

Geochemical and isotopic analyses of river waters from the Okayama Prefecture, Japan.

\*Katsuyuki Yamashita<sup>1</sup>, Takahiro Kamei<sup>1</sup>, Yuga Kishimoto<sup>2</sup>, Aya Ooi<sup>2</sup>, Ayaka Onishi<sup>2</sup>, Yoko Kurihara<sup>2</sup>, Hitoshi CHIBA<sup>1</sup>, Takanori Nakano<sup>3</sup>, Ki-Cheol Shin<sup>3</sup>

1.Graduate School of Natural Science and Technology, Okayama University, 2.Faculty of Science, Okayama University, 3.Research Institute for Humanity and Nature

We have undertaken detailed geochemical and isotopic analyses of river waters from the Asahi, Yoshii, and Takahashi River systems of the Okayama Prefecture, Japan. A total of 537 samples were collected from 381 locations in Okayama and neighboring prefectures. In some locations, samples were collected periodically over a period of 4~5 years to monitor the long-term fluctuation of the geochemical signatures. All samples were filtered prior to the analyses of the major dissolved components, trace element concentrations, and O-H isotopes. For some samples, S and Sr isotopes were also determined.

Using the data obtained in this study, we constructed high-resolution geochemical maps of the rivers, which were then used to explore the geochemical and isotopic nature of the river systems. The results show that O-H isotopes display a regional variation that exceeds the seasonal variation. The deuterium excess is high in the upstream of the river systems near the Chugoku-mountains, and gradually decreases towards the downstream.

The concentrations of the major dissolved components and trace elements also display a regional variation. For example, the Ca concentration is highest in the areas where limestones are exposed, indicating that breakdown of  $\text{CaCO}_3$  has a significant impact on the Ca concentration of the river waters. The Sr concentration follows a similar pattern. The Sr isotopic signature is low in the area where the Quaternary volcanic rocks are exposed, and high in the areas where the Carboniferous to Jurassic sedimentary rocks are exposed. Such a geographical correlation between the Sr isotopic signature and rocks exposed in the area imply that the breakdown of Ca, Sr bearing minerals has an important impact on the geochemistry of the river waters.

The concentration of  $\text{SO}_4$  is lowest in the northern region of the Okayama prefecture near the Chugoku-mountains, but gradually increases in the areas south of Tsuyama and Kuse basins. The increase in  $\text{SO}_4$  is accompanied by shift in sulfur isotopic composition towards  $\sim 0\%$ . This correlation may imply that decomposition of fertilizers used in agricultural activities is, at least in part, responsible for the change in the  $\text{SO}_4$  concentration.

Keywords: Okayama Prefecture, River Water, Geochemistry

## The geochemical and stable isotope characteristics of the Chikusa River in Hyogo Prefecture

\*Ken'ichi Ohkushi<sup>1</sup>, Takanori Nakano<sup>4</sup>, Ichiro Tayasu<sup>4</sup>, Tadashi Yokoyama<sup>2</sup>, Tamihisa Ohta<sup>4</sup>, Yukiko Kusano<sup>4</sup>, Hiromune Mitsuhashi<sup>3</sup>, Masayuki Itoh<sup>1</sup>, Kuniyoshi Ebina<sup>1</sup>

1.Kobe University, Graduate School of Human Development and Environment, 2.Hyogo Prefectural Nishi-Harima School for Students with Special Needs, 3.Museum of Nature and Human Activities, 4.Research Institute for Humanity and Nature

The simultaneous survey of water temperature in the Chikusa River was performed by Chikusa River Conservation Committee on August 9, 2015. The activity of the simultaneous survey has been putting it into effect by cooperation with a hundred of areal residents on Sunday of the beginning of August every year since 2002. In the survey, water samples were collected at 74 sites in total from Chikusa-cho Mimuro in the upstream and Amako seller to the Ako City coastal part in downstream. The cooperative geochemical study for the Chikusa River between the Chikusa River Conservation Committee and Research Institute for Humanity and Nature with Kobe University and Museum of Nature and Human Activities, Hyogo has started from the 2015's survey. In this study, we analyzed the water samples collected in 2015 by the Chikusa River Conservation Committee and areal residents in order to construct an environmental map for conservation in the Chikusa River area. The hydrogen and oxygen isotope composition and an ion chromatography analysis were performed about the water samples.

## Monthly monitoring of multiple water-quality to diagnose the linkage between surface water and groundwater in the Saijo plain, Ehime prefecture

\*Minoru Tokumasu<sup>2</sup>, Takanori Nakano<sup>1</sup>, Ki-Cheol Shin<sup>1</sup>, Yukiko Kusano<sup>1</sup>, Tamihisa Ohta<sup>1</sup>, Saitoh Yu<sup>1</sup>, Yoriko Yokoo<sup>4</sup>, Yoshihiro Yamada<sup>3</sup>

1.Research Institute for Humanity and Nature, Inter-University Research Institute Corporation National Institutes for the Humanities, 2.Minicipal office of Saijo , 3.Faculty of Agriculture, Kagawa Univbersity, 4.Faculty of Sciences and Engineering, Doshisha Univbersity

Coastal plain of Saijo city in Ehime prefecture is divided into eastern Saijo plain and western Shuso plain, and is known to be rich in groundwater irrespective of low precipitation in the Setouchi district. This is ascribed to be the presence of Ishizuchi mountainous area in the back of the plain, where the amount of precipitation increases with elevation. For the sustainable use of the groundwater, we collected samples of groundwater and river water over the whole plain area in cooperation with residents of Saijo city. Spatial analysis for the concentrations of 54 elements and stable isotope ratios of H, O, S, and Sr of these water showed that (1) the groundwater is divided into several areas dependent on the watershed and flow areas, and (2) the unconfined groundwater in the eastern plain flows in shallow aquifer recharged from the head of alluvial fan of the Kamo river, whereas the artesian water, which is representative and good quality of Saijo citizens, flows in deeper aquifer recharged from more mountainous area. Based on this finding, we started to monitor water-quality monthly at two Kamo river sites (Funagata bridge and Isonohashi bridge), Ohmachi elementary school site for shallow groundwater, Uchinuki hiroba site for artesian groundwater, and Tokumasu house site for a mixture of both waters. Temporal analysis of water quality data obtained during 2007 to 2015 is summarized as follows:

(1) The concentrations of most elements (Sb, As, V, Rb, Si, Al, Ti) in river water become high in summer and low in winter or spring, whereas those in groundwater at the Ohmachi site are high in winter and low in spring or summer and those in groundwater at the Tokumasu site are high in autumn and low in winter or spring. From the temporal analysis of these water-quality data, we can estimate the flow rate of the shallow groundwater to be about 10 cm per day.

(2) This seasonal variation is not so distinct for most elements in the artesian water at the Uchinuki site; the concentrations of Cl, B, Na, Sb, and As increase, whereas those of Ca and Sr decrease monotonously with weak seasonal change. Other elements (Si, V, Mg, Ti, SO<sub>4</sub>) show more complex variation. This result indicates that the recharge area and flow rate of the artesian water differ significantly from that of shallow one, and other water source in addition to the Kamo river is involved.

It is concluded that the monthly monitoring of water quality is effective to evaluate the linkage of the surface water and groundwater system, but further continuous monitoring is required especially for elucidating the flow system of artesian water.

Keywords: groundwater, surface water, monitoring, flow rate, water quality diagnosis, recharging area

Spatiotemporal variations in oxygen-hydrogen and strontium isotopic and trace elemental compositions of precipitation, Saijo, Ehime

\*Yoriko Yokoo<sup>1</sup>, Syuhei Ito<sup>2</sup>, Ki-Cheol Shin<sup>3</sup>, Shota Kato<sup>4</sup>, Takanori Nakano<sup>3</sup>, Minoru TOKUMASU<sup>5</sup>

1.Faculty of Science and Engineering, Doshisha University, 2.Graduate School of Science and Engineering, Doshisha University, 3.Research Institute for Humanity and Nature, 4.Kanazawa University, 5.Saijo City

We collected monthly precipitation at 6 sites with different altitudes in Saijo city of Ehime prefecture over 9 years from 2007 to 2015, and determined their  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and Sr isotopic and elemental compositions and to elucidate the precipitation process.

The values of deuterium excess (d-excess) ranged from 20 to 30‰ during winter and from 3 to 10‰ during summer in precipitations. The values of d-excess at the location "Jojusha (1,280 m above sea level)" were 3~10‰ higher than those of another sites during summer from 2009 to 2012. On the other hand, the values of d-excess at Jojusha had same as those of another sites during summer from 2013 to 2014. These results indicate heterogeneity of the isotope ratio within the investigation area and were ascribed to the origins of clouds, process of condensation from clouds and massive heavy rain.

The enrichment of As, Cu, Pb, Sb and Zn concentrations in the precipitation at lowest altitude site (20 m on the roof of city office) suggests the input of industrial anthropogenic activities from the urban area in the Saijo city and/or surrounding Setouchi region.

The concentrations of Al, Mn, Fe, Zn, V, Cu, As, Rb, Sr, Mo, Cd, Sb, Cs and Ba were high at city office site, Fujinoishi (700 m) and Jojusha from winter to spring. The Sr isotope ratio of precipitation at Jojusha also showed a seasonal variation with high in spring, indicating the contribution of the eolian dust from the Asian continent.

Keywords: precipitation, oxygen-hydrogen isotpe, Sr isotope, trace element

## Seasonal and Secular Change in Sulfur, Hydrogen, Oxygen and Strontium Isotopic Ratios of Precipitation Across Chugoku District.

Huixing Mao<sup>1</sup>, Kai Tsukada<sup>1</sup>, Tatsuya Yodose<sup>1</sup>, Katsuyuki Yamashita<sup>1</sup>, \*Hitoshi CHIBA<sup>1</sup>

1. Graduate School of Natural Science and Technology, Okayama University

We have sampled precipitations at 7 sampling points in Tottori and Okayama prefectures. Sampling method is bulk sampling by which both wet- and dry-deposition are sampled together. We measured major chemical composition, sulfur isotopic ratio of sulfate ion, hydrogen, oxygen and strontium isotopic ratios of water, and considered the origin and seasonal and secular change of precipitation and its dissolved components from 2011 to 2015.

Sulfur isotopic ratio of non-sea-salt sulfate ion decreases with increase in the distance from the Sea of Japan in most seasons. It shows seasonal change, high in winter and low in summer.

Therefore, cross-border pollution from mainland China seems to affect strongly at the Sea of Japan side than at the Seto Inland Sea side, and affect stronger at winter season. The maximum and minimum sulfur isotopic ratio of non-sea-salt sulfate ion seems to increase gradually from 2011 to 2015. It is necessary to monitor sulfur isotopic ratio of non-sea-salt sulfate ion continuously in order to find whether this increase is due to the increase of cross-border pollution or not.

The d-index of precipitation calculated from its hydrogen and oxygen isotopic ratio shows seasonal variation, high in winter and low in summer, at every sampling point. Furthermore, d-index of the Sea of Japan Sea side precipitation is lower than that at Seto Inland Sea side precipitation in summer season, and the former is higher than the latter in winter season. It indicates that winter precipitation is caused by the air mass coming from the mainland China and that summer precipitation is caused by the air mass coming from the Pacific Ocean. It supports that the cross-border pollution indicated by high sulfur isotopic ratio of non-sea-salt sulfate ion is brought by the air mass coming from mainland China.

Non-sea-salt Sr isotopic ratios in Yurihama and Misasa, both close to the Sea of Japan, show seasonal variation with higher ratio ( $>0.7010$ ) at spring and lower ratio ( $\sim 0.7070$ ) at summer and autumn. The higher ratio at spring reflect the contribution of yellow sand from the mainland China. On the other hand, low isotopic ratio at summer and autumn seems to be affected by the low isotopic ratio material derived from local rock, which accords with the low material transfer from the mainland China indicated by sulfur isotopic ratio of nss-sulfate and d-index of precipitation. The moderate Sr isotopic ratio at winter seems to result from the small yellow sand transport during winter season.

Keywords: precipitation, Chugoku district, non-sea-salt sulfate, S isotope ratio, H and O isotope ratio, Sr isotope ratio

## Characteristics of River Water Quality in Shodo-shima Island -Drawing a material Map in Rivers -

\*Yoshihiro Yamada<sup>1</sup>

1.Faculty of Agriculture, Kagawa University

### [Introduction]

In Kagawa Prefecture, where water resources are low, the accumulation of organic matter in the rivers downstream has become a problem (Yamada et al. 2015). For the cause analysis of organic contaminant, it is necessary to clarify its origin and load process and is essential to make a material map as the database of substance concentration.

So far, we have reported a material map in rivers in Shikoku Island. This time, by drawing a material map of Kagawa Prefecture, including Shodo-shima Island, the relationship between the river water quality and the river's basin environment will be analyzed, especially regarding Shodo-shima Island.

### [Methods]

In 27 rivers and 125 points of the entire area of Shikoku Island (Kagawa Prefecture) and Shodo-shima Island, water sampling was performed in August 2011. The items analyzed were main dissolved ions, chlorophyll *a* (Chla + Pheo), particulate organic carbon (POC) and particulate organic nitrogen (PON), and dissolved silicate (D-Si).

### [Results and Discussion]

In Shikoku Island, POC was from 26 mg L<sup>-1</sup> to 3232 mg L<sup>-1</sup>. As POC and Chla have a correlation ( $r^2=0.54$ ,  $p < 0.001$ ), it can be said that the main components of POC in the rivers are algae.

Additionally, when multiple regression analysis was performed by setting the population density, domestic animal wastes, the density of reservoir and the amount of precipitation as explanatory variables, as the effects of the density of reservoir were shown to be especially significant (standard partial regression coefficient 3.54,  $p = 0.001$ ), it can be considered that the algae produced in the reservoirs are the origin of POC in the rivers.

In Shodo-shima Island, POC was from 90 mg L<sup>-1</sup> to 5277 mg L<sup>-1</sup>, which was higher compared to Shikoku Island, especially in the southern part. Furthermore, as POC and Chla have no correlation and C/N was as high as 14 on average, it can be said that higher forms of life contribute greatly to the organic matter within the rivers of the southern part of Shodo-shima Island. When comparing the ratio of forest in the basin of the river with C/N of the downstream end, both the ratio of forest and C/N ratio were high in most of the points in the southern part of Shodo-shima Island.

Accordingly, it seems that the ratio of forest has a great influence on the composition of POC. Additionally, examining the relationship between the quantity of river water and POC, POC became high at the points when the quantity of the river water was small.

The D-Si of Shodo-shima Island became higher compared to that of Shikoku Island (Shikoku Island average: 7.53mg L<sup>-1</sup>, Shodo-shima Island average: 13.6 mg L<sup>-1</sup>). In particular, it tended to be high at the points of granites, while it became low at the points where there is basalt in the upstream that contains Hyp-Aug-01 basalt containing a small amount of silicon. When comparing the D-Si of the source of the rivers in Shikoku Island and Shodo-shima Island, which include granite with the amount of precipitation of the basin, it was found that there was a negative correlation. It was found that, as Shodo-shima Island has a small amount of precipitation, D-Si become high.

Furthermore, by setting up the prediction formula for precipitation at the granite area points in Kagawa Prefecture, the D-Si of the other nature of the soil of Shodo-shima Island was corrected by the amount of precipitation. As a result, it was found that D-Si was higher at the points of

andesite compared to the points of granite. It is considered that much silicate has been eluted because the geological age of andesite of Shodo-shima Island is new.

[Acknowledgments]

This study was supported in part by the River Fund from the Foundation of River and Watershed Environment Management, Japan.

Keywords: Shodo-shima Island, River, Water Quality

## Temporal and spatial variation of anthropogenic sulfur deposition in Japan by using sulfur isotopic ratio

\*Yayoi Inomata<sup>1</sup>, Tatsuyoshi Saito<sup>1</sup>, Yukimasa Morohashi<sup>1</sup>, Naoyuki Yamashita<sup>1,2</sup>, Hiroyuki Sase<sup>1</sup>, Tsuyoshi Ohizumi<sup>1,3</sup>, Katsuyuki Takahashi<sup>4</sup>, Naoki Kaneyasu<sup>5</sup>, Daisuke Funaki<sup>6</sup>, Aya Iwasaki<sup>7</sup>, Kazunori Nakagomi<sup>8</sup>, Tomoaki Shiroma<sup>7</sup>, Takashi Yamaguchi<sup>9</sup>

1.Asia Center for Air Pollution Research, 2.Forestry and Forest Products Research Institute, 3.Niigata Prefectural Institute of Public Health and Environmental Sciences, 4.Japan Environmental Sanitation Center, 5.National Institute of Advanced Industrial Science and Technology, 6.Shimane Prefectural Institute of Public Health and Environmental Sciences, 7.Okinawa Prefectural Institute of Health and Environment, 8.Nagano Environmental Conservation Research Institute, 9.Environmental and Geological Research Department

### [Introduction]

It is well recognized that non-sea salt (nss) sulfur isotopic ratios are useful to identify the sources because the sulfur isotopic ratio have source specific values. We have measured sulfur isotopic ratio in precipitation by using Japanese monitoring sites for the Acid Deposition Monitoring Network in East Asia (EANET). In this study, we investigated the spatial and temporal distribution of anthropogenic sulfur deposition and evaluated the contribution from transboundary transport from the Asian continent to Japan,

### [Observation and analysis]

We collected precipitation samples at 12 sites (Rishiri, Tappi, Ochiishi, Sadoseki-misaki, Niigata-Maki, Niigata-Kajikawa, Oki, Happo, Tokyo, Ijira, Hedo, Ebino, Ogasawara) after 2014. The sampling interval was 2 weeks, 1 month, and seasonally depending on the sampling schedule at each site. The sulfur isotopic ratios were measured by stable isotope mass spectrometer. Canyon Diablo Troilite (CDT) was used as the standard material. The analytical precision was  $\pm 0.16\%$ . The nss-sulfur isotopic ratio was calculated assuming that  $\text{Na}^+$  is originated from sea water.

### [Results and discussion]

At the monitoring sites located in the coast of the Sea of Japan, temporal variations of nss-sulfur isotopic ratio were characterized by seasonal variation with high in winter and low in summer season (e.g. Niigata-Kajikawa,  $+2$ - $+4.9\%$ ). Similar seasonal variations were also found in Tokyo and Ijira, where locates the Pacific coast sites. However, nss-sulfur isotopic ratio in Tokyo and Ijira was lower with smaller seasonal variation in comparison with those at the coastal site of the Sea of Japan (e.g. Tokyo,  $-0.73$ - $+4.0\%$ ). It was reported that sulphate in the air mass in China were strongly affected by coal combustion ( $0$ - $15\%$ , Xiao et al., 2011), whereas that in Japan were derived from oil combustion, which was negative values ( $-2.7\%$ , Ohizumi et al., 1997). Furthermore, it was reported that nss-sulfur isotopic ratio in aerosol in central China is  $4.5 \pm 1.3\%$  (Li et al., 2013). The difference of nss-sulfur isotopic ratio and these seasonal amplitude between coastal site of Sea of Japan and Pacific coast suggests that transboundary transported sulphate were mixed with the emitted sulphate from domestic (Japan) sources.

At Happo, mountain monitoring site (1850 m asl), nss-sulfur isotopic ratio were almost constant value ( $4.7 \pm 1.2\%$ ) except for several samples in spring. Contribution of Asian dust will cause the higher values. Almost constant value at Happo suggests that nss-sulfur isotopic ratio is minor contribution from local anthropogenic sources, indicating the transboundary transport from the Asian continent.

At Ogasawara, remote marine site, nss-sulfur isotopic ratios were high in spring-summer and low in winter, which were opposite seasonal variation. The higher nss-sulfur isotopic ratio in



spring-summer was possibly the biogenic emissions.

Relative contributions of sulfur with different sources have been evaluated with mass balance model. It was clear that the transboundary transported sulphur deposition in the coastal site of Sea of Japan (e.g. Niigata-Kajikawa  $1.1-20 \text{ mg m}^{-2} \text{ day}^{-1}$ ) is two-three times larger than those in the Pacific coast (e.g. Tokyo  $0.03-6.7 \text{ mg m}^{-2} \text{ day}^{-1}$ ).

[References]

Li, X., Bao, H., Gan, Y., Zhou, A., Liu, Y. 2013. Multiple oxygen and sulfur isotope compositions of secondary atmospheric sulfate in a mega-city in central China, *Atmospheric Environment*, 81, 591-599.

Ohizumi, T., Fukuzaki, N., Kusakabe, M., 1997. Sulfur isotopic view on the sources of sulfur in atmospheric fallout along the coast of the sea of Japan, *Atmospheric Environment*, 31, 13339-1348.

Xiao, H.Y., Liu, C-Q., 2011. The elemental and isotopic composition of sulfur and nitrogen in Chinese coals, *Organic Geochemistry*, 42, 84-93.

Keywords: sulfur isotopic ratio, precipitation, transboundary transport

## Annual and vertical variation of strontium isotopic ratio in two forest catchment in Japan

\*Tatsuyoshi Saito<sup>1,2</sup>, Naoyuki Yamashita<sup>1</sup>, Masayuki Morohashi<sup>1</sup>, Yayoi Inomata<sup>1</sup>, Shigeki Uchiyama<sup>1</sup>, Makoto Nakata<sup>2</sup>, Takanori Nakano<sup>3</sup>, Ichiro Tayasu<sup>3</sup>, Ki-Cheol Shin<sup>3</sup>, Tsuyoshi Ohizumi<sup>1</sup>, Hiroyuki Sase<sup>1</sup>

1.Asia Center for Air Pollution Research, 2.Niigata University, 3.Research Institute for Humanity and Nature

## [Introduction]

In the case of light elements such as sulfur, when it is used by plants in the ecosystem, isotopic ratio is varied by isotopic fractionation. It is caused by that light isotope is easier taken up to plants than heavier isotopes. On the other hand, in the case of heavy elements such as strontium (Sr), isotopic fractionation is almost negligible level, and isotopic ratio is only varied by component mixture from different sources. Therefore, such as elements are more suitable to estimate the contribution of some sources in the ecosystem. In this study, we discuss about annual and vertical variation of Sr isotopic ratio in two forest catchment, Kajikawa catchment in Shibata city, Niigata Pref. and Ijira catchment in Yamagata city, Gifu Pref.

## [Methods]

We collected rainfall, streamwater and soil solutions in the slope soil in each catchment and determined Sr isotopic ratio of samples which collected from Dec. 2013. Soil solutions were collected at the three plot, upper, middle and lower slope and two depth, 20 and 60 cm. Sr isotopic ratio was determined by thermal ionization mass spectrometry (TIMS) of Research Institute for Humanity and Nature (Kyoto city, Kyoto Pref.). Sr isotopic ratio is shown as  $^{87}\text{Sr}/^{86}\text{Sr}$  calculated based on the standard substance NBS987.

## [Results and discussion]

Figure shows analysis results of  $^{87}\text{Sr}/^{86}\text{Sr}$  in both catchment. In the case of rainfall as input side, annual variation range is comparative larger than streamwater as output side. In Kajikawa catchment, the highest value was shown in spring season when the amount of yellow sand increased. Second highest season was winter when sea salt contribution and amount of Sr derived from the continent increased by monsoon. These variation of Sr isotopic ratio indicate the contribution from different sources. In winter season, sea salt contribution rate became high level, and  $^{87}\text{Sr}/^{86}\text{Sr}$  value became close to seawater which value is about 0.709. In spring season, dust including soluble mineral ( $^{87}\text{Sr}/^{86}\text{Sr}$ :  $0.711 \pm 0.001$ ) derived from the continent made  $^{87}\text{Sr}/^{86}\text{Sr}$  value higher than winter season. On the other hand,  $^{87}\text{Sr}/^{86}\text{Sr}$  values of streamwater were stable throughout the year, and so far from rainfall value in both catchment. Sr concentration of streamwater was higher than rainfall over than one digit, and suggests correlation between calcium and magnesium. In addition, streamwater of Ijira catchment which geology include middle Paleozoic marine sedimentary rocks indicated higher  $^{87}\text{Sr}/^{86}\text{Sr}$  value than Kajikawa catchment which include rich granite. These results suggests that major part of Sr which flowed out to stream in both catchment was not derived from atmospheric deposition, probably from geologic origin.

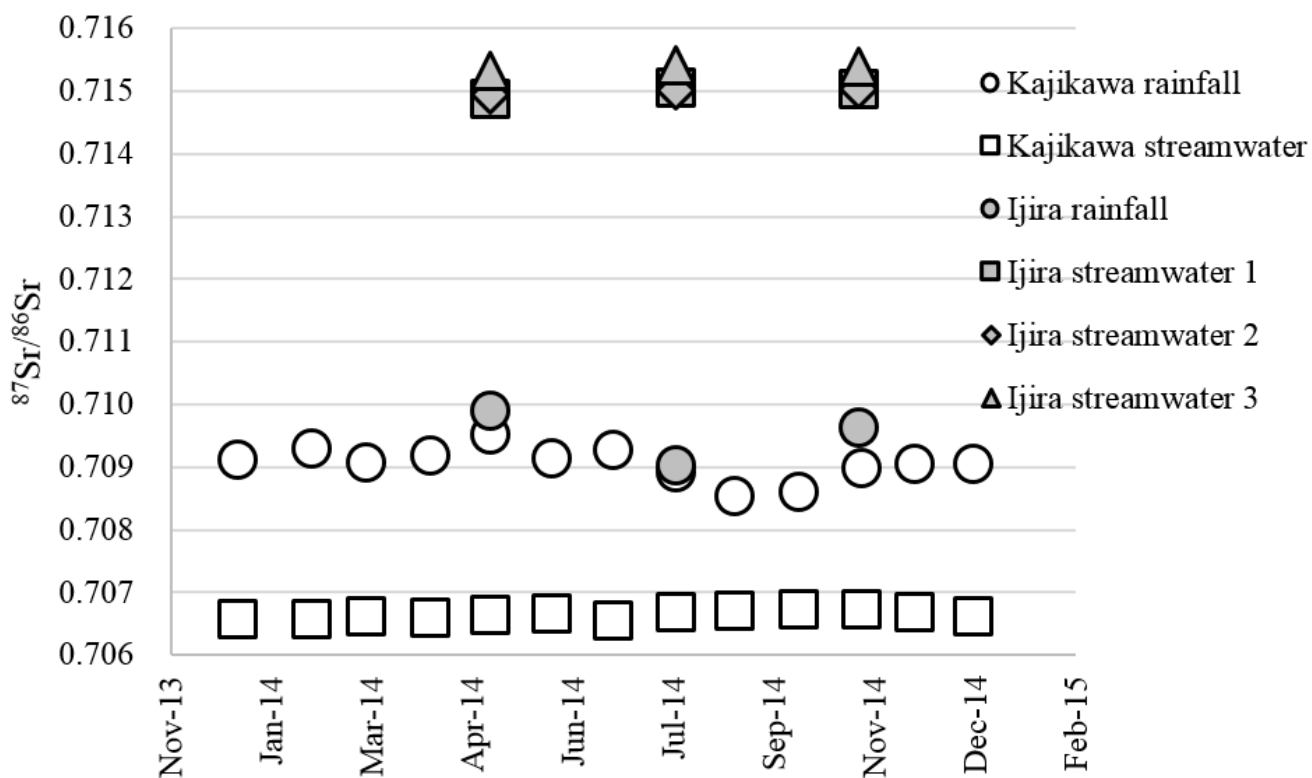
In this study, we also discuss about the vertical variation including soil solution value and comparison with sulfur (S) isotopic ratio.

## [Acknowledgements]

This study was conducted based on the monitoring data from the Ministry of the Environment of Japan and the related research outputs. Sr isotopic ratio analysis was conducted by the support of Joint Research Grant for the Environmental Isotope Study of Research Institute for Humanity and Nature. S isotopic ratio analysis was conducted by the support of Asia Pacific Network on Global change Research: ARCP 2013-13 CMY-Sase. Authors thank officers, experts and scientists in the relevant

organizations.

Keywords: strontium isotopic ratio, rainfall, streamwater



## Chemical separation of environmental materials for Stable Isotope Analysis

\*Ki-Cheol Shin<sup>1</sup>

## 1. Research Institute for Humanity and Nature

Stable Isotopes (SI), especially Sr-Nd-Pb isotopes, had been widely used as powerful geochemical tracers in Earth sciences. In recent, these isotope ratios have been applied to the biogeochemical tracer in traceability research. Since its invention, multi-collector ICP-MS (MC-ICP-MS) has been widely used for isotope analysis of metal and metalloids, including Sr and Pb because of their higher ionization efficiency of the ICP ion source, the enhanced sample throughput, and the flexibility of sample introduction. However, the chemical separation is still adapted from those developed for TIMS, and not modified for the use of MC-ICP-MS. The higher ionization efficiency makes almost all introduced component to ionize, causing matrix effect to the analyzed data and deterioration of the machine. Diverse environmental samples, especially organic materials cause a problem during chemical separation that could not expect. It should need that the element for MC-ICP-MS analysis should be clearly separated from matrix component not only cation elements but also organic materials.

The purpose of this study is to describe a newly developed sequential separation of Sr, Pb, and Nd with Sr resin and nitric acid solution reducing the processing time, the amount of acid reagent solution, and evaporation steps.

Two type of separation methods has developed depending on the elements. One is single separation method and the other is multi-separation ones. Single separation method separates a small amount of Sr (~1 $\mu$ g Sr) or Pb (~1 $\mu$ g Pb) only with restricted volume of the resin. This method merits fast recovery of the target element and direct analysis of Sr isotope ratios with MC-ICP-MS. The Pb solution recovered by hydrochloric acid evaporated and dissolved in nitric acid for isotope analysis. Multi-separation method uses a large amount of the resin to separate REE, Sr, and Pb in a row. The REE solution follows further separation of matrix elements with a cation exchange resin to purify rare earth elements. Nd elements purified from REEs with Ln resin.

To reduce organic materials from the Sr resin, a polymeric adsorbent resin is used in the lower layer of the Sr resin. For water samples, it is recommended to use hydrofluoric acid during sample evaporation, because natural water contains silica as a major component and poor separation in the resin. During these methods, the elements recovered up to 95% of Sr and 99 % of Pb of the loaded samples, respectively. The blank levels of Sr and Nd in the separation process were ~10pg and ~20pg, respectively.

Keywords: Stable isotope, MC-ICP-MS, chemical separation, Sr resin

Evaluation for information on paleoclimate and event recorded in stable isotopic compositions of an annually-laminated tufa, Asama volcano, central Japan

Masahiro Yuhara<sup>1</sup>, \*Nagayoshi Katsuta<sup>1</sup>, Osamu Abe<sup>2</sup>, Sayuri Naito<sup>1</sup>, Shin-ichi Kawakami<sup>1</sup>

1.Faculty of Education, Gifu University, 2.Graduate School of Environmental Studies, Nagoya University

Here we present analytical results of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in an annually-laminated tufa Asama volcano, deposited from AD. 1999 to 2012, and discuss its implication of paleoclimate and volcanic activity around Asama volcano.

Keywords: Tufa, Stable isotope, Volcano

## Tracing of the freshwater fish movement patterns and water dynamics by strontium stable isotope ratios and the elements concentrations analysis

\*Konomi Fudamoto<sup>1</sup>, Ki-Cheol Shin<sup>2</sup>, Takanori Nakano<sup>2</sup>, Seiichi Mori<sup>3</sup>, Manabu Kume<sup>4</sup>, Syotaro Nishida<sup>3</sup>, Ichiro Tayasu<sup>2</sup>

1. Graduate School of Science, Kyoto University, 2. Research Institute for Humanity and Nature, 3. Gifu-keizai University, 4. National Institute of Genetics

In coastal area of Otsuchi, Iwate prefecture, spring water is abundant and thereby the rare freshwater three-spined stickleback (*Gasterosteus aculeatus*), which prefer cold water environment, inhabit here. This area was damaged by the tsunami caused by the 2011 off the Pacific coast of Tohoku Earthquake. During the reconstruction and recovery works, the understanding of the habitat range and the environmental conditions of the three-spined sticklebacks contributes to the appropriate ecosystem management. Strontium stable isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) has been used as a powerful indicator to trace the past movement patterns of fish because of the same  $^{87}\text{Sr}/^{86}\text{Sr}$  value between fish and the water of its habitat. Therefore, we used  $^{87}\text{Sr}/^{86}\text{Sr}$  indicator to elucidate the three-spined stickleback movement patterns.

First, we investigated the relationship between the  $^{87}\text{Sr}/^{86}\text{Sr}$  of three-spined stickleback whole otoliths (ear bone) and the water in isolated water bodies. We confirmed that both water and fish have almost same  $^{87}\text{Sr}/^{86}\text{Sr}$ .

Second, by analyzing the water of different rivers and tributaries in Otsuchi, we found that, just in one tributary of Kozuchi mainstream,  $^{87}\text{Sr}/^{86}\text{Sr}$  and many element concentrations (e.g. Ca, Sr) were remarkably different between the upstream and downstream. Using  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration values of water, the downstream water was estimated to be mix of the upstream water, mainstream water and seawater (Contribution ratio; upstream: 82.6%, mainstream: 16.7%, seawater: 0.6%). Then, using  $^{87}\text{Sr}/^{86}\text{Sr}$  and elemental concentration of otoliths of fish captured in the upstream and downstream, we estimated their past movement patterns. We compared the water  $^{87}\text{Sr}/^{86}\text{Sr}$  between the upstream and the downstream and the  $^{87}\text{Sr}/^{86}\text{Sr}$  of otolith. As a result, it was possible to identify that stickleback lived in either upstream or downstream within single tributary; three-spined sticklebacks captured in the upstream (40 individuals in total) were not likely to move from downstream, while the fish caught at downstream (13 individuals in total) were estimated to have moved from the upstream or the mainstream. Furthermore, in the downstream, some fish otoliths showed a larger value of Sr/Ca than the others, which means that those fishes lived in high salinity environment in the past suggesting that the downstream population of three-spined stickleback was able to live in both fresh and brackish water environments.

Keywords: strontium stable isotope ratio, otolith, fish, water

The apterous winter stonefly fauna and its feeding on seasonal snowfields in Japan  
- Analysis of the food web using C and N Stable Isotope -

\*Chika Okamoto<sup>1</sup>, Nozomu Takeuchi<sup>1</sup>, Ichiro Tayasu<sup>2</sup>, Tamihisa Ohta<sup>2</sup>

1.Chiba University, 2.Research Institute for Humanity and Nature

In snow and ice environments, there are diverse living organisms that can be active and grow in cold temperature. For example, snow algae, heterotrophic bacteria, and insects can be found on snow fields in Japan. An apterous winter stonefly is one of the typical insects that appear on snow surface in mountainous regions during winter or spring in Japan. However, their food web, particularly food resources of the stoneflies on snowfields, is still not well-known. It is important to clarify the food web of the organisms living on snowfields to understand carbon and nitrogen cycles quantitatively in the snow and ice environments. The stable isotope ratios of carbon and nitrogen of the specimens provide a means of analyzing their food resources. In this study, we analyze the food webs of the winter stoneflies and other organisms on Japanese snow fields using C and N stable isotope analysis.

The stonefly specimens were collected on the snow surface at five sites in Japan during 2015. The study sites included snow fields in Shinjo in Yamagata (altitude: 150 m), in Ushitakeonsen in Toyama (490 m), in Uonumakyuryo in Niigata (210 m), in Mt. Gassan (1300m altitude), in Tateyama Mountains (2300 m). Furthermore, other specimens including springtails, spiders, leaves, snow algae and particulate organic matter in snow were collected. The stable isotopes showed that potential food sources of apterous winter stoneflies are springtails, aphids, small spiders, snow algae, particularly dead leaves.

Keywords: stonefly, food web, stable isotope





## Effects of additional nitrogen input and different river slope on the outflow from upstream nitrogen-saturated forests

\*kenichi Shinozuka<sup>1</sup>, Masaaki Chiwa<sup>1</sup>, Ichiro Tayasu<sup>2</sup>, Chikage Yoshimizu<sup>2</sup>, Atsushi Kume<sup>1</sup>

1.Kyushu University Faculty of Agriculture, 2.Research Institute for Humanity and Nature

Non-point source nutrients, such as excess fertilizers from agriculture and human sewage water, are main cause of eutrophication of lakes, streams, and coastal areas. The upstream areas of suburbs of Fukuoka are covered with nitrogen-saturated forests, and supplied high concentration  $\text{NO}_3^-$  river water to the downstream. Such nitrogen-saturated forests have large impact on the downstream water quality (Chiwa et al., 2012), but less information was available of the mechanism of the changes in  $\text{NO}_3^-$  concentration from upstream to the downstream.

The objectives of this study were to clarify (1) whether the nitrogen dynamics (the concentration of  $\text{NO}_3^-$ ,  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) in the downstream were affected by the nitrogen-saturated forests in the upstream, (2) the influence of nitrogen runoff from agriculture and urban area in the downstream, and (3) the influence of the river gradient on denitrification.

$\text{NO}_3^-$  concentration and the stable isotopes,  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  were measured in the Tataru River Basin, located in northern Kyushu, western Japan. Water samples were mainly collected from branch rivers; Ino River, Sue River and Umi River. Deciduous mature forest dominates the ridges in the upstream, with paddy, farmland and urban dominating in the middle and downstream. Topographic Index (TI) was calculated by using Digital Elevation Model (DEM) with ArcGIS software.

Our results showed that the  $\text{NO}_3^-$  concentration in the upstream of three rivers (33.9-82.8  $\mu\text{mol/L}$ ) were higher than the other non-saturated forests. Lower  $\delta^{18}\text{O}_{\text{NO}_3}$ , higher  $\text{NO}_3^-$  and  $\delta^{15}\text{N}_{\text{NO}_3}$  in the downstream were be found in Sue River and Umi River. On the other hand, Ino River showed different trend that lower  $\text{NO}_3^-$  concentration, higher  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  concentration in the downstream. The higher  $\text{NO}_3^-$  concentration in the downstream in Sue River and Umi River was affected by the increasing agriculture and urban areas in the downstream. However, the  $\text{NO}_3^-$  concentration in the downstream of Ino River decreased with the increasing agriculture and urban areas.

The average TI value showed no difference between rivers. However, the distribution of TI values in Ino River was different from other rivers. Ino River has smaller changes in gradient from upstream to downstream and fewer agriculture and urban areas in the downstream than the other two rivers. These differences could result in the higher probability of denitrification occurring and the lower  $\text{NO}_3^-$  loading in the downstream in Ino river.

The nitrogen-saturated upstream forests in this watershed has large impact on the nitrogen sources to the downstream. In the areas with steeper gradient, the high concentration of nitrogen runoff was supplied to the agriculture and urban areas. On the other hand, in those areas with gentle gradient, the nitrogen loading in the downstream also decreased due to the gentle gradient of the watershed and it was suggested that the rate of denitrification and decrease  $\text{NO}_3^-$  concentration in the downstream was also high.

Keywords: nitrogen saturation, stream water quality, nitrogen isotope, land use, Topographic Index

Trial application of oxygen, carbon and strontium isotope analysis in tooth enamel for identification of past-war victims for discriminating between Papuan, Japanese and US soldiers

\*Hidetoshi Someda<sup>1</sup>, Takashi Gakuhari<sup>2</sup>, Akai Junko<sup>1</sup>, Araki Yoshiyuki<sup>1</sup>, Ki-Cheol Shin<sup>3</sup>

1.National Defense Medical College, 2.Kanazawa University, 3.The Research Institute for Humanity and Nature

Stable isotope analysis has undergone rapid development in recent years and yielded significant results in the field of forensic sciences. In particular, carbon, oxygen and strontium isotopic ratios in tooth enamel obtained from human remains can provide useful information for prescreening for identification of remains. The aim of this study is to evaluate this method for discriminating remains between local people, Japanese and US soldier in the battlefield of New Guinea of World War 2.

In this study, the carbon, oxygen and strontium isotopic ratios in the tooth enamel of the examined Papuan (South highland, East New Britain and Bougainville) and Japanese (Tottori) individuals is compared to previously reported data for US individuals, and statistical analysis is conducted using a discriminant analysis.

US populations can be extracted from these groups accurately. The discrimination between the Papuan and Japanese is found to be partly accurate. Thus, the present method has potential as a discrimination technique for these populations for use in the examination of mixed remains comprising Papuan, Japanese and US fallen soldiers.

Keywords: Stable isotope analysis, War victim, Geographic origin

## Stable isotope analysis and radiocarbon dating on human skeletal remains from the Yoshigo shell mound of the Jomon period

\*Soichiro Kusaka<sup>1</sup>

1.Museum of Natural and Environmental History, Shizuoka

The author investigated radiocarbon ages and carbon and nitrogen stable isotope ratios in human skeletal remains excavated from the Yoshigo shell mound in the Aichi Prefecture. Although a large number of skeletal remains has been excavated from the Yoshigo shell mound, ages of these skeletal remains are still unclear. Radiocarbon dating on human bone collagen can estimate the ages of the individuals, but the precise estimate on marine food dependence is needed to correct marine reservoir effect on radiocarbon dates. This study investigated radiocarbon ages and carbon and nitrogen stable isotope ratios of human skeletal remains from the Yoshigo shell mound during the Late-Final Jomon period. By using the Bayesian mixing model on the carbon and nitrogen isotope ratios, the dietary dependences on marine food of each individual were estimated. Then, the results of radiocarbon dating were corrected. The results of this calibrated ages of human skeletal remains exhibited the ages during the Late-Final Jomon period, and it can enable us to analyze the dietary difference through time.

Keywords: Human skeletal remains, Stable isotope, Diet

Building an ontology of isotope environmental science

\*Yasuhisa Kondo<sup>1</sup>, Terukazu Kumazawa<sup>1</sup>, Tatsuki Sekino<sup>1</sup>, Ichiro Tayasu<sup>1</sup>, Takanori Nakano<sup>1</sup>

1. Research Institute for Humanity and Nature

In its Midterm Master Plan Phase 3 (FY 2016-2021), the Research Institute for Humanity and Nature (RIHN) will promote research and development in the visualization of isoscapes, or spatial information on environmental isotope ratios, including the disclosure and sharing of measured isotope data. As a preliminary study in this area, the authors built an ontology of isotope environmental science using the following method. First, in a brainstorming session with researchers of informatics and isotope environmental science, participants sorted the relationships of vocabularies extracted from lectures in the RIHN citizen seminars by posting sticky notes on a wall. This brainstorming session successfully organized the ontological relationships of terms in isotope environmental science, particularly in hydrology, ecology, geochemistry, and the social sciences. Then, the ontology was structured and visualized by using an analytical program called Hozo (<http://hozo.jp>). To continue this approach, the ontological model should be extended to other related fields of research, such as archaeology and geography. Furthermore, the authors plan to apply the RDF (Reference Description Framework) for describing the ontological relationships within the triple of subject, predicate, and object.

Keywords: Isotope environmental science, ontology, knowledge base, terminology

