontological engineering and can provide participatory GIS (geographical information systems) in order to promote such a participatory citizen science. This study validates the usability of these tools by applying the ontological engineering technique to the researchers' talk on multi-isoscapes and water quality monitoring in public lectures for analyzing their knowledge systems and by applying the spatial principal component analysis to multiple chemical elements of the underground water in Ohno City (Fukui Prefecture, Japan).

Keywords: Multi-isocpaces, Information visualization, Ontology engineering, Participatory GIS, Spatial principal component analysis, Citizen science

Measurement technique of the nitrogen isotope ratio of NOx collected by the filter-pack method and its application.

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NOx (NO and NO2) is quite important in atmospheric chemistry as well as in the biogeochemistry. Although natural abundance of stable nitrogen isotope is a promising tool for the the investigation of NOx dynamics in the enviornments, nitrogen isotopic measurement of NOx is quite difficult due to its high reactivity. We combine the filter-pack method (Watanabe et al. 2006) to capture NOx with the denitrifier method (Sigman et al. 2001) to measure nitrogen isotopic signature of NOx in the actual enviornments.. We found that the filter-pack method can be applied for atmospheric NOx samples including the soil-emitted NOx. We present our preliminary data obtained from the field and discuss the limitation and possibility of our filter-pack method in the presentation.

Keywords: d15N, NO gas, denitrifier method

Using environmental tracers to evaluate dynamics of nitrate sink in Japan Sea stratovolcano areas.

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Atmospheric deposition of nitrogen transported from the East Asia is modifying terrestrial ecosystem of Japan. Although increasing trends of nitrate concentration are reported in several rivers facing to the Sea of Japan, there are little long-term data on the relationship between atmospheric nitrogen deposition and nitrate concentration of stream water. To clarify the relationship, we have retrospectively evaluated the impact of atmospheric nitrogen deposition on three watersheds (Site A: Mt.Daisen, Site B: Mt.Haku, Site C: Mt.Chokai) by using nitrate triple oxygen isotope ($D^{17}O$) and sulfur hexafluoride (SF₆) in spring water and groundwater.

Keywords: nitrogen deposition, eutrophication, triple oxgen isotope, Sea of Japan

Recovery of stream water from acidification due to declining atmospheric sulfur deposition in a Japanese cedar forest near the Sea of Japan

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Introduction: Atmospheric environment in Northeast Asia has been dynamically changing recently. Although SO₂ emissions in China peaked in 2006 and started declining thereafter, emissions of N compounds and related air pollutants have still been increasing. As shown in previous studies in Europe/North America, decline of S deposition promotes recovery of ecosystems from acidification but its process is not uniform. Since the deposition in Asia has just started declining, response of ecosystems should be studied as one of the current subjects in biogeochemistry. In this paper, in addition to the long-term monitoring data, isotopic analysis was applied to discuss the recovery process of ecosystems from acidification due to declining S deposition in a forested catchment.

<u>Methods</u>: The Kajikawa site (3.84 ha) was established in a small catchment within a Japanese cedar plantation in Shibata City, Niigata Prefecture. Rainfall outside the canopy (RF), throughfall and stemflow (TF+SF), and stream water (SW) have been collected biweekly or monthly since January 2002. Discharge of the stream water was measured continuously using the weir. The pH, electrical conductivity, alkalinity (only for SW) and major ions were measured for the water samples. Additionally, soil solutions have been collected since 2012, and then measurement of the sulfur isotopic ratio (δ^{34} S) was started. Moreover, isotopes in Sr, Pb and water (H and O) were also measured for part of the water samples. The water year (WY) in the site was defined from June to May in the next year.

Results and discussion: Fluxes of SO_4^{2-} by RF and TF+SF increased in winter with those of CI^- and Na^+ . This suggested that the area suffered from long-range transported air pollutants due to seasonal winds through the Sea of Japan in winter. The long-term data indicated that the annual flux of non-sea salt SO_{A}^{2-} by TF+SF started declining after the peak in WY 2006/2007, reflecting the sulfur emissions in China. SO₄ ²⁻ concentrations in SW declined significantly, and pH and alkalinity increased. This may be the recovery process from the past acidification. The δ^{34} S values in RF and TF+SF were also lowering in summer (ca. 4‰) and increasing in winter (ca. 12‰). In winter, the rainwater may be affected by high- δ^{34} S sulfur derived from sea-salt (20.3%) and coals in China (6.6%: Ohizumi et al. 2016). On the other hand, the δ^{34} S values in SW were stable (ca. 9‰). The annual weighted mean δ^{34} S value in RF was also around 9‰. According to the input-output budget until WY 2013/2014, approximately 76% of the sulfur input was discharged into SW in the study catchment. The δ^{34} S value in RF and SW suggested that the sulfur input was once cycled and/or retained in the soil-plant system and then the isotopically homogenized sulfur was discharged into SW. Therefore, in the recovery process, the circulation/retention in the plant-soil system may sensitively respond to decline of the sulfur input. In seven lakes monitored by the Ministry of the Environment of Japan (MOEJ), similarly, SO_4^{2-} concentrations started declining after peaks in 2006/2007/2008, and the δ^{34} S values were stable without seasonality. This suggests that inland water in Japan sensitively responded to decline of the atmospheric sulfur input. In the presentation, results of other isotopic measurements will also be discussed.

<u>Acknowledgements:</u> The surveys in Kajikawa site were conducted under approval by Niigata Prefecture and assisted by the manager, Mr. Takanori Funayama. Monitoring on lake water and part of isotopic measurements were conducted as the Long-term Monitoring on Transboundary Air Pollution and Acid Deposition by MOEJ. Isotopic measurements of elements other than sulfur were conducted as Environmental Isotope Study in Research Institute for Humanity and Nature. The authors thank relevant persons and organizations.

References: Ohizumi, T. et al. 2016. Atmospheric Environment 140, 42-51.

Keywords: sulfur, acidification, recovery

Origin of Sulfate Ion in Precipitation of Chugoku District Estimated by Sulfur and Oxygen Isotope Ratios

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Origin of Sulfate Ion in Precipitation of Chugoku District Estimated by Sulfur and Oxygen Isotope Ratios

We have sampled monthly precipitations at 6 sampling sites in Tottori and Okayama Prefecture in order to observe seasonal and secular change of cross-border pollution from mainland China. We have measured chemical composition, H-O and Sr isotope ratios of precipitation, and S isotope ratio of sulfate ion. Origins of sulfate and their contribution to sulfate ion in precipitation has been estimated using S isotope ratio. In this study, we measured O isotope ratio of sulfate ion to try to restrict the origin of sulfate ion more accurately.

Oxygen isotope ratio of sulfate ion was measured by TC/EA-IRMS. Barium Sulfate precipitated from precipitation occludes nitrate ion and cannot be used directly oxygen isotope measurement. It is purified by dissolving using chelating agent (DPTA) and re-precipitation. Remaining DPTA is removed by heating at 450°C for 3 hours. Purified barium sulfate is used for oxygen isotope analysis.

Measured isotopic ratios are the mixture of isotopic ratios of seawater sulfate, sulfate resulted from fossil fuel combustion (coal combustion in China and petroleum combustion in Japan) etc. Non-seawater sulfate (nss) oxygen and sulfur isotope ratios of sulfate ion were calculated using chemical composition of precipitation, and oxygen and sulfur isotope ratios of seawater. In a plot of oxygen isotope ratio vs. sulfur isotope ratio, the measured results split into three groups. Group A includes winter high δ^{34} S group ($\delta^{18} O \approx 7\%$, $\delta^{34} S \approx 7\%$), which is influenced by Chinese coal combustion. Group B includes summer low δ^{34} S group ($\delta^{18} O \approx 7\%$, $\delta^{34} S \approx 2\%$), which is mainly influenced by Japanese petroleum combustion. Group C includes intermediate δ^{34} S and high δ^{18} O group ($\delta^{18} O \approx 15\%$, $\delta^{34} S \approx 4\%$) in March. Nss-Sr isotope ratio of group C is highest among samples, indicating the contribution of soluble component of yellow sand. Thus, high δ^{18} O of group C may be due to the soluble sulfate ion of yellow sand. Measurement of δ^{18} O for soluble component of yellow sand is necessary to prove this hypothesis. Unfortunately, oxygen isotope ratio of sulfate is found not to be a good indicator to discriminate between sulfate from Chinese coal combustion and that from Japanese petroleum combustion.

Keywords: precipitation, Chugoku district, Sulfate ion, S isotope ratio, O isotope ratio

Geographic variation of Japanese cedar (*Cryptomeria japonica*) may have a different effect on soil ecosystem

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Soil organisms can be affected by differences in aboveground vegetation, often driven by the chemical quality of the soil and litter. C. japonica is the most popular plantation tree species in Japan, and plantations of C. japonica account for 12% of the total land area in Japan. C. Japonica has many geographic variations such as Yakusugi and Yoshinosugi, and has been planted at each provinances. Our previous studies showed plantation of C. japonica affect community structure of soil invertebrate by altering calcium availability in soil. However, we have not estimated whether the effects of plantation on soil organisms vary depend on the geographic variation. In Wakayama Experimental Forest, Hokkaido University, there are common gardens that planted various provenances of C. japonica. We investigated the soil solution and leaf litter chemistry, root exudation rates of organic acids and soil invertebrate community, and we compared between plots that planted a different provenances of C. japonica (Yakusugi, Yanasesugi, Yoshinosugi and Itoshirosugi). Our results showed the diversity of soil invertebrate and concentrations of essential nutrients (calcium and phosphorus) in soil and litter significantly higher at the plot where native provenance, Yoshinosugi, was planted. Furthermore, root exudation rates of organic acids were also significantly higher at the plot where Yoshinosugi was planted. Supply of the organic acids from root systems of tree can alter dynamics of soil nutrients. Therefore, variation of rhizosphere environment might create differences in soil nutrients availability and soil invertebrate community.

Keywords: Soil invertebrate, Calcium availability

Ecology of collembola (springtails) living on seasonal snow in the deciduous forest in Yamagata Prefecture, Japan

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There are diverse organisms living in snow and ice environments. They are adapted to cold temperature, thus they are active and growing on snow and ice. For example, snow algae, heterotrophic bacteria, and insects can be found on snow fields in Japan. Collembola is one of the typical insects living on snow surface. However, their ecology is still not well-known. It is important to understand the ecology of such organisms for quantification of the carbon and nitrogen cycles in the snow and ice ecosystems. In this study, we investigated life history and food resources of the collembola living on the snow surface in the deciduous forest in Yamagata Prefecture in Japan. We described their population density and body size on the snow surface. We also analyzed their carbon and nitrogen stable ratio to identify their main food resources. The study site is located at 750 m a.s.l. in elevation close to Mt. Gassan (altitude). The collembola specimens collected there were mostly *Desoria yukinomi*, which is common species living on snow surface. They were also found in a trunk of trees in the season without snow (Octorber), suggesting that they migrate seasonally between the tree trunk and snow surface. The introgen isotope of two species of lichens, grown on a trunk of trees, was lower than that of collembola, suggesting that they are most likely food source of collembola.

Keywords: Snow and ice organisms, soil organisms, carbon stable isotope, nitrogen stable isotope

Stable isotope ratios of Sr, Nd and Pb as environmental traceability index

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The stable isotopic ratios of Sr, Nd and Pb in environmental and artificial materials reflect the regional values of rock minerals and ores which are their origin. In this presentation, I introduce recent examples applied to atmospheric and terrestrial environments of Sr-Nd-Pb isotopes, which have been used in geological studies.

The isotope ratios of Sr, Nd, and Pb in Asian dust are known to differ depending on the particle size and constituent minerals and also to differ from those of coal ash and road dust. It also becomes clear that the Sr-Nd-Pb isotopic ratio of wet precipitation in Japan changes both locally and temporally, and the weak-acid soluble substances in the atmospheric aerosol have Sr-Nd-Pb isotopic ratios which are similar to the wet precipitation but are different from the acid-insoluble substances. These information suggests that the Japanese atmosphere is contributed by a variety of transboundary substances from the Asian continent as well as the substantial amounts of domestic substances. The areal and temporal change in the Sr-Nd-Pb isotopic ratio of the atmospheric precipitation is different from the sulfur isotope ratio, suggesting that the emission area and the atmospheric behavior of primary particles containing Sr, Nd, and Pb is different from secondary particles containing sulfur.

The Sr-Nd-Pb isotopic ratio of the atmospheric fallout is effective for the discrimination and of elements from basement rock, Asian dust, and volcanic ash, which are the source materials of Japanese soil. While the Sr and Nd isotopic ratio of river water and plants changes in accordance with the basement geology, the Pb isotopic ratio reflects the value of atmospheric fallout. Sr-Nd-Pb isotopes can be used as a traceability index of environmental materials and agricultural products. The Sr isotopic ratio of Japanese vegetables tends to be low in Northeast Japan and in the central and southern parts of Kyushu, where volcanic materials of Neogene-Quaternary time are dominant, while to be high (>0.708) in Southwest Japan and especially in the Kinki district, where Jurassic and Cretaceous-Paleogene accretionary prism and Cretaceous granitic rocks are widely distributed, However, the contribution of Sr from fertilizer is obvious in Japanese vegetables, suggesting that stable isotopes of Sr as well as Nd may be used for artificial impact assessment like Pb isotopes. In order to advance Sr-Nd-Pb isotopes as environmental traceability index, distribution on the Sr-Nd-Pb isotopic ratio for river water and groundwater are indispensable.

Keywords: Stable isotopes of Sr, Nd and Pb, traceability index, atmospheric environment , soil and vegetation ecosystem, product area identification of vegetables

Nd isotopic variation of seawater along the Pacific coast of Tohoku district and its causal factor

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Nd isotope ratio of seawater is known to vary between regions or water masses in the ocean. This contrasts to the fact that Sr isotope ratio of seawater is quite homogeneous. Therfore, Nd isotope ratio has the potential to become an effective tracker of marine animals or marine products. However, Nd isotopic variation in coastal sea region is not investigated well compared to that in global scale. In this study, we investigate the alongshore variation of the Nd isotope ratio of seawater and its causal factor at the Pacific coast of Tohoku district, northeast Japan, of which hinterland is composed of varied geology. The Nd isotope ratios of seawater samples, which were taken from 14 coastal sites located between 38.17N and 40.55N, vary from -8 to +1 in ε_{Nd} . These values are well correlated (r=0.72) with Nd isotope ratios of river water samples taken from the adjacent river of each coastal site, which ranges from -8 to 2 in $\epsilon_{\rm Nd}$. This indicates that the $\epsilon_{\rm Nd}$ of coastal seawater is largely defined by the value of land water. On the other hand, the range of Sr isotope ratios of seawater samples is quite narrow and high (0.70916 to 0.70919) despite that the value of river water ranges widely from 0.7055 to 0.7085. The Nd isotope ratios of seawater and water of the adjacent river differ from each other in most sites although they are correlated significantly. Nd contribution from offshore seawater should be considerable. Mixing of river water and offshore seawater of Tohoku district (-4 to -3 in ε_{Nd} ; Amakawa et al, 2004) is consistent with the linear regression expression of ε_{Nd} of seawater to that of river water (y=0.65x-0.83). Contribution of land water is suggested to be limited to nearshore regions. Surface seawater samples were taken along an offshore-directed line from the Abukuma River mouth in December 2015 (winter) and July 2016 (summer). Nd isotope ratios in summer were almost uniform around -9 in ε_{Nd} in the interval between 2km and 60km from the shore, whereas in winter it increases offshore from -6 to -2 in the interval between 35 km to 60 km from the shore. The ϵ_{Nd} of about -9 is considered to be that of the Kuroshio Current (Amakawa et al., 2004), which dominates in summer at the region, whereas that of -2 is consistent with the value of the Oyashio Current (Amakawa et al., 2004). On the other hand, the ε_{Nd} of the Abukuma River water (-2.9) is not reflected even at the site only 2 km apart from the shore. In spite of this regional limitation, Nd isotope ratio can newly provide a tool to trace animals and products at least in coastal seas.

Keywords: Nd isotope ratio, seawater

Using Sr isotopes to determine the contribution of volcanic ash to Sr and Ca in stream waters, a preliminary study in a chert watershed.

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The sources of Ca in Japanese forest ecosystems have been assumed to be sea salt, bedrock, and Kosa (Asian dust). Volcanic ash may also be an important contributor of Ca in volcanic areas. In our previous study (Koshikawa et al. 2016), an attempt was made to estimate the contribution of volcanic ash to Sr and Ca in stream waters and plants in a granite watershed. The fraction of atmospherically derived Sr in the stream water was evaluated using Sr/Cl ratio of stream water and atmospheric precipitation. Then, the fractions of Sr in stream water derived from granite and volcanic ash were estimated using Sr isotope ratios. The results confirmed that information about the Sr-isotopic composition is useful for determining the sources and contributions of Sr and Ca in stream waters and plants, even in complex systems containing volcanic ash and bedrock weathered products. Now, we are planning to apply this estimation to other regions where the Ca supply from parent materials is anticipated to be low. In this study, we report Sr isotope ratios of stream waters in a chert watershed, Mt. Amemaki (Tochigi, Japan), and a preliminary estimation of the contribution of volcanic ash to Sr in stream waters.

Keywords: Volcanic ash, Sr isotopes, Stream water, Ca sources, Chert

Assessing strontium isotope mixing model to reveal human diet and migration of the Jomon period

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Strontium isotopes are a useful tool to reveal past human migration directly from the skeletal tissues of human. Although strontium isotope ratios of skeletal remains from Yoshigo and Inariyama shell mound of the Jomon period were revealed, the concentrations of strontium and its relationship with the isotope ratios were still unclear. This study investigated the concentrations of Sr against Ca of teeth and bones from the Yoshigo and Inariyama shell mound. The concentration of Sr were highly varied in enamels and bones, and the relationship between the concentrations and Sr isotope ratios in enamels suggested several sources of Sr. The concentration. The results of this study indicated that the utility of measuring strontium concentrations in addition to strontium isotope ratios is important to reveal past human diet and identify migrants in human population.

Keywords: Isotope, Strontium, Bone

Food web analysis of Toyama Bay and seasonal changes of zooplankton: Using stable carbon and nitrogen isotopic ratios

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The isotopic ratios of stable carbon and nitrogen can be a key to finding out the influence that the environmental changes such as rising seawater temperature have on marine food web. The main aims of this study were i) to explore the food web in Toyama Bay, which has separate water masses in the water depth shallower than approximately 200m and deeper than that respectively, and ii) to analysis primary producers by measuring zooplankton. Aquatic samples of fishes and zooplankton inhabiting in the two layers of water were collected in offshore Toyama Bay as well as sinking particles organic matter, sedimentary organic matter and POM (particulate organic matter). We also collected sample of zooplankton from Yamato Basin in the Central Japan Sea, and NYUZEN DeepSeaWater Park in order to analyze the stable carbon and nitrogen isotopic ratios.

Both on the analysis of these isotopic ratios, we reached the following findings. Aquatic creatures in Toyama Bay are located on a food web starting from POM and phytoplankton is the primary producer of both the shallow water and deep water creature. The δ^{13} C values of zooplankton collected in Toyama Bay were higher than those from Yamato Basin. It is suggested that this is because the growth rate of the phytoplankton in Toyama Bay is faster than that in Yamato Basin. The δ^{15} N in zooplankton depleted with the increase of the nitrate concentration in the surface seawater, and δ^{13} C enriched with the increase of chlorophyll*a* concentration in the surface water. Thus, it is considered that the δ^{15} N value reflects the supply of nitrate and the δ^{13} C value reflects the growth rate of phytoplankton.

Keywords: Stable isotope ratio, Toyama Bay, Zooplankton

Reconstruction of stable isotope chronology by asegmental analysis of bone.

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Isotope analysis is a powerful tool in ecological studies of animals for reconstructing their dietary sources, trophic positions, and movements. One of an important point to apply stable isotope analysis in ecological study is the timescale of the isotopic records in the target tissue, because different tissues have different turnover time of stable isotope elements.

For instance, stable isotopes in blood plasma of animal reflects information in shorter timespan which is 1 to 2 weeks, whereas that of muscle records isotopic information of last 1 to 2 month. Most of previous isotope studies focused on a single tissue and timeframe, and compared the differences of isotope values among individuals or populations within the same timescale. However, the utility of isotope analysis would be greatly improved if we could reconstruct the history of isotope values at multiple growth stages of animal using single tissue.

In this presentation, I present a new analytical method to reconstruct isotope chronology of multi-isotope elements by segmental analysis of bone of teleost fish and mammal species. I also show the validity of this method by incremental sulfur stable isotope analysis for an anadromous salmon, masu salmon (*Oncorhynchus masou*), and incremental radiocarbon analysis for mammals which lived in the end of 20th century. If this method correctly reconstruct stable isotope chronology of these species, I can detect isotopic information in their early life stage from their bone sections.

In all samples of masu salmon, the bone section closest to the center of the vertebral centrum had the lowest sulfur isotope ratios, which were similar to those of freshwater. The sulfur stable isotope ratios gradually increased from the center to marginal sections, finally reaching constant values similar to those of seawater. For this reason, my results show that the vertebral centra of teleost fish record isotopic information from juvenile to adult life-stages. In mammal, radiocarbon isotope ratios in later age have been detected from center and margin of femur, whereas other parts showed isotope values in former age. The result showed that the central part of femur is the subject of bone metabolisms and thereby the turnover of bone influenced the radiocarbon values in the central part of the bone. However, we also confirmed that there are few effect of turnover in the other part than central part of bone, and this method can be used for the reconstruction of stable isotope chronology of mammal species.

Keywords: stable isotope, bone, chronology

Water quality map in the lower reach of the Abe River in Shizuoka Prefecture

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The plains of Shizuoka and Shimizu, which lie on the basin of Abe River in Shizuoka Prefecture, hold a large amount of groundwater. We summarized the quality of spring, well and river waters in the area in map for the purpose of estimating the origin and recharge area of the groundwater.

The Shizuoka Plain has a typical alluvial fan and is formed with a huge amount of gravels from the Abe River. Meanwhile, the Shimizu Plain consists of delta sediments of Tomoe River originating from the northern Shizuoka Plain. In the Shizuoka Plain, the Cl⁻ concentration of groundwater was lower than those of surrounding mountain areas and Shimizu plain, and in contrast, the Sr concentration was higher, indicating the same tendency as the Abe River water quality. The water isotopic ratio of the Abe River is lower than that of precipitation in the plains of Shizuoka and Shimizu, and the groundwater in the Shizuoka plain shows low water isotopic ratio as well as Abe River, indicating the aquifer of Shizuoka Plain is recharged by Abe River. On the other hand, the water isotopic ratio in the Shimizu Plain was relatively high, suggesting that precipitation in the surrounding area is the main recharge source. The strontium isotopic ratio of the Abe River and the Warashina River is about 0.7088, which would be a value characterized by old sedimentary rocks (accretionary complex) occupying the major part of the

western mountains. Spring water and well water distributed in the Abe River fan area showed the same value as Abe River. On the other hand, the strontium isotopic ratio of the river flowing from the northern mountains composed of sedimentary rocks was 0.7060, and that of the spring water originating from the mountain of volcanic rocks was specifically low value, less than 0.7040.

Keywords: Abe River, groundwater, water quality, stable isotopes

The geochemical study about the aqueous environment of Chikusa River in Hyogo prefecture

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The Chikusa River belongs a class B river system, which runs through the southwestern part of Hyogo prefecture. Because of heavy rain, this river sometimes flows over and its basin is damaged, so Hyogo prefecture has carried out river reforming works to improve the capacity of flow until May, 2016. But the works changed the environment of this river, the impact on the quality of river water and the river ecosystem is concerned and we need the basic data of this river to measure this impact scientifically. In this study, we analyzed concentrations of dissolved ion and trace elements, stable isotopes of water (δD , $\delta^{18}O$), nitrate ($\delta^{15}N$, $\delta^{18}O$), strontium (${}^{87}Sr/{}^{86}Sr$). In addition, we plotted the result of analysis on a basin map with a geographical information system so that the result could be seen easily and we aimed to offer the basic data which was easy to use. Furthermore, we estimated the formation factor of dissolved ion, trace elements and stable isotopes through a comparison between the result of analysis and the land use, geological features and topography of the basin.

In the Chikusa River, Chikusa River Conservation Committee has been holding "The simultaneous survey of water temperature all around Chikusa River" in every August since 2002. In this survey, the committee and many local residents measure water temperature at 94 sites, from headwaters to river-mouth and some tributaries. From 2015, Research Institute for Humanity and Nature, Kobe University and University of Hyogo has joined in this survey and started collecting water samples. In the survey of 2016 (held in August 7, 13:00~16:00), we received the water samples from local residents and we filtered them at once, with cellulose acetate filters whose diameters of holds are 0.2 μ m. After filtering, we subdivided the samples into some polyethylene bottles and a glass vial and stored them at 20°C or -30°C. We analyzed concentrations of trace elements and bicarbonate ion, δD , $\delta^{18}O$ (water) and ${}^{87}Sr/{}^{86}Sr$ 20°C samples. We also analyzed concentrations of dissolved ion, δ^{15} N and δ^{18} O (nitrate) with -30°C samples. As a result of the analysis, the concentrations of dissolved ion were gradually increased from the upstream toward the downstream. From the upstream to the middle reaches, most of the dissolved ion were likely derived from the rock or the precipitation. On the other hand, the downstream and the tributaries flowing through well-populated areas, the concentrations of it were higher because of living or agricultural wastewater. The concentrations of nitrate or phosphate ion were higher from the upstream to the middle reaches and lower in the downstream. At the high concentrations points, most of them were likely derived from nitrogen load from nitrogen saturated forest areas or livestock wastewater. At the downstream, low concentrations points, the water temperature was higher, so aquatic lives became active and they likely consumed nitrate or phosphate ion.

 δ D and δ ¹⁸O were lower in the upstream and higher from the middle reaches to the downstream. From the upstream toward the middle reaches, they became lower as the altitude became higher because of the precipitation affected by the altitude effects. On the other hand, they were higher from the middle reaches to the downstream in spite of the altitude. These areas' river became shallower and wider in the river reforming works, so the effects of sunlight on the river became big and the evaporation from the surface of river became more active. This is why δ D and δ ¹⁸O became higher in these areas. Furthermore, rice farming is flourishing in these areas, so the paddy water having high δD and $\delta^{18}O$ likely flowed into the river. This is also why they became higher.

There are other analysis points affected by the rock or the wastewater. We will also discuss results of these points in this presentation.

Keywords: Hyogo prefecture, the Chikusa River, river water, concentrations of dissolved ion, stable isotopes, geochemistry

Meridional distribution of isotopic composition of precipitation in the Nobi Plain, central Japan

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The weekly isotopic compositions of precipitation in the Nobi Plain, central Japan was investigated in the period from August 2016 to December 2016. Rain gauges were installed at six observation sites along the 42km survey line from near the Ise Bay to inland of the Nobi Plain (Gifu city). We made simple rain gauges from 18 cm diameter funnels and wasted 2-litter plastic beverage bottles. The precision of the rain gauge is $\pm 0.5\%$, that is good enough for practical use. The weekly precipitation and their hydrogen and oxygen isotope ratios obtained show clear seasonal variations from summer to winter. The north to south distribution of precipitation and their isotope ratios varied weekly and seasonally, then we classified them from their characteristics and the weather conditions. We also observed isotope ratios of typhoon precipitation collected half-hourly during the passage of typhoon Malakas on 20th September 2016, and their significant changes were discussed in relation to cyclone systems.

Keywords: precipitation, oxygen isotope ratio, hydrogen isotope ratio, meridional distribution, Nobi Plain

Stream Water Chemistry in a Mountain Forest near the Tokyo Metropolitan Area and the Impact of Atmospheric Deposition (3)

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In the Tanzawa mountains, which is located in the western part of Kanagawa prefecture, it has been reported that fir trees decayed and surface soils were acidified. We have revealed that high concentrations of nitrate run off through stream water on Mt. Oyama (1252 m a.s.l.), which is located in the southeastern part of the Tanzawa mountains and easily affected by air pollutants transported from the Tokyo metropolitan area.

We here report stream water chemistry during the 9 years from 2007 to 2015 in the eastern Tanzawa mountains and evaluate the impacts of atmospheric deposition using stable isotopes of hydrogen and oxygen in water. Total dissolved nitrogen (TDN) concentration (the sum of nitrate nitrogen; NN, ammoniumnitrogen; AN, and dissolved organic nitrogen; DON) in stream water in the eastern Tanzawa mountains during 9 years was 1.12 mgN/L in the southeastern area on average, 0.99 mgN/L in the southwestern area, and 0.67 mgN/L in the northern area. The ratio of the TDN concentration in 2007 to that in 2015 was 0.60 in the northern area, 0.62 in the southeastern area, 0.69 in the southwestern area, respectively. TDN decreased in three areas of the eastern Tanzawa mountains, especially in the northern area. The contribution of NN decreased while the contribution of DON increased in all three areas, especially in the northern area. ANdidn't have a clear trend in all areas. Decrease of TDN was due to the decrease of NN in stream water, which could be the decrease of atmospheric inorganic nitrogen deposition and/or the suppression of nitrification in surface soils.

The stable isotope ratios of hydrogen and oxygen in stream water on the eastern Tanzawa mountains declined with the increase of altitude. Such a tendency is also reported in surface water in Japan, and is generally due to the evaporation effect, namely light water easily evaporates as surface water runs from the upper reaches to the lower. The stable isotope ratios in throughfall of cedar at the top of Mt. Oyama were higher than those in rainfall and stable isotope ratios in stream water distributed between them. The amount of throughfall in the lowland forest is generally about 70% of rainfall amount due to canopy interception, which makes isotope fractionation occur due to the evaporation in the canopy. Then the stable isotope ratios of hydrogen and oxygen inthroughfall become heavy, but the amount of Cedar throughfallwas 1.8 times more than rainfall amount at the top of Mt. Oyama. The difference in stable isotope ratios between in throughfall and in rainfall could be due to fog water deposition because fog occurs frequently on Mt. Oyama.

Keywords: Stable Isotope, Nitrogen Saturation, Nitrate Nitrogen, Ammonium Nitrogen, Dissolved Organic Nitrogen, Nitrification

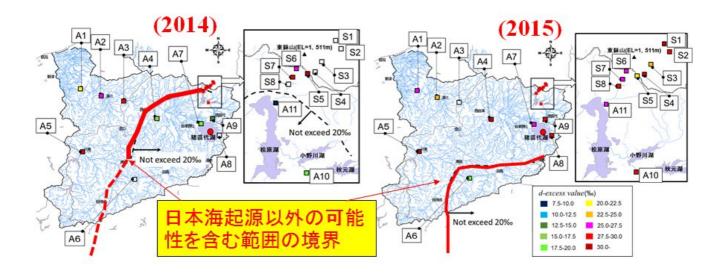
Study on regional snow distribution effect using isotope ratio

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The regional water resource managemnt is estimate difficult opreration in the future because climate change has a connection with snow variation. It is inportant to predict snow environment using climate model outputs to this solution. However this data can not use for regional water management according large grid size. It is necessary to develop this management to export small spatial resolution. we tried to study detail climate information using isotope ratio as tracer. The regularity to spatial feature was obtained vy chamical characteristic in this study. And we also understood water effect due to snowconditon. As result, snow depth variation changes depend on sbowfall source as spatial characteristic. Therefore, we could recognize new regularity of acid snow.

Keywords: isotope ratio, snow environment, regional scale



Role of chemical forms for transportation of metals in Tama-Omono Rivers, Akita Prefecture, Japan

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Chemical forms of elements in river water of Tama and Omono Rivers containing acidic thermal water were determined by successive filtration technique. The chemical forms of elements were divided into the particulate (>0.2 μ m), colloidal (0.004 - 0.2 μ m) and dissolved (<0.004 μ m) forms. This study proposes that the chemical compositions of elements in river water are controlled by variation of chemical forms of elements according to change in geology along the rivers. Tama River which is one of the tributaries of Omono River, runs through the area composed of Quaternary volcanic rocks at the upstream site through the area composed of Miocene volcanic rocks and Quaternary sedimentary strata from Lake Tazawa to Daisen City. Inflow of acidic thermal water into Tama River in upstream changes the pH of the river water to acidic and concentrations of dissolved metals into high concentrations except for Fe and As. Dissolved Fe and As easily change into colloidal and/or particulate forms in river water in upstream of Tama River. According to qualitative analyses by SEM-EDX, the reddish particulate is thought to be Fe hydroxide. Arsenic was adsorbed on the surface of Fe hydroxide. This indicates that Fe hydroxide controls the mobilization of As. The pH of river water of Tama River changes from 4.6 in upstream to 7.1 in downstream. At the downstream site, the influence of acidic thermal water becomes small due to supply of particulate material from the erosion of Quaternary sedimentary rocks. The particulate forms of AI, Fe and trace metals in river water contribute to increase of concentration of these elements. Based on observation and analyses by SEM-EDX and XRD, the particulate materials are thought to be phyllosilicate and clay minerals: chlorite, illite/montmorillonite. Uptake of Al, Fe and trace metals onto these minerals decrease concentration of dissolved metals in river water of Tama River. The amounts of AI and As that are transported by river water of Tama River decreased from upstream to downstream. This suggests that precipitation of these elements in natural lake and dam lakes along Tama River. Therefore, the natural lake and dam lakes could play an important role in reducing the environmental impact. Omono River runs through the area mainly composed of Miocene to Quaternary volcanic rocks in the upstream to the area mainly composed of Quaternary strata covering Miocene sedimentary rocks in the downstream. The difference in geology along Omono River accords with the difference in the distribution of elements in the particulate form in the river water of Omono River. At the upstream site of Omono River, Fe in the river water is present as particulate Fe hydroxides, resulting from river water mixing between Omono River having neutral pH (7.2) and Takamatsu River containing acidic thermal water of pH 3.2. Towards downstream site, reddish gravels along river bank disappear. However, concentrations of Fe as colloidal and particulate forms in the river water increase. This observation and chemical analysis by SEM-EDX and XRD suggests that these particulate materials are clay minerals. The clay minerals derived from the sedimentary rocks along Omono River could be the host of Fe as particulate form in river water of Omono River. The particulate form as clay minerals derived from sedimentary rocks increase concentration of Al, Fe, Mn and trace metals in river water of Omono River. Concentration of Al, Fe, Mn and trace metals in particulate form of river water of Omono River are higher than those of Tama River. The difference of these concentrations accords with the difference in dominance of Quaternary and Miocene sedimentary rocks between Omono and Tama Rivers. Concentrations of elements of river water are controlled by concentration of elements adsorbed on the surface of suspended particles such as clay minerals in river water having near neutral pH.

Keywords: chemical forms, acidic thermal water, river water, geology setting

Applicability of ⁸⁷Sr/⁸⁶Sr in examining surface-groundwater interactions in extensively irrigated paddy watersheds

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Repeated cycles of water diversion from and return flows to main channels have substantial impacts on the flow regimes of watersheds containing extensive areas of irrigated paddy fields. Numerous studies have attempted to decipher the hydrological processes in such irrigated areas; however, surface-groundwater interactions hinder the understanding of the fate of the irrigation water. Although the stable isotopes of water, deuterium and ¹⁸O are the major tracers used to decipher hydrological processes of watersheds, these isotopes cannot be used to track the fate of irrigated water because of mixing of precipitation and irrigation water and fractionation during evaporation from water surfaces. The ratio of strontium isotopes (⁸⁷Sr/⁸⁶Sr, hereafter Sr ratio) can be used to complement the shortcomings of the stable isotopes of water because it has the following characteristics: (1) temporal changes in the Sr ratio can be ignored at less than geological time scales, and (2) the effects of fractionation are negligible. In other words, the Sr ratio of water will change only because of interactions with the porous media it flows through (soil/rock), or mixing with water that have different Sr ratios. Although the use of the strontium isotopes for studying hydrological processes is increasing, their applicability in irrigated watersheds has not yet been examined.

We carried out the study described here in a typical agricultural watershed located on the alluvial fan of the Kinu River, namely the Gogyo River. The aim was to examine the potential for using the Sr ratios by investigating the following: (1) the variation in Sr ratios between water sources (i.e., precipitation, irrigation water, shallow aquifer, and streamflow), and (2) the temporal variation in the Sr ratios in relation to irrigation periods. We sampled water sources in irrigated (June) and non-irrigated (October) periods and analyzed the Sr ratios and concentrations as follows: (1) 23 samples of streamflow along the Gogyo River at 500 m intervals, (2) 56 samples of shallow aquifers, (3) precipitation in June and October, and (4) irrigation water of the main irrigation channel in June.

The Sr ratios of the samples were plotted against 1/Sr concentration. The streamflow samples were plotted linearly on the diagram, and the Sr ratio and 1/Sr concentration decreased along the direction of flow, indicating that the streamflow was composed of two end-members. One potential end-members was the irrigation water, which plotted near the higher end of the streamflow plot. The other was the water from the shallow aquifer, which plotted near the lower end of the plot.

The Sr ratios of soil water within paddy fields decreased as sampling depth increased. This suggests that as irrigation water percolates into the shallow aquifer, its Sr ratio decreases as it mixes with the soil water; whereas when irrigation water drains from paddies via surface channels, the Sr ratio will be less likely to change. The continuous decline in the Sr ratio along the stream suggests a conceptual model of exfiltration of irrigated water from the shallow aquifers. The water samples in the Gogyo River during the non-irrigated period had lower in Sr ratios and higher in Sr concentrations, suggesting a relative increase in contributions of the water from the shallow aquifers.

The stable isotopes of water also supported the above conceptual model that the streamflow was composed of water originating from the surface drainage system and the shallow aquifers. For stream water samples of the Gogyo River, δ^2 H was highly correlated with δ^{18} O. The slope of the regression line was approximately 6.0, suggesting that the streamflow was characterized by water that had been

subjected to high levels of evaporation in the paddies.

Our study shows that the Sr ratio-1/Sr concentration diagram can be used to elucidate the mixing ratio of the water from the surface and subsurface flow paths. The temporal changes in the contributions of flow from each flow path over the duration of the irrigation period will shed new lights on the hydrological processes in irrigated watersheds.

Keywords: strontium isotopes, irrigated paddies, surface-groundwater interactions

Characteristics of water quality and stable isotopes (O, H, and Sr) in 15 rivers of Sado Island, Niigata Prefecture

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The interactions between water and rocks during chemical weathering release water-soluble substances and form secondary minerals (e.g., clay minerals) with consumption of atmospheric CO_2 . The determination of dissolved chemical substances in rivers gives us important information concerning chemical weathering processes including the weathering rate and amount of CO₂ consumption. Since the weathering processes is closely related to sediment disaster such as landslide and debris flow, it is significant to investigate river water quality for better understanding the weathering processes in detail. On the other hand, the Sado Island of Niigata Prefecture has been developed with a gold mine during the Edo Period. In recent years, Japanese crested ibis, a protected species, is steadily increasing by extensive breeding programs. The conservation of water environment in the island is most necessary to preserve natural animals and resources. Based on our investigation, we reveal the characteristics of water quality and isotopic composition (O, H, and Sr) in 15 rivers of the Sado Island. Our findings suggest that water quality and Sr isotopic composition (⁸⁷Sr/⁸⁶Sr) in 15 rivers were contaminated by airborne sea salt from Japan Sea surrounding the island. The values of O and H isotope ratios (d¹⁸O and dD) range from -9.34 to -8.44 per mill and from -53.48 to -47.87 per mill, respectively, and are affected by the average altitude of each watershed. Next step of this study is to investigate and analyze spatiotemporal variations in water quality and isotopic composition.

Keywords: Sado Island, river water quality, isotopic composition (O, H, and Sr)

Multi isotopic analysis of rainwater and inland water in acid sensitive areas

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Introduction: Acid deposition and other materials from atmosphere accumulates in ecosystem and may cause acidification of soil and inland aquatic environment. We' ve studied about dynamics analysis and ecological impact evaluation of atmospheric deposition by sulfur isotopic analysis in high sensitivity areas for acid deposition. From 2014, we started strontium (Sr), lead (Pb), oxygen and hydrogen of water isotopic analysis for multilateral analysis by isotopic information of multiple elements. In this presentation, we outline isotopic ratio data in our study sites.

<u>Method:</u> Study was conducted in 2 catchments and 6 lakes shown in the figure. We collected rainwater, soil solution and streamwater in catchments and surface water in lakes. We determined Sr isotopic ratio by thermal ionization mass spectrometer (TRITON, Thermo Scientific), Pb isotopic ratio by double focusing type multi-collector ICP-MS (NEPTUNE, Thermo Scientific), oxygen and hydrogen of water isotopic ratios by water isotopic analyzer (L2120-i, Picarro).

Results and discussion: Sr isotopic ratio was determined from Dec. 2013 to Sep. 2015. In both catchments, ⁸⁷Sr/⁸⁶Sr of rainwater showed seasonal variation in range of 0.709±0.001 by contribution of soluble minerals (0.711±0.001) contained in continental dust in spring and sea salt (about 0.709) in winter. On the other hand, streamwater ratios were stable around 0.707 in Kajikawa and around 0.715 in Ijira, and these were widely different from rainwater. Soil solution indicated middle value of rainwater and streamwater. Sr concentration of rainwater were several μ g/L even though in high concentration period, but streamwater were stable around 20 μ g/L even though in lower concentration catchment Ijira. These results suggest that Sr leaching into streamwater is strongly contributed by geological Sr. In overviewing lakes data based on these results, Sr concentration of Ohataike, Oike and Banryu were around 15 μ g/L, so these suggests that geological contribution is strong in these lakes. On the other hand, Sr concentration were around 3 μ g/L in Yashagaike, Meike and Sawanoike which seems to be acid sensitivity is particularly high. In the case of these lakes, effect of bedrock weathering may be small and contribution of atmospheric deposition may be relatively large.

Pb isotopic ratio was determined from Apr. 2014 to Aug. 2015. In the case of ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb, contribution of rainwater clearly appeared in streamwater ratios and response speed was also fast. Particularly in Kajikawa which catchment area is small, response time rag was shorter than one month. In plotting with two components of ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb, all values of our study sites fit in the range of previous reported values of aerosols in East Asia (Nakano *et al.* 2006),especially plotted near range of Russia and Mongolia values.

Oxygen and hydrogen isotopic ratios of water were determined from Jun. 2014 to Jul. 2015. In both catchment areas, rainwater δ ¹⁸O and δ D showed seasonal variations, but streamwater ratios were stable around yearly average of rainwater, so it suggests that streamwater may leach from rainwater after recharged and averaged in catchments in calm water situation. In both catchments, d-excess values of rainwater showed similar trend with variation range from 5 to 35, and effect of dry continental air masses appeared clearly in winter.

In poster presentation, we also discuss about mutual relationship between these isotopic ratios.

<u>Acknowledgment:</u> Samples used in this study were collected as a part of long-term monitoring of transboundary air pollution and acid deposition by MOEJ. Isotopic analysis was conducted as Environmental Isotope Study in Research Institute of Humanity and Nature. The authors thank relevant persons and organizations.

<u>Reference:</u> Nakano, T. *et al.* 2006. Determination of seasonal and regional variation in the provenance of dissolved cations in rain in Japan based on Sr and Pb isotopes. *Atmospheric Environment* 40, 7409–7420.

Keywords: strontium isotopic ratio, lead isotopic ratio, water isotopic ratio



High-resolution isotope analyses of annually-laminated tufa, Asama volcano

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In this study, we present results of the high resolution δ^{13} C and δ^{18} O isotopes of annually-laminated tufa and its paleotufa from R. Nigori of Asama volcano, central Japan, and then examine the causes of their variations.

Keywords: Tufa, Stable isotope, Asama volcano

Evaluation of environmental stress on roadside trees in Kyoto city using stable carbon isotope ratio

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Roadside trees have many important roles and functions such as absorption / trapping of air pollutants, preventing heat reflections of the road surface by the formation of tree canopy, and as a result, prevention of temperature rising in urban area in summer. The increase in air pollutants and atmospheric temperature by industrialization and urbanization are serious enviromental problems in Japan as well as in other industriarized and developping countries, and thus, the roles of roadside trees such as alleviating urban warming and reducing air pollutants are very important in these countries. However, many roadside trees seem to "reducing activity", e.g., fallen leaves and increased numbers of dead branches, in the summer. Our previous studies showed that the influence of air pollutants (Kume et al. 2006), as well as a combination of environmental stresses caused by soil and air drought, which are affected by urban warming, reduced photosynthetic capacity in roadside trees (Kagotani et al. 2013). However, it is difficult to evaluate the decline of the physiological activity of roadside trees from their appearance, because photosynthetic capacity often declines during the summer without any changes in their appearance. In addition, significant interspecific differences were found in the decline of photosynthetic capacity in the summer, which was about 50% decrease in Prunus yedoensis, contrasting the no decrease in Ginkgo biloba (Hanba et al. 2010). However, genetic and physiological factors inducing such interspecific differences in reduction in photosynthetic capacity have not been clarified.

In order to maximize the functions of roadside trees mitigating the high temperature of summer, it is essential to suppress "decline of activity in summer" due to combined environmental stress including air pollution and drought. In order to evaluate the activity of roadside trees, the "4 rank evaluation method" which evaluate the activity by their appearance has been widely performed (Science and Technology Agency Resource Research Committee). However, in this method, it is not possible to evaluate the roadside trees that only the physiological activity is declining. If we can distinguish the influence of environmental stress before its effect appears on their appearance, we can take measures to improve activity of roadside trees by appropriate management. Previous studies showed that stomatal closure occurs at the earliest stage among a series of reactions in response to environmental stress such as air pollution and drought stress. Since the carbon stable isotopic ratio (δ^{13} C) of the photosynthetic product in the leaf reflects the averaged stomatal pore opening, it is widely used for stress determination of natural plants. Although there is a possibility that it can be applied to plants in urban areas, there are only a couple of applications in urban areas, because there are no established methods for correcting the influence of atmospheric δ^{13} C of fossil fuels on leaf δ^{13} C (Wang et Al. 2011).

We used δ^{13} C of roadside tree leaves for major roadside trees to determine the environmental stresses on the roadside trees through stomatal closure in urban areas in Kyoto City. We focus on environmental stress such as (1) drought stress and (2) air pollutants. We performed drought experiment for major roadside trees to investigate their physiological responses. We also performed environmental monitoring and measurement of physiological functions of roadside trees in Kyoto city. The main results obtained so far are as follows. (1) In response to artificial soil drought, remarkable differences were found in physiological functions among species of roadside trees. Specifically, some species sensitively closed stomatal pores in response to drought and maintaining water content in plants, but the other species maintained photosynthetic function by stomatal closure in response to drought. In addition, one month' drought did not affect δ^{13} C of leaves of roadside trees. (2) We selected some study sites with different air pollutant levels in Kyoto city, and the physiological functions and δ^{13} C of *Ginkgo biloba* and *Rhododendron* x *pulchrum* were examined. As a result, no difference was found between the study sites in both tomatal pore opening and leaf δ^{13} C for the tall tree *G. bilova*, but for the shrubs *R. pulchrum*, the stomata tended to close in the study site where the air pollutant level was high, with the high values of δ^{13} C in leaves. These results suggested that evaluation of the effect of long - term environmental stress on roaadside trees is possible using δ^{13} C of leaves at the site where roadside trees are being planted.

Keywords: Stable carbon isotope ratio, Photosynthesis, Stomata, Atmospheric polllutant

Influence of atmospheric pollutants on roadside trees in Kyoto city

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Atmospheric pollutants impair physiological activities of plants. The concentration of photochemical oxidant (O_x), which is one of the atmospheric pollutants, has been increased year by year in Kyoto city from 1981 to 2015. Thus, trees growing in Kyoto city are possibly influenced by O_x . In this study, we investigated the effect of O_3 on the roadside trees. We measured O_3 concentration at three study sites in Kyoto city where O_3 concentration is expected to be different, to evaluate the physiological activities of the roadside trees in these sites.

We selected three study sites in Kyoto city, such as Omiya ($35^{\circ}01'08.N 135^{\circ}75'20.E$), Yamashina (34° 97'18.N 1 $35^{\circ}81'45.E$), and Nishinokyo ($35^{\circ}01'83.N 135^{\circ}73'08.E$). These sites were selected according to the NO_x concentration in order to compare effects of different levels of O₃ on roadside trees. The species investigated were *Rhododendron pulchrum* and *Prunus yedoensis*, which are major roadside trees in Kyoto city. Average concentration of O₃ were measured twice at study sites, using passive samplers for 7 days in early June and late November in 2016. It is expected that the trees growing in a study area with a high concentration of O₃ have more decreased physiological activity. Photosynthetic activity was evaluated by gas exchange parameters using a portable photosynthesis system, Li-6400 (LI-COR). In addition, stable carbon isotope ratios, which are indicators for long-term water use efficiency, were measured using CN-IRMS. In order to identify factors affecting photosynthetic activity, the relationship between environmental and photosynthetic variables were analyzed by Pearson's moment correlation analysis.

 O_3 concentration in early July was 75.8 ppb at Omiya, 80.8 ppb at Yamashina, and 55.6 ppb at Nishinokyo. The photosynthetic rate of *P. yedoensis* measured at PPFD of 1500 μ mol m⁻² s⁻¹ was significantly higher in Yamashina than those in the other study sites. The same tends were obtained for stomatal conductance (g_s). Maximum carboxylation rate of Rubisco (V_{cmax}) and electron transport rate in thylakoid membrane (*J*) were high in Nishinokyo for *R. pulchrum*, which suggests that biochemical activity in photosynthesis was high in Nishinokyo in *R. pulchrum*. Although there was a difference in the photosynthetic activity of these roadside trees between the study sites, correlation analysis showed that there was no correlation between O_3 concentration and photosynthetic activity. The carbon isotope discrimination in leaves of *R. pulchrum* showed high values in Omiya and Yamashina, which suggested that water use efficiency was high at these two sites.

We conclude that O_3 concentration was not related to the photosynthetic rate of the roadside trees in Kyoto city. Possibility the concentration of O_3 in the all three study sites was not so high as to affect the roadside trees.

The comparison of photosynthetic function and water status between roadside shrub trees under drought stress

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Roadside trees are expected to play roles for CO_2 absorption and cooling by transpiration. However, plants in urban area are exposed to high temperature and drought stress condition during summer. Drought stress decreases photosynthetic rate of roadside trees because of the stomatal closure. Therefore, summer drought will affect CO_2 absorption and cooling by transpiration of roadside trees, and thus, will reduce mitigation effect on urban warming. Many previous studies have shown that different plant species show different response to drought stress. In this study, photosynthetic function, water status and carbon stable isotopic ratio in five representative roadside shrub trees under drought stress were measured to compare their drought tolerance and recovery from drought stress.

Rhododendron pulchrum, Rhododendron obtusum, Rhaphiolepis umbellate var. integerrima, Forsythia suspense and Camellia hiemalis were used for the experiment. Seedlings of trees were pot-grown in a greenhouse in Kyoto Institute of Technology. Drought and recovery experiments were performed sequentially. First, watering was stopped during the drought experiment. Stomatal conductance was measured several times using Li-6400 for a fully matured leaf. When soil fully dried, plants were re-watered to perform recovery experiment. $A-C_i$ curve was obtained using Li-6400. Water potential was measured using pressure chamber in three stages: pre-drought (control), post-drought (when stomatal conductance value becomes 20%~30% compared with pre-drought value), recovery (when increases in pot weights were mostly stopped for three days). Leaves for carbon stable isotope ratio measurement were collected at each stages.

Photosynthetic rate and water potential significantly decreased in all tree species at the post-drought stage, with these values were recovered to those at the pre-drought stage. Maximum decreasing rate of photosynthesis from pre-drought to post-drought was 84% observed for *R. obtusum*, while minimum value was 55% observed in *F. suspense*. Maximum recovery rate of photosynthesis at the recovery stage was 99% observed for *C. hiemalis*, while minimum recovery rate was 67% observed for *R. obtusum*. Minimum decreasing rate of water potential at the post-drought stage was 470% observed in *R. pulchrum*. These results suggest that *F. suspense* can maintain high photosynthetic rate during drought stress, while *C. hiemalis* has high recovery rate from drought stress. R. ×pulchrum has the highest ability to maintain plant water status in post-drought and recovery stages. These results will help for the effective selection of roadside trees.

Characteristics of nutrient supply from forest areas in eastern river in Toyama prefecture read from attached algae

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It is pointed out that the origin of nutrient salt flowing from Hayatsuki River located in the eastern part of Toyama Prefecture to Toyama Bay is a forest area upstream from the nitrate nitrogen stable isotopic ratio (δ^{15} N - NO₃) (Zhang ·Sano , 2014). However, in previous studies, the area has remained at an altitude of 1000 m or less, and research has not been conducted on altitudes of more than 1000 m at which alpine forest areas serving as a source spread, and for multiple catchment areas. The aims of this study is to grasp the dynamics of water from the uppermost stream and to the estuary and evaluate nutrient supply.

Magnesium isotope analysis of environmental samples

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Stable isotopes (SI) is utilized as a fingerprint of an element to trace its behavior in the environment. Magnesium is a major element of terrestrial rocks and widely distributed throughout the lithosphere and biosphere. The element has been utilized to provide valuable information about geological, biological, and atmospheric processes. With the advent of multi-collector ICP-MS, it is possible to measure precise value of 25 Mg/ 24 Mg and 26 Mg/ 24 Mg in Mg solution.

To promote the environmental SI fingerprint, RIHN is desired to determine the isotope ratios of magnesium in an environmental sample with high precision and accuracy, rapidness, and convenience. Further, as biota, soil, and rock is composed of different components (bone, meat, mineral, etc.), whose magnesium concentrations and isotope ratios differ one another. Analytical precision affected sensitively by matrix component of Mg solution according to various sample processing should be evaluated. Here, I report a simple and efficient one-step separation method and the resulting matrix component of various environmental standards samples. Furthermore, an analytical method was tested using cool plasma and hot plasma-middle resolution by environmental standards from the National Metrology Institute of Japan (NMIJ) and international rock standards (AIST and USGS) with high-resolution multi-collector ICP-MS of NEPTUNE (Thermo Fisher Scientific K. K.).

Keywords: magnesium isotope, environmental standard, cool plasma