Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-01 Room:304 Time:May 27 11:00-11:15

Geochemical and isotopic map of stream water as a basis of environmental traceability an example of northeastern Japan

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Traceability, which can trace the route of a material from its utilization to production area, is a key concept based on the precautionary principle of global environmental issues. All materials in the earth is composed of 92 elements, most of which have stable isotopes (SI). The ratio of SI of an element can be utilized as a traceability index regarding the source and process of the element in the environment. In order to establish a traceability method in earth environment using multiple elements and SI, Research Institute for Humanity and Nature (RIHN) has been installed analytical instruments of elements and SI in the laboratory, and started a project of making water quality map, which aims to elucidate the spatial distribution of the concentration and SI ratios of elements in terrestrial water. This is because elements in organisms and agricultural-fishery products are derived ultimately from ambient water, and the concentrations and SI ratios of elements in the water vary geographically rather than seasonally. This geographical variation of terrestrial water is attributed to the amount and quality of atmospheric precipitation and the geology and human activities in the watershed. Accumulating the data of water quality map provides basic information on traceability studies including water-material circulation, biodiversity, and climate change as well as agricultural and fishery products and food.

In order to elucidate the impact of atmospheric precipitation and the role of chemical weathering and human activities on fresh water, we determined the concentrations of 6 major ions and 46 trace elements and the isotopic ratios of hydrogen, oxygen, and strontium for about 1000 stream waters in the Iwate, Miyagi, Akita, and Yamagata prefectures of northern Tohoku, and compared them with geomorphology, geology and the geochemical map of river sediments.

The δD and δ^{18}O values of stream water tend to decrease with latitude and elevation, but their relation is expressed as δD=6.6δ^{18}O. The slope value of 6.6 is lower than 8.0 in the precipitation and it becomes low in the water of high δD and δ^{18}O values, indicating that river water experienced with evapotranspiration, particularly in southern and coastal areas where both values are high.

The ^{87}Sr/^{86}Sr ratio of stream water in igneous rock watershed ranges from 0.704 to 0.706, which is slightly higher than that of water in the Green Tuff region (0.706-0.707). The ^{87}Sr/^{86}Sr ratios of sedimentary rocks in the north Kitakami region (0.7085-0.7124) are higher than those in the south Kitakami one. The distribution of Sr/Ca ratio of stream water in the igneous rock watershed also resembles to that of watershed rocks. This correspondence of the Sr isotopic ratio and the Sr/Ca ratio of stream water with those of watershed rock reflects the major source of Sr as well as Ca in the water is largely derived from rocks.

However, although the distribution patterns of alkali-earth elements (Sr and Ca) in the water is similar each other, it is different from those in the river sediment. The distribution pattern of other major and trace elements is also different between river water and river sediment. This inconsistent pattern of elements indicates the important role of element fractionation during the chemical weathering of rocks into water, such as the adsorption and desorption of elements on the sediment particles.

Rare-earth elements of river water in the Miyagi prefecture tends to be higher than those in the Iwate prefecture. As REE are present as colloidal form, this tendency suggests that rocks in the Green-tuff region supply colloidal particles than granite and sedimentary rock which widely distribute in Iwate prefecture. Adsorption-desorption reaction play an important role on the water quality of water.

Keywords: geochemical map, isotopic map, stream water, traceability, northeastern Japan

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-02 Room:304 Time:May 27 11:15-11:30

Sources of atmospheric lead inferred from isotope ratios of HCl-soluble Pb and the residual Sr-Nd of aerosol particles

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Lead is one of the major pollutants of atmospheric environment. Around the East Asia, China is known as the major emission source of atmospheric lead. It is obvious that the influence reaches Japan across the sea. However, it is not clear which part of China is the major pollutant source of Japanese air and if there is seasonal change of sources. In order to reveal these, we conducted Pb isotope analysis of HCl-soluble component of aerosol particles sampled with high temporal resolution from August 2011 to August 2012 at the Omura City, north Kyushu. In association with Sr-Nd isotope ratios of HCl-insoluble component and air-mass back trajectory analysis, the four regions, the north, inland, south China, and Korea, were recognized as the discrete sources of atmospheric lead. Among the four areas, the north China is important in amount of lead. Atmospheric lead in the Omura City is mainly derived from the north and inland China during fall and winter. On the other hand, it is transported from Korea during a few days in fall, and from the south China during a few days in summer.

Keywords: Aerosol, Atmospheric lead, cross-border pollution

Japan Geoscience Union Meeting 2015
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HTT31-03 Room:304 Time:May 27 11:30-11:45

Multi-tracers approaching to groundwater and surface water interaction in Ono basin surrounded by steep mountains, Japan

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Mountainous headwaters and lower stream alluvial plains are important as water recharge and discharge areas from the view point of groundwater flow system. Especially, groundwater and surface water interaction is one of the most important processes to understand the total groundwater flow system from the mountain to the alluvial plain.

We performed tracer approach and hydrometric investigations in a basin with an area 948 square km surrounded by steep mountains with an altitude from 250m to 2060m, collected 258 groundwater samples and 112 surface water samples along four streams flowing in the basin. Also, Stable isotopes ratios of oxygen-18 (^{18}O) and deuterium (D) and strontium (Sr) were determined on all water samples.

The ^{18}O and D show distinctive values for each sub-basin, due to different average recharge altitudes among four sub-basins. Also, Sr isotope ratio shows the same trend as ^{18}O and D, due to different geological covers in the recharge areas among four sub-basins.

The ^{18}O, D and Sr isotope values of groundwater along some rivers in the middle stream region of the basin show close values as the rivers, and suggesting that direct recharge from the river to the shallow groundwater is predominant in that region. Also, a decreasing trend of discharge rate of the stream along the flow supports this idea of the groundwater and surface water interaction in the basin.

Keywords: Groundwater flow system, Circulatory system of groundwater and surface water, Hydrogen and oxygen isotope ratio, Sr isotopic composition, Multi tracers approach

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-04 Room:304 Time:May 27 11:45-12:00

Plantation of Cryptomeria japonica might alter dynamics of metal element

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In this study, we found dynamics of many metallic elements in catchment areas may be altered by plantation of Cryptomeria japonica.

Organisms can alter nutrient dynamics in ecosystems via physiological results such as respiration, decomposition and excretory processes. Many studies have established importance of the alteration of nutrient dynamics by organisms in ecosystems. Especially, dynamics of carbon, nitrogen and phosphorus can be altered by physiological responses of organisms. However, there are few studies that focused on effects of organisms on dynamics of metallic elements in ecosystems.

Our previous studies showed that the vegetation in catchment area might alter calcium concentration in the soils and water of streams, and affect the community structure of invertebrates in soils and streams. In these studies, we observed that concentration of exchangeable calcium in the Japanese cedar (C. japonica) plantations is about three times higher than in the evergreen broad-leaved forests. This might indicate C. japonica has characteristics that alter dynamics of metallic elements in soil. We focused on organic acids extracted from roots of tree because some studies showed root exudation of organic acids could elute materials in soil particles and base-rocks.

We conducted field survey and a pot experiment in Wayakama Experimental Forest of Hokkaido University. And we determined the reason why the elevation of calcium concentration in plantation of C. japonica occurs. In consequences, our results showed plantation of C. japonica might increase exchangeable metallic ion in soils through increased supply of organic acids to soil systems. And the some eluted metallic ions might be supplied to streams.

Keywords: stream, soil, metallic ion, plantation of Cryptomeria japonica, organic acids

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-05 Room:304 Time:May 27 12:00-12:15

Usefulness of strontium isotope composition for determining the geographical origin of Japanese horseradish

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The geological conditions in Shizuoka prefecture vary widely, from young volcanic rock area in the eastern part to old sediment or metamorphic rock in the western area. Dissolved element and isotopic compositions in springwater, which is located at the top of a river, would reflect the geological characteristics with the exception of effects of atmospheric deposition and human activity. This study aims to evaluate the usefulness of strontium isotope ratio ($^{87}Sr/^{86}Sr$) for determining the geographical origin of Japanese horseradish (*Wasabia japonica*) cultivated in the springs. We collected 58 springwater samples and 59 horseradish samples from 21 sites in Shizuoka prefecture. These samples were subjected to trace elements and $^{87}Sr/^{86}Sr$ analyses. The $^{87}Sr/^{86}Sr$ values differed, based on the geological characteristics of their site locations, and the value of horseradish sample was well accorded with that of water sample in the same location. The combination of trace element content, e.g. vanadium, and $^{87}Sr/^{86}Sr$ value of the horseradish allowed us to distinguish the production area clearly.

Keywords: geographical origin, Japanese horseradish (Wasabia japonica), strontium isotopic composition, trace element, Shizuoka prefecture

Japan Geoscience Union Meeting 2015
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HTT31-06 Room:304 Time:May 27 12:15-12:30

A possibility of the elucidation of smelting process in pre-modern Japan by stable lead isotope ratio analysis

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Keywords: stable lead isotope ratio, pre-modern Japan, smelting process

Japan Geoscience Union Meeting 2015
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HTT31-07 Room:304 Time:May 27 12:30-12:45

Recent progresses in the ICP-mass spectrometry as rapid, accurate and flexible analytical tool for isotopes geosciences

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[1]Kyoto University

Rapid and unremitting developments in inorganic mass spectrometry, including a multiple collector-ICP-mass spectrometry (MC-ICPMS), have revolutionized the precision of the isotopic ratio measurements, and the applications of the inorganic mass spectrometry in geochemistry, metrology and biochemistry were beginning to appear over the horizon. Analytical community is actively solving problems, such as spectral interference, mass discrimination drift, high-yield chemical separation and purification processes, or reduction of the contamination of analytes. The variations in isotopic ratios of the heavy elements can provide new insights into past and present geochemical and biochemical processes.

Stable isotope tracers are now increasingly being used in studies of elemental metabolism, bioavailability or toxicity of nutrients, as well as evaluating the elemental turnover time. Besides an absence of harmful radiation, this approach has the further advantage of enabling multi-element studies, in which different isotopes can be added to the same meal. The metabolism of higher organisms can be transcribed as stable supply of the most essential elements through transfer, absorption, and storing processes, which form the basis of homeostasis function. Because of the homeostasis control, fluctuations or changes in the concentration of the essential nutrients would be highly restricted to maintain the biochemical functions. This suggests that the impairments in the metabolism or nutritional status of both the essential and toxic metal elements could not be evaluated only by the concentration of the elements in fluids. Variations in the isotopic composition of the elements induced through dietary or metabolism processes have potential to become novel biochemical markers for assessing impairments in metal metabolism or nutritional status of the elements.

Iron is one of the most important inorganic nutrients for all terrestrial plants and animals, and the natural variations in isotope ratio of Fe have been used to trace the food chain. For land organisms, it is widely recognized that the Fe isotope ratios (^{56}Fe/^{54}Fe and ^{57}Fe/^{54}Fe) changes by 0.1% with increase the trophic level (Walczyk and Blankenburg, 2002, 2005). In contrast, the Fe isotope data for marine organism of lower trophic levels (plankton, shrimp and tuna) did not vary significantly from the Fe isotope ratio for the seawater. The small variations in the Fe isotope ratios for marine organisms could be explained either by higher intake efficiency of Fe from the dietary foods, or by the smaller isotope fractionation due to intake of hemo-Fe (Fe(II)). However, it should be noted that the reported Fe isotope ratios for marine organisms were very limited, and therefore, possible link between the ^{56}Fe/^{54}Fe and ^{57}Fe/^{54}Fe ratios and the trophic level was not clearly demonstrated. To investigate this, we have measured the ^{56}Fe/^{54}Fe and ^{57}Fe/^{54}Fe for series of marine creatures of various trophic levels using multiple collector-ICP-mass spectrometer (MC-ICPMS). The measured ^{56}Fe/^{54}Fe isotopes for marine organisms of higher trophic levels became significantly lower than those for lower trophic levels animals. Several important features of the Fe isotopes for marine creatures could be derived from the present results. The obvious changes in the Fe isotope ratios could be due to different Fe biocycling for higher trophic level animals. Another important feature obtained from the Fe isotopes was that the definition of the trophic level, based on the ^{13}C/^{12}C and ^{15}N/^{14}N isotope, would not reflect the food chain for inorganic nutrients including Fe. The details of the mechanism in the variation of the ^{56}Fe/^{54}Fe ratios for both the marine and land organisms will be discussed in this presentation.

Keywords: stable isotope, isotope signature, MC-ICP mass spectrometry, Fe biocycle, trophic level

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-08 Room:304 Time:May 27 14:15-14:30

Use of multiple isotope tracers to study coastal ecosystem

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Environmental traceability method is based on material cycling, thereby applicable to the studies on various environmental issues. Especially, the method is useful to evaluate human impacts on ecosystem properties. However, comprehensive use of the method is under development. In this study, we show potential applicability to use multiple isotope tracers in the study of coastal marine ecosystem, using isotope elements of terrestrial origin as well as the elements circulating in the system.

Elements constituting living organisms are obtained from the environments. From ecological point of view, the living organisms are obtaining environmental information where they live and what they eat. In other words, the living organisms record indicators of surrounding environmental conditions. Elements in hard tissue, e.g. otolith, sequentially record environmental variables as they grow. The calcium carbonate and trace metals in otolith are primarily derived from the water, therefore, they contain information of the water bodies that the fish have previously occupied. In contrast, elements in soft tissue are continuously metabolized and have each turnover time. Some elements in the organism are derived from the surrounding water, others are derived from the diet. These things considered, multiple tracers in organisms have various information.

Our project, ”Development of multi-isotope tracer techniques for evaluating functions of coastal ecosystem” funded by JST-CREST, is aiming at developing a method to evaluate coastal ecosystem using multiple isotope tracers. We show potential advantage of the use of multiple isotope tracers to study coastal ecosystem.

Keywords: Stable isotope, Traceability, Coastal ecosystem

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-09 Room:304 Time:May 27 14:30-14:45

Stable nitrogen isotope ratios of amino acids reveal the differences in trophic position of benthic fishes in Sendai Bay

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Coastal area provides many ecosystem services such as fishery resources, while it is one of vulnerable ecosystems affected by overfishing, pollution, and development. For the suitable conservation and management, it is necessary to clarify the food web structure and its dynamics. In coastal ecosystem, since some fish species show a widespread migration, their spatio-temporal scales are critical for unraveling the food web dynamics.

Estimation of trophic positions using carbon and nitrogen isotope ratios of bulk tissues are powerful approach for clarifying the food web structure. In the management of fishery resources, trophic positions estimated by stable isotope ratios are regarded as important index of fish resources.

Recent studies reveal that stable nitrogen isotope ratio of individual amino acids ($\delta^{15}N_{AA}$) is useful for estimating trophic levels (TLs) of organisms. In the amino acid metabolism of organisms, glutamic acid experiences deamination and transamination, which consequences great isotopic enrichment per TL. On the other hand, phenylalanine conserves its amine during metabolism, resulting in little isotopic enrichment per TL. Therefore, the TLs of organisms can be determined by following equation:

$$TL = (\delta^{15}N_{Glu} - \delta^{15}N_{Phe} + \beta)/7.6 + 1$$

where $\delta^{15}N_{Glu}$ and $\delta^{15}N_{Phe}$ are stable nitrogen isotope ratios of glutamic acid and phenylalanine of an organism, respectively, and β is the nitrogen isotopic difference between glutamic acid and phenylalanine of a primary producer. For accurate estimation of TL, β values for aquatic and terrestrial primary producers are defined as -3.4 ‰ and +8.4 ‰, respectively.

In this study, we estimated TLs of bastard halibut (*Paralichthys olivaceus*) and stone flounder (*Kareius bicoloratus*) in Sendai Bay using $\delta^{15}N_{AA}$ values. After hatch and settling, juvenile fishes inhabit shallow sea areas (water depth $<$10m), and most of them move to deeper offshore areas with growth. However, some large adult fishes are caught at shallow sea areas.

To reveal the changes of TL with growth and differences of TL among different habitats in these fishes, we collected fish samples from various habitats in Sendai Bay from 2012 to 2014. Amino acids of fish muscle tissues were purified by HCl hydrolysis, followed by N-pivaloyl/isopropyl derivation. The values of $\delta^{15}N_{AA}$ were determined by isotope ratio mass spectrometry coupled to a gas chromatograph via combustion and reduction furnaces.

Analysis of $\delta^{15}N_{AA}$ clarified increase of TL from juveniles to larger adults of bastard halibut and stone flounder. Furthermore, difference of TL between adult fishes with even body size collected in shallow sea areas and deeper offshore areas suggested that some adult fishes stay at shallow sea areas for a long period. In offshore areas, difference of TL among habitat areas and seasons suggested the variation of food resources. Furthermore, we considered the possibility for tracing the migrations of individual fish using information from $\delta^{15}N_{AA}$.

Keywords: coastal ecosystem, food web, fishery resources, migration tracing

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-10 Room:304 Time:May 27 14:45-15:00

The effects and solution of ”mixing problem” in the dietary analysis using stable isotopes

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Dietary analysis using stable isotopes can reveal dietary information in the long timeframe, and it can be applied to ancient animals. These advantages of stable isotope analysis allowed them to be used in the various field of science including anthropology, ecology and archaeology. Especially, stable isotope analysis using dual isotopes; carbon ($d^{13}C$) and nitrogen ($d^{15}N$) is the most widely used in every field. Carbon stable isotopes possess distinctly different isotope ratios between C_3 and C_4 plants due to fractionation during photosynthetic carbon fixation. The stable nitrogen isotope ratios increase along with food chain. In this reason, stable isotope analysis using these stable isotopes provides highly reliable dietary information. In addition, recent studies sometimes use stable isotope mixing model, which can evaluated the proportional contribution of each food resource to the diets of individual or groups of target animal.

However, there are several points to be kept in mind when we interpret the result of stable isotope analysis, and the ”mixing problem” is one of them. This is attribute to the geometry of sources and mixtures in a mixing diagram, and the problem sometimes diffuses or constrains the possible source contributions. The mixing problem frequently occurs as the number of sources increases (e.g. over 4 sources in dual isotopes). If the geometry of sources and mixtures were likely to involve the mixing problem, the interpretation of stable isotope analysis should be undetermined regardless of the use of mixing model. However, this problem is not sufficiently recognized even in modern times.

In this presentation, we show the effect and solution of the mixing problem using field data of Hokkaido brown bears (*Ursus arctos*). Brown bears are opportunistic omnivore and they consume various diet items including C_3 plants, crops (including C_4 plants), terrestrial animals and salmon. Previous studies showed that the mean $d^{13}C$ and $d^{15}N$ values of C_3 plants, terrestrial animals and salmon of Hokkaido were almost linearly distributed, and the points of Hokkaido brown bears were also mostly plotted on the line. This is exactly the case of mixing problem, and we tried to evaluate the effects of the mixing problem using mixing model analysis and additional use sulfur stable isotopes which can isotopically separate the marine and terrestrial diet.

We collected bone collagen of brown bears in Shiretoko peninsula and their diet items (C_3 herbs, C_3 fruits, corn, terrestrial animals and salmon), and measured carbon, nitrogen and sulfur stable isotope ratios. Then we estimated proportional contribution of each diet items to individual bear’s diet using mixing model (SIAR) both in dual (carbon and nitrogen) and triple isotopes (carbon, nitrogen and sulfur), and compared the results of these estimates.

In the results of SIAR using dual isotopes, proportions of each diet items (C_3 herbs, C_3 fruits, corn, terrestrial animals and salmon) were 33.2%, 28.1%, 8.4%, 19.0%, 6.4%, respectively. On the other hand, dietary proportions estimated by triple stable isotopes were 36.5%, 28.3%, 6.8%, 11.4% 10.5%, respectively. Mean absolute differences of proportions of each diet items were highest in terrestrial animals (12.0%). In the dual isotope analysis, the proportion of terrestrial animals tended to be overestimated (max: 53.3%) and salmon and C_3 herbs were likely to underestimated.

Our results showed that the mixing problem practically results in the bias of dietary estimation by stable isotope mixing model. When the geometry of sources and mixtures were likely to involve the mixing problem, the proportions of diet items in the intermediate position of mixing diagram should be overestimated. In this case, interpretation of stable isotope data is difficult, and therefore, addition of other stable isotope elements or discussion about the expected bias should be needed.

Keywords: stable isotope, carbon, nitrogen, sulfur, mixing model, brown bear

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-11 Room:304 Time:May 27 15:00-15:15

Marine ecological study using long-lived radionuclides

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Recent advance in technology enables us to monitor fish migrations and marine mammals behaviors to understand their ecological information. These fundamental data is critical to establish management programs of marine resources. However the logger size limits their applicability to smaller size tests and no information is available for the period before the capture and release of loggers.

We therefore have been trying to develop methods to monitor ecology and environmental data using geochemical fingerprints remaining in the body of marine organisms. That includes radiocarbon, iodine and other trace amount of nuclides. In the presentation, we will introduce our recent studies on this topic in particular using radiocarbon that is measured by Single Stage Accelerator Mass Spectrometry installed at the Atmosphere and Ocean Research Institute, the only and the first machine in Japan. The success of the study is depending on the reduction of sample sizes for each measurements but this new AMS provides stable and reliable measurements with trace amount of samples.

Keywords: isotope, radionuclides, accelerator mass spectrometry, ecology

AMS building (left) and Single Stage Accelerator Mass Spectrometer (right)

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-P01 Room:Convention Hall Time:May 27 18:15-19:30

Chemical compositions and Sr-Pb isotope ratios of precipitation of Saijo city in Ehime prefecture

YOKOO, Yoriko[1*] ; KAMEYAMA, Takuya[1] ; SHIN, Kicheol[2] ; KATO, Shota[3] ; TOKUMASU, Minoru[4] ; NAKANO, Takanori[2]

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We collected monthly precipitation at 2 sites with different altitudes (20 m on the roof of city office and 1280 m in Jojusha) in Saijo city of Ehime prefecture over 5 years from 2008 to 2012, and determined their chemical compositions and Sr-Pb isotope ratios. The concentrations of Al, Mn, Fe, Zn, V, Cu, Ga, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, and P were high at both sites from winter to spring. The concentration and isotope ratio ($^{87}Sr/^{86}Sr$) of precipitation also showed a seasonal variation with high in spring, indicating the contribution of salinization minerals mainly of Ca-carbonate in Asian dust.

Throughout a year, the concentrations of Ni, U, Pb, Cs, Sr, Li, Rb, V, Sb, Al, Mn, and Co in the precipitation of the city office site were 1.3 to 3.0 times higher than those in the precipitation at the Jojusha site. For Ga, As, W, Cd, Zn, Ba, Si, and Mo, the enrichment in the city office precipitation were 3.7 to 6.5 times and the enrichment in the city office precipitation were 17 times for Cu. The increase of dissolved elements in the winter precipitation is likely ascribed to the long-range transport from the Asian continent. However, the enrichment of elements in the precipitation at the city office suggests their major source to be the urban area in the Saijo city and/or surrounding Setouchi region. This contention is consistent with the Pb isotope ratios of precipitation at Jojusha, which are indistinguishable from those in aerozols in Japan.

Keywords: precipitation, trace element, Sr isotope, Pb isotope

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

HTT31-P02 Room:Convention Hall Time:May 27 18:15-19:30

Spatiotemporal variations in isotopes of oxygen and hydrogen of precipitation at Saijo city in Ehime prefecture

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The isotopic compositions of oxygen (δ^{18}O) and hydrogen (δD) of wet precipitation provide fundamental information for atmosphere-hydrosphere cycle. Global change of δ^{18}O and δD has relation to meteorological components such as air temperature and precipitation amount. Spatiotemporal information of δ^{18}O and δD of precipitation is important to understand the atmosphere and water cycle in local basin. However, there have been few studies of local basin due to the difficulty of long-term collecting precipitation.

We determined δ^{18}O and δD of monthly wet precipitation at 6 sites in Saijo from November in 2008 to December in 2014 to elucidate the precipitation process in local basin. The isotopic compositions of precipitation were heterogeneity within the investigation area (<several hundreds km^2). This result is assumed to concern the origins and formation processes of clouds and precipitation process. We compared the seasonal variation in the δ^{18}O and δD of precipitation among the different altitude sites.

The inclinations of monthly meteoric line had distinct values, approximately 8, at each site. On the other hand, the values of deuterium excess (d-excess) ranged from 20 to 30 ‰ in winter and from 3 to 10 ‰ in summer. The values of d-excess at Jojusha (1,280 m above sea level) is 3 ~ 10 ‰ higher than those of another sites during spring and autumn. In spring, the values of d-excess at Jojusha showed higher and the δ^{18}O and δD had 3 ‰ and 20 ‰ lower than those of precipitation at the lowest altitude site (20 m on the roof of city office), respectively. On the other hand, during summer and early autumn, the δ^{18}O and δD of precipitation at Jojusha had 1 ‰ and less than 10 ‰ lower than those at the city office, respectively. These results indicate that the isotopic compositions of precipitation in Saijyo had obviously seasonal variations. Re-vaporized vapor generate precipitation including higher values of d-excess. Therefore, the isotopic signatures of precipitation at Jojusha in spring were ascribed to vapor from evapotranspiration, requiring any more consideration. The precipitation at the city office had low d-excess and high δ^{18}O and δD in winter, suggesting that the re-evaporation effect for condensation of raindrop from clouds.

Keywords: precipitation, oxygen isotope ratio, hydrogen isotope ratio

Japan Geoscience Union Meeting 2015
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HTT31-P03 Room:Convention Hall Time:May 27 18:15-19:30

Estimating source of atmospheric aerosols by Sr and Pb isotopes in Noto peninsula, Japan

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Due to the prevailing high pressure system in the Pacific, it has been generally accepted that the air quality near the ground surface of central Japan is relatively unaffected by the polluted air-mass originating from the continent. However, there is increasing number of observations reporting high $PM_{2.5}$ episodes even in summer periods. With respect to the origin of such high $PM_{2.5}$ episodes, it has been suggested that the polluted continental air-mass may reach the region even in summer especially when certain condition of atmospheric pressure pattern is met. However, it may also be partly explained by the particles originating from domestic volcanoes (e.g. Sakurajima) which are increasingly active in recent years. Therefore, the exact source and contribution responsible for such high $PM_{2.5}$ episodes remain controversial.

Stable isotopes of Sr and Pb are powerful tools for fingerprinting as the source areas because minerals and rocks have distinct isotopic ratios depending on their geological development. Also, these isotopes are relatively unaltered by the weathering, transportation, and deposition. Thus, Sr and Pb isotopes are useful tools to estimate source of atmospheric aerosols. In this study, we present the Sr and Pb isotopic ratios of the aerosols collected in Noto peninsula, Japan in July 2014, in order to identify the sources of atmospheric aerosols.

The sampling site is NOTO Ground-based Research Observatory (NOTOGRO) at 37 ^{0} 45'N, 137 ^{0} 36'E. All of the samples were collected weekly on the roof of a building (about 15 m high) using a High-volume air sampler (AH-600F, SHIBATA) with a constant flow rate of 700 L/min. Only the coarse fraction exceeding 2.5 μm in diameter was collected on a 12.6 $\times$ 16.6 cm^2 SiO_2 filter through an impactor. Filters samples were extracted with 5% HOAc solution. Residual fraction after extraction with HOAc were digested in HF-HCl-HNO_3 solution. Isotopic ratios of Sr and Pb were measured using a Thermo Scientific Neptune multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS).

The HOAc-leachate materials are characterized by low $^{87}Sr/^{86}Sr$ ratios and approach to sea salt value of approximately 0.70918, whereas the HOAc-residue materials have high $^{87}Sr/^{86}Sr$ ratios. In addition, sample of 16 July (collected from 9 to 16 July) have the highest value and similar to values observed in north China which was indicated to be 0.71432 on average (Nakano et al., 2004), providing strong support that the continental air-mass may reach Japan even in the summer season.

Keywords: Sr-Pb isotopes, Sakurajima volcanic eruption, Transboundry air pollution, Air pollution in summer

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Estimation of sulfur dynamics in a small forest catchment by isotopic ratio analysis

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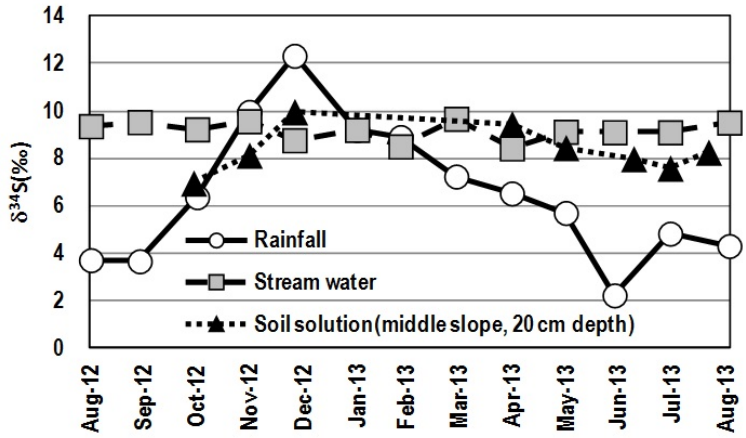
This study is conducted to clarify the dynamics of sulphur derived from atmospheric deposition, by sulphur isotopic analysis.

The study plot was selected in a small catchment of a Japanese ceder forest in Kajikawa, Niigata prefecture, Japan which suffered large amount of deposition from transboundary air pollution. Rainfall, stream water and soil solution were collected from the study site at least once a month. In addition, throughfall and stemflow were also collected. Sulphur isotopic ratio(δ^{34}S) and also water chemicals in these samples were determined.

Seasonal variation of δ^{34}S from Aug. 2012 to Aug. 2013 is shown in Figure. Clear variation is shown in rainfall, but δ^{34}S in stream water is stable at 9 ‰. It suggests that sulphur in rainfall does not directly reach to stream. Sulphur deposition may be retained once in ecosystem and δ^{34}S changed by some processes for example soil adsorption. We'll discuss about the data include throughfall, stemflow and soil solutions in presentation.

The study was supported by the grant from APN (ARCP2013-13CMY-Sase). Authors thank them for their support and cooperation.

Keywords: sulphur isotopic ratio, rainfall, stream water, soil water



Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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Effects of nitrogen-saturated forests on downstream water quality in Fukuoka City

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Nitrogen is often limiting nutrient for plant growth and is mainly supplied from atmosphere. Forests can act as a filter for atmospherically deposited nitrogen and maintain background concentration levels of nitrogen in streams. However, recent increases in atmospheric nitrogen deposition have resulted in a shift from net-nitrogen retention to high levels of net-nitrogen loss from forested, resulting in high nitrogen concentration stream water.

In the Tatara River Basin, Fukuoka City, nitrogen retention capacity of upland forests has decreased and nitrate concentrations in downstream water have been increasing (Chiwa et al., 2012). This study analyzed NO_3^--δ^{15}N, NO_3^--δ18O in addition to NO_3^- concentrations in stream water in the Tatara River Basin to assess the impact of nitrogen saturation forest on downstream water quality.

In northern part of the basin, NO_3^- concentrations of upstream were lower than downstream. In contrast, in southern part of the basin, NO_3^- concentrations in upstream were lower than downstream. NO_3^--δ^{15}N in upstream was significantly lower than downstream in both northern and southern parts of the basin. In contrast, little difference of NO_3^--δ^{18}O was observed between upstream and downstream in both parts. It has been known that the value of δ^{15}N and δ^{18}O ratio due to human wastewater is 10 to 20 ‰ and -5 to 7 ‰, respectively (Kendall and others, 1995). Therefore, the different trends in NO_3^- concentrations from upstream to downstream between two parts could be caused by different amounts of human sewage to the downstream between two parts.

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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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Effect of atmospheric deposition to alpine ecosystem in Mt. Tateyama

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Forest soils are often produced by the weathering products of bedrock and litter supplied from the forest, but in which the influence of the substance supply by air deposition is not much considered. However, the strong influence of the monsoon brings many rain and snow in Japan, and leaching from plant and soil is prevailing. Therefore, the influence of bedrock is directly observed limited on the outstanding region serpentine and limestone, geomorphic elements such as slope direction, inclination and position on the slope are major impact on plants growth and distribution. This suggests that atmospheric deposition is significant impacts on the nutrient circulation in places other than the valley and plains the sediment from the top is supplied. In particular, the main nutrient flows source on the vicinity of the ridge line of the mountainous areas is only to wet and dry deposition, so it is considered to be able to understand the actual condition of the nutrient circulating in the alpine ecosystem by assessing atmospheric deposition.

Result of observation of material dynamics on canopy of *Pinus pumila* Regal in Jodo-daira (2839m a. s. l.) in Chubu-Sangaku mountainous area in central Japan, P. pumila uptakes ~70% of inorganic nitrogen supplied from rain and fog adhering to the needle surface. In addition, considerable amounts of potassium (K^+) and magnesium (Mg^{2+}) ions are supplied to the soil as throughfall, which was derived from canopy leaching. The $^{87}Sr/^{86}Sr$ ratio of groundwater and surface water are almost identical to that of soil and bed rock, suggesting that Sr in the surface and ground water is largely derived bedrock through chemical weathering. The $^{87}Sr/^{86}Sr$ ratio of forest rain of *P. pumila* is 0.70934, and similar to rain and sea water value. The ratio of leaf and branch of *P. pumila* are different from surface water and bedrock, and similar to yellow sand dust. The most notable feature is that *P. pumila* has high $^{87}Sr/^{86}Sr$ ratios. Most small alpine plants have lower $^{87}Sr/^{86}Sr$ ratios.

In order to examine the nutrient circulation changes in each forest types at different altitude in Tateyama, we measured chemical properties of forest rain and $^{87}Sr/^{86}Sr$ ratio of shoot and litter and surface horizon soil at Bijo-daira (*Cryptomeria japonica*, 977m a. s. l.) , Buna-daira (*Fagus crenata*, 1200m a. s. l.), and Midaga-hara (*Abies mariesii* forest, 1930m a. s. l.). $^{87}Sr/^{86}Sr$ of *C. japonic*a and *A. mariesii* leaves, branches, litter and forest rain are close to rain, but F. crenata leaves and forest rains are almost the same as the value of the yellow sand dust. Results of ion analyses suggested the existence of interaction between canopy and rain in any type of canopies. A large amount of K^+ leaching has occurred in the *F. crenata* forest and calcium (Ca^{2+}) leaching has occurred in the A. mariessi forest. In addition, the values of $^{87}Sr/^{86}Sr$ in the surface horizon soil of any soils closed to the value of yellow sand dust.

These results suggested that in any of the forest stand in Tateyama, ion supply from atmosphere forms a main body of material circulation, the influence of the bedrock is very small, and also yellow sand dust has become an important cation source, nutrients such as Ca^{2+} supplied to the forest floor salts, to form a nutrient pool in root zone containing litter, and nutrients are used by circulating to resorption by root.

Keywords: Asian dust, Alpine, Sr isotope, plant ecophysiology, Forest hydrology, material cycle

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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Distribution of chemical and isotopic components in the stream water of Otsuchi town, northeastern Japan

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Otsuchi town in Iwate prefecture, northeastern Japan, was totally devastated by giant tsunami on March 11, 2011. This town is mainly composed of watersheds with three rivers (Otsuchi, Kozuchi, and Unosumai rivers) flowing into the Otsuchi Bay. The coastal plain area is small, but it is rich in groundwater of good quality and has been used for daily lives and industries such as Japanese sake, Tofu, and salmon hatchery. The wise use of this groundwater is expected to play an important role toward the rehabilitation of this town. In order to get basic information regarding the recharge area and flow system of the groundwater, we collected river water samples at about 200 sites in the tributaries and main streams of the three rivers and determined their chemical compositions and isotopic ratios. The distribution of water quality component was analyzed using ARC-GIS software.

The δD and δ^{18}O values of tributaries tend to decrease, whereas the excess-deuterium (d) value tends to increase, with the distance from the coast and/or elevation. The value of δD is expressed as $7\delta^{18}$O+5, showing the small evaporation of atmospheric precipitation. Accordingly, the high d-value in inland, mountainous area seems to suggest the high input of winter snow or re-precipitation of water vapor evaporated from the watershed area. The concentration of Cl, Na, Mg, and B tends to decrease along with the hydrogen and oxygen isotope ratios, indicating the decrease of sea-salt particles toward the inland atmosphere.

The watershed geology is composed of granite of Cretaceous age and sedimentary rocks of sandstone and shale in the Paleozoic to Mesozoic age. Sedimentary rocks contain chert blocks in the vicinity of the coastal area and basaltic rocks in the inland area. The strontium isotope ratio (^{87}Sr/^{86}Sr) of tributary water is correspondent to the distribution of watershed rocks; it is low in granite area (0.705-0.706) and is high in chert-dominant downstream areas (0.709-0.712). The Sr/Ca ratio is also high in the granite area but is low in other areas. This correspondence of water quality and watershed geology demonstrates the major source of Sr and Ca in the water is derived from rocks through chemical weathering. However, the distribution of the concentration of Sr and other elements in the water is not correspondent to the watershed geology, indicating other processes play a role in the chemical composition of water.

Heavy metals such as lead and cadmium in the water are low, indicating a negligible role by human impacts. However, some waters contain arsenic (As) whose concentration is above 2 mgL-1. As there are many abandoned gold deposits in the area, which accompanies As-bearing sulfides, it is likely some As in the water is ascribed to sediments derived from Au deposits.

The chemical and isotopic compositions of main stream are different from those of tributaries due to the mixing of waters. This difference becomes large in the main stream at downstream sites, indicating that the water quality map is based on the river with the same watershed area. Groundwater in the coastal area can be divided into three recharging areas, which are downstream waters of Otsuchi and Kozuchi rivers and small dale waters from Mt. Shiroyama in the west. The quality of the three recharging waters is consistent with the present river water data. In particular, strontium isotope ratios can separate three types' groundwater, demonstrating the usefulness of ^{87}Sr/^{86}Sr as an index of recharging water.

Keywords: Otsuchi town, groundwater, chemical compositions, stable isotopic ratios, Sr isotope

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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The origin of nitrate in river water in Tohoku region based on the nitrogen and oxygen stable isotope ratios

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Nitrogen is one of the most important limiting factors of biological production, and regarded as a major factor of water pollution. Therefore, nitrogen concentration in aquatic environment has been monitored in the past. However, because the components of such environment are non-conservative, changes in these concentrations usually provide insufficient information for clarification of origins and pathways of nitrogen. On the other hand, the nitrogen stable isotope ratio can provide useful information to clarify the dynamics of nitrogen, as it reflects the organism-driven metabolism including uptake, nitrogen fixation, nitrification, and denitrification, as well as having the information related to the origin of these compounds.

Recently, nitrogen pollution assessment using the stable isotope technique has been recognized, as the nitrogen stable isotope ratios of anthropogenic nitrate originating from sewage and fertilizers have a unique range of δ^{15}N values, and a nitrogen removal process such as denitrification increases nitrate nitrogen δ^{15}N. In this study, we determined nitrogen and oxygen isotope ratios of nitrate for 372 river water samples in Iwate and Miyagi prefectures to examine the origin of nitrogen and environment of rivers.

Nitrogen isotope ratios tended to be high in urban and agricultural areas and low in mountain areas. These trends are consistent with the empirical knowledge that the nitrogen isotope ratio increases as the anthropogenic impact increases. A few high isotope values were observed in mountainous areas, however, there were some livestock farms up the river of the sampling points. It suggested the waste water from these farms has a significant influence on river water.

Oxygen isotope ratios tended to be high in mountain areas, such as Hayachine and Kurikoma, suggesting that atmospheric deposition (snow) was major source of nitrogen at that areas. High isotope ratios of both nitrogen and oxygen in some agricultural areas suggested the possibility of denitrification.

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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Geochemical maps of river waters in Toyama Prefecture: major and trace element distributions and Sr isotope signatures

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Toyama is located central Japan, and abundant in water resources. To understand river and groundwater quality, water circulation patterns recharged from high-altitude areas, and anthropogenic nitrogen fertilization, major ion chemistry, oxygen and hydrogen isotopes, and nitrogen isotopes of nitrate in river and groundwater have been studied so far. However, trace elements and Sr isotope ($^{87}Sr/^{86}Sr$ ratio) data, that can be used as hydrological tracers, have not yet been studied although such hydrological tracers will provide insight into our comprehensive understanding of (1) water circulation patterns recharged from high-altitude areas and (2) anthropogenic and geological influence on water quality. In this study, we aim to comprehend geographical distributions of major and trace elements and Sr isotopes in river waters through geochemical maps and statistical analysis. River water samples were collected at 76 sites in September?November 2013. The major elements, trace elements, oxygen isotopes of water ($\delta^{18}O$) and $^{87}Sr/^{86}Sr$ were measured by ion chromatograph, sector-field ICP-MS, IR-MS, and TIMS, respectively.

The $^{87}Sr/^{86}Sr$ ratios of river waters varied from 0.70594 to 0.70989. The highest value was obtained in the upper stream of Shogawa, and the lowest value was found in a Tateyama stream. The relatively lower $^{87}Sr/^{86}Sr$ ratios were found in the eastern part of the studied area, Kurobegawa and Jyogannjigawa, where there are input of hot spring waters to rivers. In the western part of the studied area, we found strong correlations between Na^+ and Cl^- and between Cl^- and $\delta^{18}O$, suggesting the influence of the sea salt on river water quality. However, such influence of the sea salt on river water quality cannot be identified from $^{87}Sr/^{86}Sr$ ratio. We will present geochemical maps on 7 major elements, 15 trace elements, DIC, $\delta^{18}O$, and Sr isotopes in a poster session, and discuss water circulation patterns recharged from high-altitude areas and anthropogenic and geologic influence on water quality based on these data set.

Keywords: geochemical map, Sr isotope, trace metal, Toyama, oxygen isotope, river water

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(May 24th - 28th at Makuhari, Chiba, Japan)

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Groundwater flow regime in Kyoto basin estimated from hydrogeochemical characteristics

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[1]Ryosuke Fumita, [2]Koki Kashiwaya, [3]Katsuaki Koike, [4]Yohei Tada, [5]Ki-Cheol Shin, [6]Makoto Taniguchi, [7]Takanori Nakano

Groundwater is valuable water resource used for a variety of uses because it has generally better water quality compared to surface water. Flow velocity of groundwater is slow, so it takes a long time to recover if it receives pollution or water level drop. In order to maintain the quality and quantity of groundwater, management method that enable to use groundwater appropriately. Final goal of this study is development of hydrogeological model that can be used to predict groundwater flow regime with high accuracy. Kyoto basin was selected as study area.

This year, groundwater samples were collected from 19 wells around Katsura River, Uji River, and Kizu River, and pH, oxidation-reduction potential (ORP), electrical conductivity (EC), and dissolved oxygen concentration (DO) were measured on site. The samples were analyzed together with groundwater samples collected by Fumita et al. (2014) from 28 wells around Kamo River and Takanogawa river. for main dissolved ions, hydrogen and oxygen isotopic ratios, and strontium isotope ratio. Principal component analysis (PCA) was applied to the analysis results of the components except for strontium isotope ratio.

The analysis results showed that groundwater from wells in southern region has higher concentration of main dissolved components. From the PCA, it was clear that the eigenvector coefficients of the first principal component were positive except for ORP, DO, and SO_4. In the eigenvector coefficients of the second principal component SO_4, K, and EC were positive, and pH was negative. Additionally, the wells were distributed in different domain in scatter diagram of the first and second principal component, depending on the watershed. The water quality is presumably reflect the differences in the geological features of the watersheds.

In the watershed of Kamo River and Takanogawa River, Fumita et al. (2014) indicated that groundwater is recharged and surface water and groundwater are mixing around the confluence of the two river. Additionally, distribution of underflow water around the Kamo River was implied in downstream area of the confluence. $^{87}Sr/^{86}Sr$ was 0.715 in the most northerly well in the studied wells, and $^{87}Sr/^{86}Sr$ values of groundwater from wells in the east area near from granite body were about 0.712. Each ratio is similar to the values of Tanba formation and granite (Wada, Komatsu, 2010). In addition, the ratios of the samples collected in southern wells were 0.708˜0.709. In this area, groundwater flow from mountains in east is estimated (Kyoto newspaper company, 1983), so it is indicated that the origin of groundwater was different from it of the upstream of the Kamo River.

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Keywords: groundwater flow, geochemistry, principal component analysis, isotope

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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87Sr/86Sr of threespine sticklebacks and water in Otsuchi: Implications for the current habitat range and past movement

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All living organisms have various interactions with surrounding organisms and their physical environment. For conservation and management purposes, it is important to understand the environmental condition not only in the present but also in the past. Strontium isotope ratio ($^{87}Sr/^{86}Sr$), often measured in otoliths of a fish, has been used as an indicator to estimate current habitat range and past movement of the fish. The method is based on two assumptions. 1, $^{87}Sr/^{86}Sr$ of a fish is almost the same as that of the ambient water. 2, $^{87}Sr/^{86}Sr$ of river water is characterized by the underlying bedrock geology. If there are significant differences among $^{87}Sr/^{86}Sr$ of the habitats in the study area, it is possible to estimate the past movement of a fish. However, the method cannot be used when there are no significant differences within the area. Wide study area potentially provides high probability that there are significant differences of $^{87}Sr/^{86}Sr$ among the habitats, so that most studies using this method subjected fishes that move widely. In this study, we propose to develop the $^{87}Sr/^{86}Sr$ method to reconstruct the movements of a small fish, threespine stickleback (Gasterosteus aculeatus). Japanese marine threespine sticklebacks can be classified into two genetically divergent groups, the Pacific Ocean anadromous form and the Japan Sea anadromous form. In Otsuchi area, Iwate Prefecture, both the Pacific resident freshwater form and the Japan Sea anadromous form of threespine sticklebacks occur, and there are many freshwater habitats including new coastal habitats that were made by a natural disaster of tsunami in 2011. For conservation and ecological understanding of threespine sticklebacks, it is important to know the past movement of the individual fish.

In this study, we analyzed $^{87}Sr/^{86}Sr$ of back bones of the freshwater form threespine sticklebacks and compared with that of ambient water in order to estimate the current habitat range and the past movement. Results and discussions are shown as follows.

1. $^{87}Sr/^{86}Sr$ of ambient water can be grouped into three regions (more than 0.709156, 0.708165~0.709156, and less than 0.708165). The result suggests that there are significant differences among the habitat of threespine sticklebacks in Otsuchi area.
2. There was a significant correlation between 87Sr/86Sr of threespine sticklebacks and that of environmental water in each sampling point. The result indicates that Sr of threespine sticklebacks mainly derived from the environmental water.
3. $^{87}Sr/^{86}Sr$ of threespine sticklebacks can be grouped into three regions as well as the ambient water. The result suggests that threespine sticklebacks moved only within each region.
4. There were significant differences between $^{87}Sr/^{86}Sr$ of threespine sticklebacks and that of the ambient water in each sampling point. The result implies that threespine sticklebacks moved among sampling points within each region. However, the detected differences were small, and the temporal changes of water $^{87}Sr/^{86}Sr$ need to be studied.
5. In the coastal area, $^{87}Sr/^{86}Sr$ of threespine sticklebacks was higher than that of the ambient water, probably because the water was affected by the sea water ($^{87}Sr/^{86}Sr$ = 0.70918) at high tide. However, there was a significant positive correlation between them. The result suggests that although these sampling points were expected to have connected with each other at the flood, threespine sticklebacks did not move among the points frequently.

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

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Stable isotope analysis of food-web system in subarctic to subtropical region of western North Pacific

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Carbon and nitrogen isotope ratios of biota are controlled by two factors, a metabolic system and a life style of predator and a regional variability of environmental parameters on food-web system. To evaluate the environmental factors (*i.e.*, nutrients and temperature) on the basic food-web in marine ecosystem, we studied the seasonal variation of nitrogen and carbon isotope ratios of zooplankton and ambient water in the subarctic site of K2 (47^{o}N, 160^{o}E) and the subtropical one of S1 (30^{o}N, 145^{o}E) in the western Pacific ocean, both of which are JAMSTEC observation site.

Biota were collected in eight depths (0-50, 50-100, 100-150, 150-200, 200-300, 300-500, 500-750, 750-1000m) at both sites using IONESS from February 2010 to July 2011. We also collected water samples from seasonal and vertical (˜1,000m depth) profiles in δ^{15}N (NO_3^+ + NO_2^-) together with zooplankton δ^{15}N at K2 and S1 in special reference to nitrogen cycles. Biota samples were freeze-dried on board immediately after the sampling, and dried one day and delipidated before the analysis. The δ^{15}N and δ^{13}C values of zooplankton ware determined at SI Science and Research Institute for Humanity and Nature, whereas the δ^{15}N ratio of nitrate ions (NO_3^-+NO_2^-) in the water was determined using denitrifying method (Casciotti et al., 2002; Sigman et al., 2001) at Tokyo University of Agriculture and Technology and the University of California, Davis.

The δ^{15}N and δ^{13}C values of amphipods and copepod, omnivorous zooplankton in the surface ocean, showed a large seasonal variation. The δ^{15}N values of zooplankton and nitrate ions in the water at the S1 site tended to be lower than those at the K1 site, indicating that the basic food-web is affected by nitrogen fixation. We further compared the trophic fractionation of carbon and nitrogen isotopes ($\Delta\delta^{13}$C, $\Delta\delta^{15}$N) at these two sites statistically with previously databases for food chains in four marine environments of the Antarctic Ocean, gulf of Alaska, Oyashio, and Kuroshio. It is observed that a simple relationship exists in the $\Delta\delta^{15}$N/$\Delta\delta^{13}$C regardless of species and ecosystems. This result demonstrates that the $\Delta\delta^{15}$N/$\Delta\delta^{13}$C, which is an isotope fractionation in the baiting process of food-web system, is determined by energy metabolism mainly driven by amino-acids and decarbonation. This contention suggests an unified regularity is maintained in the lower to higher trophic level in the marine ecosystem.

Keywords: nitrogen stable isotope, carbon stable isotope, food web, isotope fractionation

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Carbon isotope ratios of human tooth enamel record the evidence of terrestrial resource diet during the Jomon period

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Archaeological remains strongly suggest that the Holocene Japanese hunter-gatherers, the Jomon people, utilized terrestrial plants as their primary food source. However, carbon and nitrogen isotope analysis of bone collagen indicates that they primarily exploited marine resources. We hypothesize that this inconsistency stems from the route of protein synthesis and the different proportions of protein-derived carbon in tooth enamel versus bone collagen. Carbon isotope ratios from bone collagen reflect that of dietary protein and may provide a biased signal of diet, whereas isotope ratios from tooth enamel reflect the integrated diet from all macronutrients (carbohydrates, lipids, and proteins). In order to evaluate the differences in inferred diet between the archaeological evidence and bone collagen isotope data, this study investigated carbon isotopes in Jomon tooth enamel from four coastal sites of the Middle to Late-Final Jomon period (5000-2300 years BP). Carbon isotope ratios of human teeth are as depleted as coeval terrestrial mammals, suggesting that C_3 plants and terrestrial mammals were major dietary resources for the Jomon people. Dietary dependence on marine resources calculated from enamel was significantly lower than that calculated from bone collagen. The discrepancy in isotopic ratios between enamel and collagen and the nitrogen isotope ratio in collagen shows a negative correlation on individual and population levels, suggesting diets with variable proportions of terrestrial and marine resources. This study highlights the usefulness of coupling tooth enamel and bone collagen in carbon isotopic studies to reconstruct prehistoric human diet.

Keywords: diet, collagen, enamel, human, Holocene

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Estimation of groundwater flow at northern part of Mt. Bandai using the stable isotopes

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The Mt. Bandai which is an active volcano of the Quality period is located at Fukushima prefecture. There is a lot of groundwater storage in the mountain, because of volcanic geological permeable geology. The groundwater flow system at the northern part of Mt. Bandai has not been obvious. Then, the objective this study is to make clear the groundwater flow at the northern part of Mt. Bandai with using the water quality and stable isotopes.

As a result of the field observation and analysis of water chemistry and stable isotopes in spring water, river water and lake water, the following things became clear. 1) The EC and pH values has a negative correlation. 2) The water quality of lake water and spring water which are located near the Lake Akanuma are affected by the volcanic gas. 3) The Goshikinuma Lakes can be divided into some groups by the water quality. 4) It is considered that the spring water near the Lake Bentennuma is recharged near the Lake Akanuma. 5) The water quality of Lake Akanuma and neighboring lakes show the Ca-SO_4 type, and their dissolved amounts are very high. 6) The Goshikinuma Lakes show the Ca-(Cl+SO_4) type. 7) As a result of stable isotopes of Lake Akanuma, spring water and groundwater in the slope of northern part of Mt. Bandai, it is estimated that there is the same groundwater flow from Lake Akanuma to Goshikinuma Lakes.

Keywords: northern part of Me. Bandai, groundwater flow, stable isotopes

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Mixing processes between river water and acidic hot spring water in Shibukuro-Tama river

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In the Shibukuro and Tama River system, Akita, river water is acidified by inflow of acidic hot spring water (pH=1.2, T=98 ℃). 80% of hot spring water is fed into a neutralization plant and neutralized with limestone. The effluent is released into the Shibukuro River. Sulfur isotopic ratio of Tamagawa hot spring water is 31.8 ‰, and Sr isotopic ratio of the neutralized effluent is 0.7068. These higher isotopic ratios and lower ratio of river water as well as the chemical composition of dissolved components lead to understanding of mixing process of confluent river water. The mixing ratio of waste water with Shibukuro River water was estimated 1 to 1, and at the confluence of Shibukuro and Tama Rivers the mixing ratio of these two was estimated 3 to 7 or 4 to 6. These mixing ratios were consistent with those obtained from the concentrations of dissolved chemical components. These consistent mixing ratios suggest that the chemical composition of river water was mainly controlled by the mixing of the waste water and the tributary river waters, and the influence of precipitation of insoluble salts was negligible. The contribution of the waste water was about 10% at Tose located down the confluence of Shibukuro and Tama Rivers.

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S, H, O and Sr isotopic Study of precipitation in Chugoku district

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Monthly precipitations at 7 sampling points along Tottori-Okayama line in the Chugoku district have been collected in order to reveal regional impact, and seasonal and secular change of cross border pollution from mainland China. We report here the results during January 2011 and August 2014. Major dissolved species, hydrogen and oxygen isotope ratios of water, sulfur isotope ratios of sulfate ion, and strontium isotope ratios were measured after filtration by 0.45um membrane filter.

On the Sea of Japan side, sulfur isotope ratio of non-sea salt sulfate is high in winter and low in summer. High sulfur isotope ratio indicates the contribution of sulfate originated from northern China, cross border pollution. Constancy of this high sulfur isotope ratio in winters during study years suggests no change in the source of pollution. In summer of 2013, high sulfur isotope ratio of sulfate was found. It is probably due to the washout of sulfate of high sulfur isotope ratio by heavy rains in this summer, and is local phenomenon.

On the Seto Inland Sea side, no seasonal change in sulfur isotope ratio of sulfate was found and sulfur isotope ratio of non-sea salt sulfate is lower than that on the Sea of Japan side. This indicates that sulfate with high sulfur isotope ratio originated from mainland China is largely removed before crossing the Chugoku Mountains.

The deuterium excess in both of the Sea of Japan and the Seto Inland Sea sides is high in winter season and low in summer. It indicates that water vapor responsible for winter precipitation is provided from the Sea of Japan in both sides, and that the water vapor responsible for summer precipitation is from the Pacific Ocean. In winter at the Seto Inland Sea side, though water vapor from the Sea of Japan is responsible for precipitation, no signature of sulfate with high sulfur isotope ratio originated from main land China is found. This indicates that sulfate originated from mainland China is mainly removed in the process of the precipitation/snowfall in the Sea of Japan side.

Sr isotope ratio measured at Yurihama close to the Sea of Japan shows clear seasonal variation. In April, May, and June it is higher than that of seawater, and in July and August it is lower than that of seawater. It is almost equal to that of seawater in other months. High Sr isotope ratio in spring is due to the soluble component of yellow sand brought from mainland China and low Sr isotope ratio in autumn and winter is mainly influenced by sea salt. The timing of change in sulfur isotopic ratio of sulfate does not agree with that in Sr isotope ratio, indicating the transport process of sulfate and yellow sand are independent of each other.

Keywords: cross- border pollution, precipitation, sulfur isotope ratio, hydrogen isotope ratio, oxygen isotope ratio, strontium isotope ratio

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Compositions of Mesopotamian tablet clay for identification of source area

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Clay tablets are excavated from all over Mesopotamia and some contain date of issue. Thus, if we can decode information on paleo-environment from grains and microfossils included in the tablet clay, the use of the clay tablet wold be greatly widen. However, many tablets are stored in the museums in West Asia without any information of the excavated sites. In this paper, we report results of compositional analyses on the tablet clay using material stored in the Slemani Museum, Iraq, aiming to understand where they were made.

Keywords: clay tablet, composition, isotope

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

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A detailed geochemical and isotopic analyses of water samples collected from the Asahi River (197 samples at 140 points), Yoshii River (180 samples at 118 points), and Takahashi River systems (62 samples at 62 points) of the Okayama Prefecture, Japan were undertaken. Samples were collected during March 2011 to November 2014. In several locations, samples were collected periodically in order to monitor the long-term fluctuation of the geochemical properties.

The result of this study shows that the deuterium excess (DE) is high in the upstream ($>$20) and gradually decreases towards the downstream ($<$12). This is interpreted to be the result of different air mass contributing to the meteoric water of different locations. Seasonal variation at a specific location was approximately 3˜4 ‰.

Sr isotopic signature of the river water is generally low in the northern region where the Quaternary volcanic rocks and Cretaceous granitic rocks are exposed, and high in the regions where the Carboniferous to Jurassic sedimentary rocks are exposed. Geographical variation in the Sr isotope ratio seems to correlate well with the change in the type of rocks exposed in the river basin.

The concentration of SO_4 increases towards the downstream. This is accompanied by shift in $\delta^{34}S$ towards ˜0 ‰. This may be a result of human activities such as decomposition of fertilizers used in agricultural activities.

Keywords: Geochemical map, Okayama Prefecture

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Geochemical comparison of adsorped elements on sediments with dissolved ones in the river waters of Tohoku area

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River sediment adsorbs many elements on its surface, which is considered to affect the chemical composition of the river water. However, there are few studies regarding the geochemical relationship between the sediment and the water in the river system.

To evaluate the role of the adsorbed elements on the geochemical properties of fresh water, we sampled sediments and waters at 342 sites in the rivers of Iwate and Miyagi prefectures of northeastern Japan. Approximately 10g of sediment particles (less than 2 mm) were reacted with 50 ml of 2 mol/L ammonium acetate solution for 2 hours. The solution was subsequently diluted by a factor of 25 using 1% nitric acid, and the concentrations of 51 elements were determined using Agilent7500cx ICP-MS.

The concentration of most elements in adsorped solution (ADS) increased with that of ambient river water (RW), while the adsorption coefficient of ADS to RW (ADS/RW) decreased. This result indicates that sediment has a limitation with respect to the adsorption capacity. The adsorption coefficient of most cations was greater than 1.0, whereas that of anions such as V and B was low. It was particularly high for heavy metals and rare-earth elements, reflecting their strong partitioning on the surface of the sediment. The adsorption coefficient of REEs decreased with the atomic number with positive Ce anomaly and negative Eu anomaly, indicating the REE fractionation in the aquatic system.

As the study area is composed of a variety of rock types, including volcanic to plutonic rocks, and metamorphic to sedimentary ones, the observed result is not attributed to the geological heterogeneity. It is likely that the adsorption of elements on the sediment surface plays a dominant role on the geochemical composition of the river water.

Keywords: river water, sediment, geochemistry

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Analysis of river organic pollution in a low precipitation region based on water isotopes and phytoplankton species

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The river organic pollution was studied in the Shin River in Kagawa Prefecture, Japan. In Kagawa Prefecture, where water resources are scarce, the use of water is efficient and a large proportion of water is retained within the river basin. The retention time of water within the river basin becomes longer and algae increase in water areas represented by irrigation ponds. The dynamics of particulate organic matter (POM) in the Shin River was significantly influenced by the natural and artificial hydrological environment in the river basin. The degree of organic pollution in the Shin River was high and most of the organic matter was algae.

δ^{18}O of water of the middle and lower reaches of the Shin River was high, and it was found that water subjected to evaporation for a long time in the basin flows in the river. The concentration of organic matter in the Shin River increased along with the rise of δ^{18}O, and it was found that algae increased in the stay waters in the basin of the middle?lower reaches and flows in the Shin River. It was thought that the irrigation ponds in the basin were the main sources of water and organic matter for the river. This tendency was notable during the non-irrigation season in that the volume of water in the basin decreased. On the other hand, the proportion of algae in the organic matter in the river decreased when there was much precipitation.

During the non-irrigation season, the number of algal cells increased to 2.3×10^4-7.8×10^4 cells mL^{-1} in accordance with the increase in the concentration in irrigation ponds, and species composition changed to Pseudanabaena sp. as well as irrigation pond. Although Microcystis sp. was also dominant in the middle/lower reaches as well as the irrigation ponds during the irrigation season, cell numbers were lower than in October. In addition, the number of algal cells in the river correlated well with δ^{18}O in the river water; irrigation pond phytoplankton is supplied to rivers when water flows from irrigation ponds to the river. The influence of irrigation ponds on rivers was found to increase during non-irrigation seasons when irrigation water is scarce and precipitation is low, and so the quantity of river water decreases.

This study found that water supplied from such areas accounted for a large proportion of river water, causing organic pollution of the river by algae. It also found that this trend became stronger during the non-irrigation season when the amount of water in the river basin declined, while the trend became less obvious when precipitation was high. Therefore, to improve the state of organic pollution in the river, the inflow from irrigation ponds must be controlled. It is important to develop a method to reduce the concentration of organic matter in the river by establishing a well-planned water utilization system at a river-basin level with climate conditions and the amount of river water as underlying factors.

Keywords: Water isotopes, Phytoplankton, Organic pollution, River, Kagawa Prefecture

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Measurement of stable boron isotopic composition by MC-ICP-MS

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Boron has two stable isotopes (^{10}B and ^{11}B) and these natural abundances are approximately 19% and 81%, respectively. The stable boron isotopic composition ($^{11}B/^{10}B$) has been used to understand, for example, groundwater contamination and adsorption-desorption mechanism. The isotopic composition has been originally measured by thermal ionization mass spectrometer (TIMS). Recently, a promising new technique by using multi collector type inductively coupled plasma mass spectrometer (MC-ICP-MS) is being proposed. In this study, the measurement condition (boron solution concentration and measurement time, mainly) was optimized by using boron standard material (NIST SRM 951) for establishing accurate and high-precision determination of the stable boron isotopic composition ($^{11}B/^{10}B$) by MC-ICP-MS.

Keywords: boron isotopes, MC-ICP-MS