

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

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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 (⁸⁷Sr/⁸⁶Sr) 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 aerosols in Japan.

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

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 ($\delta^{18}\text{O}$) and hydrogen (δD) of wet precipitation provide fundamental information for atmosphere-hydrosphere cycle. Global change of $\delta^{18}\text{O}$ and δD has relation to meteorological components such as air temperature and precipitation amount. Spatiotemporal information of $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 km²). This result is assumed to concern the origins and formation processes of clouds and precipitation process. We compared the seasonal variation in the $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ and δD in winter, suggesting that the re-evaporation effect for condensation of raindrop from clouds.

Keywords: precipitation, oxygen isotope ratio, hydrogen isotope ratio

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° 45'N, 137° 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 × 16.6 cm² SiO₂ filter through an impactor. Filters samples were extracted with 5% HOAc solution. Residual fraction after extraction with HOAc were digested in HF-HCl-HNO₃ 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 ⁸⁷Sr/⁸⁶Sr ratios and approach to sea salt value of approximately 0.70918, whereas the HOAc-residue materials have high ⁸⁷Sr/⁸⁶Sr 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, Transboundary air pollution, Air pollution in summer

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

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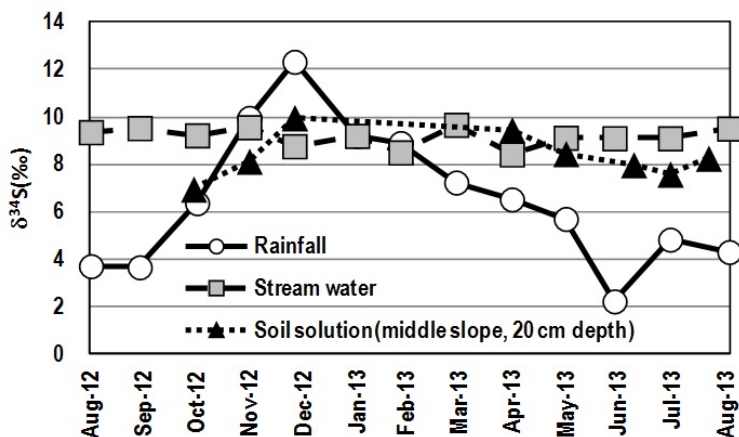
This study is conducted to clarify the dynamics of sulphur derived from atmospheric deposition, by sulphur isotopic analysis.

The study plot was selected in a small catchment of a Japanese cedar 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($\delta^{34}\text{S}$) and also water chemicals in these samples were determined.

Seasonal variation of $\delta^{34}\text{S}$ from Aug. 2012 to Aug. 2013 is shown in Figure. Clear variation is shown in rainfall, but $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ changed by some processes for example soil adsorption. We'll discuss about the data include throughfall, stemflow and soil solutions in presentation.

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



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 Tataru 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^- - $\delta^{15}\text{N}$, NO_3^- - $\delta^{18}\text{O}$ in addition to NO_3^- concentrations in stream water in the Tataru 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^- - $\delta^{15}\text{N}$ in upstream was significantly lower than downstream in both northern and southern parts of the basin. In contrast, little difference of NO_3^- - $\delta^{18}\text{O}$ was observed between upstream and downstream in both parts. It has been known that the value of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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

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 (Mg²⁺) ions are supplied to the soil as throughfall, which was derived from canopy leaching. The ⁸⁷Sr/⁸⁶Sr 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 ⁸⁷Sr/⁸⁶Sr 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 ⁸⁷Sr/⁸⁶Sr ratios. Most small alpine plants have lower ⁸⁷Sr/⁸⁶Sr 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 ⁸⁷Sr/⁸⁶Sr 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.). ⁸⁷Sr/⁸⁶Sr of *C. japonica* 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 (Ca²⁺) leaching has occurred in the *A. mariesii* forest. In addition, the values of ⁸⁷Sr/⁸⁶Sr 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 Ca²⁺ 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

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 $\delta^{18}O$ 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

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 $\delta^{15}\text{N}$ values, and a nitrogen removal process such as denitrification increases nitrate nitrogen $\delta^{15}\text{N}$. 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.

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 ($^{87}\text{Sr}/^{86}\text{Sr}$ 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 ($\delta^{18}\text{O}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ were measured by ion chromatograph, sector-field ICP-MS, IR-MS, and TIMS, respectively.

The $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $\delta^{18}\text{O}$, 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. We will present geochemical maps on 7 major elements, 15 trace elements, DIC, $\delta^{18}\text{O}$, 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

Groundwater flow regime in Kyoto basin estimated from hydrogeochemical characteristics

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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 SO₄. In the eigenvector coefficients of the second principal component SO₄, 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. ⁸⁷Sr/⁸⁶Sr was 0.715 in the most northerly well in the studied wells, and ⁸⁷Sr/⁸⁶Sr 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

$^{87}\text{Sr}/^{86}\text{Sr}$ 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 ($^{87}\text{Sr}/^{86}\text{Sr}$), 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, $^{87}\text{Sr}/^{86}\text{Sr}$ of a fish is almost the same as that of the ambient water. 2, $^{87}\text{Sr}/^{86}\text{Sr}$ of river water is characterized by the underlying bedrock geology. If there are significant differences among $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ among the habitats, so that most studies using this method subjected fishes that move widely. In this study, we propose to develop the $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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. $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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. $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ need to be studied.

5. In the coastal area, $^{87}\text{Sr}/^{86}\text{Sr}$ of threespine sticklebacks was higher than that of the ambient water, probably because the water was affected by the sea water ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70918$) 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.

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°N, 160°E) and the subtropical one of S1 (30°N, 145°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 $\delta^{15}\text{N}$ ($\text{NO}_3^+ + \text{NO}_2^-$) together with zooplankton $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of zooplankton were determined at SI Science and Research Institute for Humanity and Nature, whereas the $\delta^{15}\text{N}$ ratio of nitrate ions ($\text{NO}_3^- + \text{NO}_2^-$) 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 $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of amphipods and copepod, omnivorous zooplankton in the surface ocean, showed a large seasonal variation. The $\delta^{15}\text{N}$ 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 ($\Delta\delta^{13}\text{C}$, $\Delta\delta^{15}\text{N}$) 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 $\Delta\delta^{15}\text{N}/\Delta\delta^{13}\text{C}$ regardless of species and ecosystems. This result demonstrates that the $\Delta\delta^{15}\text{N}/\Delta\delta^{13}\text{C}$, 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 a 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

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 C₃ 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

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 Quaternary 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 of 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 have 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-SO₄ type, and their dissolved amounts are very high. 6) The Goshikinuma Lakes show the Ca-(Cl+SO₄) 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 Mt. Bandai, groundwater flow, stable isotopes

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 °C). 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.

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 mainland 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

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 would be greatly widened. 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

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 $\delta^{34}\text{S}$ towards ~ 0 ‰. This may be a result of human activities such as decomposition of fertilizers used in agricultural activities.

Keywords: Geochemical map, Okayama Prefecture

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

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.

$\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$, 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 $\delta^{18}\text{O}$ 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

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

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Boron has two stable isotopes (¹⁰B and ¹¹B) and these natural abundances are approximately 19% and 81%, respectively. The stable boron isotopic composition (¹¹B/¹⁰B) 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 (¹¹B/¹⁰B) by MC-ICP-MS.

Keywords: boron isotopes, MC-ICP-MS