

Japan Geoscience Union Meeting 2011

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AHW023-01

Room:102

Time:May 25 08:30-08:55

Application of stable isotopes to nitrate contaminated groundwater. Review and prospect

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For a last couple of decades, researches on groundwater contamination by nitrogen have been done intensively and knowledge on identification of sources, contamination processes, natural attenuation or denitrification processes has been accumulated. Since nitrate contaminations are closely related to social conditions besides scientific knowledge, measures against the contamination are still left as a big social concern.

The nitrogen stable isotope has played an important role to identify contaminant sources of chemical and organic fertilizers, livestock manure, and domestic waste, and to investigate contamination processes and natural attenuation processes, but combinations of concentrations and isotope ratios cannot necessarily solve problems.

The author will try to review last 20 years research works, including authors case studies in Numata of Gunma Pref., Sugadaira of Nagano Pref., Miyako Island of Okinawa Pref., Kanekodai of Saitama Pref., Nasunogahara of Tochigi Pref., Kagamigahara of Gifu Pref., Sangawa of Kagawa Pref., and Tsukuba of Ibaraki Pref.. Main focuses are on joint or complementary uses of nitrogen isotope with other isotopes and elements such as oxygen, sulfur and carbon isotopes, chloride, sulfate, and bicarbonate ions, and urobilin, in order to analyze groundwater contamination processes and to solve the problems. Some perspectives are referred.

AHW023-02

Room:102

Time:May 25 08:55-09:20

Nitrate sources and processes of rivers in the Lake Biwa watershed: Synoptic surveys using nitrogen and oxygen isotopes

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In order to clarify the pathways and origins of dissolved nitrate (NO₃⁻) in rivers flowing into Lake Biwa, Japan, three types of scale-coordinated surveys of concentrations and isotope compositions of NO₃⁻ were conducted: (1) synoptic river sampling of 32 representative inflow rivers, (2) two rivers in catchments with different land uses, and (3) intensive samplings in a headwater catchment. The d15N-NO₃ was significantly positively correlated with the population density of each catchment. A mass balance model assuming the d15N-NO₃ and the flow rate of sewage effluent was developed. The model simulated the relationship between the population density and the d15N-NO₃ reasonably well, suggesting that the dominant source contributing to the increase in d15N-NO₃ was the sewage effluent. The spatiotemporal distribution of d18O-NO₃ of rivers, especially in the headwater streams, suggested the possibility of the addition of atmospherically derived NO₃⁻ through precipitation and snow, although the d18O-NO₃ in soil system of forests in the headwater catchment showed the high nitrification potential and replacement of atmospheric NO₃⁻ by the microbially produced NO₃⁻. In general, the d18O of NO₃⁻ in rainwater is remarkably higher than that produced by nitrifying bacteria in soils. Accordingly, the d18O-NO₃ can often be used as an index of the impact of the atmospherically derived NO₃⁻. While soil waters in <20cm depth had a strong signal of the atmospheric NO₃⁻, the d18O-NO₃ in soil water decreased in the deeper soil horizons, indicating that the dominant source of NO₃⁻ in this soil profile was nitrification. The net nitrate production of this soil profile was about 18 kg-N/ha/year, and deposited nitrate was about 6 kg-N/ha/year. Assuming that the annual mean d18O of deposited NO₃⁻ was 60 permil, and the mean value of bacterially produced nitrate in soil was about 0 permil, the average value for soil NO₃⁻ pool could be ~15 permil. However, the observed d18O of the soil and groundwater was 0 to 6 permil and remarkably smaller than the above estimation based on annual mass balance. This suggests that the gross nitrification was sufficiently higher than net nitrification rate, and the major portion of NO₃⁻ produced in soil was reused by microbes. In forest-dominated catchments with natural drainage systems, a slightly elevated d18O-NO₃ signal remained in the stream water even during base flow conditions. This study demonstrated that multi-scale, multi-isotopic investigation is a promising strategy for describing the spatial distribution of NO₃⁻ sources synoptically and is useful for evaluating the influences of land use change. The data set used in this paper is the first comprehensive collection of isotopic composition of NO₃⁻ in rivers of a large-scale basin in Asia.

Keywords: nitrate, stable isotope, river, Lake Biwa, Forest ecosystem

AHW023-03

Room:102

Time:May 25 09:20-09:45

Environmental analysis of various aquatic ecosystems by using ^{13}C and ^{15}N natural abundances

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Natural abundance measurement techniques of stable isotopes have been utilized as an important analytical tool to study material cyclings in biogeochemical research. Nowadays, this technique has become a general research tool for ecological and environmental research fields. Because the natural abundance of stable isotopes change corresponding to the basic processes (i.e. mixing, kinetic reaction, chemical equilibrium) that control material flows, we could conduct the following three kinds of research from the isotopic analysis of the inorganic to organic materials:

- 1) The analysis of the kind of the potential sources and their contribution
- 2) The analysis of the rate limiting reaction and the factors that control the reaction
- 3) The verification on whether the status are in chemical equilibrium or not

Especially, in the environmental research field, the primary way in application of stable isotope techniques continued to be for the analysis of the potential sources and their contribution. For example, food source analysis was general done by the measurement of the isotopic composition (^{13}C , ^{15}N , ^{34}S) at the individual level of some organisms, while the food web structure could be analyzed at the community level. As for the analysis of nitrate isotopic composition (^{15}N , ^{18}O), the origin of nitrate could be revealed.

In my presentation, I would like to show you how powerful the isotope analysis is as a tool by reviewing my field isotope data in various aquatic ecosystems. The following five case studies will be introduced: 1) The diversity in N nutrition among wetland plants in Midorogaike, Kyoto, 2) The difference in food web structure between lotic and lentic ecosystems revealed by comparison between an oxbow lake and a main stream in the Shibetsu Basin, Hokkaido, 3) The food webs fueled by methane derived carbon in the Horonai river, Hokkaido, 4) The relationships between watershed characteristics and ^{15}N abundance in stream nitrate and various organic materials in Shiga, 5) The quantitative estimation of irrigation drainage by running a four source mixing model in Ibaraki.

Isotope mixing models analyzing the kind of potential sources and their contribution can be useful to examine whether river ecosystems are supported by material loading from its watershed or by regenerated compounds within river ecosystems. Because the ^{15}N natural abundance in organic and inorganic materials was roughly explained by the isotope mixing models based on the watershed landuse patterns, Japanese river ecosystems are likely to be supported by the material loading from the watershed in terms of N cycling.

Keywords: isotope mixing model, nitrogen loading, methane food web, wetland, oxbow lake

AHW023-04

Room:102

Time:May 25 09:45-10:00

Groundwater recharge and nitrogen contamination in urban area of the Kathmandu Valley, Nepal

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Groundwater is an important water resource in Kathmandu valley, Nepal. It shares about 50% of the total water supply in the valley. In recent years, there has been a marked expansion in water demand due to population and industrial growth. It has led to heavy consequences on the groundwater levels and well yields, which are being declined (JICA, 1990). And the nitrate has recognized as a major pollutants in shallow groundwater. The objective of this study is to identify the nitrate contaminations under the shallow groundwater hydrology of Kathmandu Valley, Nepal.

The 35 shallow groundwater samples were collected public and domestic wells (depth of well are 5-20m). The nitrate-nitrogen and oxygen isotopes were determined by denitrifer method for the pre-treatment and analyzed using mass spectrometry (Sercon, Cryoprep and Hydra 20-20). And the water-oxygen and hydrogen isotope were analyzed by water equilibration system (Sercon, WES and Hydra 20-20).

The water-oxygen and hydrogen isotope values are suggested that annual rain water could be the primary source of shallow groundwater recharge rather than river water. The nitrate-nitrogen and oxygen isotope values suggested that human waste is the major source of nitrate contaminations in shallow groundwater. Furthermore, the existence of a clear slope between the nitrate nitrogen and oxygen isotope values indicated the occurrence of denitrification process in the shallow groundwater.

Reference:

JICA (Japan International Cooperation Agency): Groundwater management project in the Kathmandu Valley, Final Report to Nepal water supply cooperation, 1990.

Keywords: nitrate-oxygen and nitrogen isotope, water-hydrogen and oxygen isotope, shallow groundwater, nitrate contamination, Kathmandu valley

AHW023-05

Room:102

Time:May 25 10:00-10:15

Denitrification and nitrous oxide production and consumption processes in a groundwater at Kathmandu Valley

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We investigated denitrification and its influence on nitrous oxide production and consumption processes by measuring nitrogen and oxygen isotopes ratio of dissolved nitrous oxide and nitrate, dissolved nitrous oxide concentration and other chemicals in the groundwater at Kathmandu Valley, Nepal. Nitrous oxide productions in a groundwater contaminated by nitrogen compounds were often investigated in the agricultural land. However, there are a few studies about that in urban groundwater. Nitrous oxide productions in the urban groundwater may be important as a nitrous oxide emission pathway in the case that groundwater is used as daily life water and heavily extracted.

Groundwater samples were collected from 36 shallow tube wells and dug wells (2.8-21 m) in Aug. 2009 and Aug. 2010. We collected the samples in a glass vials at plastic bucket filled with the groundwater to prevent gas exchange between groundwater and air. mercury chloride was injected to sample to decrease microbe activity in the sample. Nitrogen and oxygen isotopes of nitrous oxide and nitrate data and dissolved molecular nitrogen data showed nitrous oxide in the groundwater at Kathmandu valley was produced by denitrification or denitrification and nitrification. Moreover, dissolved molecular nitrogen data showed nitrous oxide was strongly reduced to molecular nitrogen by denitrification. Nitrous oxide production, consumption and consequent nitrous oxide concentration was considered to be mainly regulated by nitrate pool size. As the one of this reason, denitrification can easily occur in the groundwater at Kathmandu valley because of high dissolved organic carbon and low dissolved oxygen concentrations.

Keywords: denitrification, nitrous oxide, groundwater, Nepal, isotope

AHW023-06

Room:102

Time:May 25 10:15-10:30

Analysis of indicator bacteria presence affected by hydrologic factors in groundwater of Kathmandu Valley, Nepal

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Microbial contamination routinely causes water-borne diseases in Kathmandu Valley, Nepal (WHO 2007), nevertheless, qualitative & quantitative data still remains insufficient in the central area of the valley (Joshi 2003, Pradhan 2004, Prasai 2007, Warner 2007). The present study aims (i) to survey distribution of faecal indicator bacteria in wells and track the sources and (ii) to identify the microbial community structure for development of water quality assessment & control. 12 deep tube wells, 36 shallow tube wells and dug wells, river and rain waters were investigated during dry and wet seasons of 2008-2010. *E. coli* was detected from most of all wells. River waters showed extremely high levels, however, no clear relation was observed between *E. coli* conc. in any type of GW and distance of wells from adjacent rivers. According to stable isotope analyses, nitrate in river & dug wells probably originated from sewerage. These findings indicate that tube wells were rather protected and dug wells were most vulnerable for faecal contamination at very local scale. Genetic analysis of bacterial communities for deep well samples showed the existence of *Enterobacter*, *Acinetobacter* as well as methane & iron-metabolizing groups which provide information of alternative indicators for understanding the pollution system and controlling groundwater quality in the valley.

Keywords: groundwater, Kathmandu, Nepal, indicator bacteria, stable isotope ratio, hydrologic factor, *Escherichia coli*

AHW023-07

Room:102

Time:May 25 10:45-11:00

Geochemical studies on nitrate in the basin of La Paz city, Bolivia, using ^{15}N , ^{17}O and ^{18}O

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Water resources in La Paz, the capital of Bolivia, are highly dependent on runoff from its surrounding glaciers, since the city locates in a semi-arid area in the Altiplano with an annual precipitation of about 500 mm/y. This study aims at determination of nitrate cycles using its stable isotopic compositions in Tuni Lake and its basin, which is one of the important water resources of La Paz.

Samples are collected from downstream rivers of the glaciers during the dry season in September, 2010. The sampling points were allocated from an edge of the glacier to the inflow point to the lake. Samples were filtered through a 0.2 micro meter pore-size membrane filter and stored in a refrigerator until analysis. To determine the stable isotopic compositions of nitrate, the sample nitrate was chemically converted to nitrous oxide using a method originally developed for $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratios of seawater and freshwater nitrate (McIlvin and Altabet, 2005) with slight modification (Tsunogai et al. 2008). The stable isotopic compositions of nitrous oxide were determined using our Continuous-Flow Isotope Ratio Mass Spectrometry system (Komatsu et al. 2008).

Nitrate in glacial melt water had smaller triple oxygen anomalies (+4.1 permil) relative to those in atmospheric nitrate (from +17 to +35 permil), which corresponds to a mixing ratio of atmospheric nitrate to total nitrate of 12-24%, indicating the significance of non-atmospheric origins of nitrate (e.c. microbial oxidation of ammonium) within the glacier. The triple oxygen anomalies of nitrate in downstream river showed systematic variation among three basins ranging from +0.4 to +3.5 permil. The variation may be attributable to the difference in biological activity among the basins.

Keywords: nitrogen cycle, triple oxygen isotopic compositions, nitrogen isotopic composition, nitrate, Glacial melt water, Bolivia

AHW023-08

Room:102

Time:May 25 11:00-11:15

The relationship between nutrients and pH in lakes as an implication for biogeochemical cycles in continental rivers.

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In the perspective of global biogeochemical cycles, rivers are an important path transporting vast amounts of solids and solutes from land to ocean. Chemical reactions of nutrients via biological activities are likely to have a great impact on pH and carbon cycle in terrestrial water. However, previous researches focusing on this perspective were quite few. As rivers in Japan have relatively short residence time than world rivers, it is difficult to simply compare nutrient cycles in small rivers in Japan with those in large continental rivers. Thus, in this study we focused on biogeochemical cycles of lakes, which have longer and comparable residence time to large rivers in the world.

We measured carbonate chemistry of lake water from Lake Kasumigaura, Tega Marsh and Imba Marsh as typical alkaline lake systems in Japan. We also conducted a detailed survey on lake water and input rivers of Lake Inawashiro, as a representative of acidified lake.

Nutrients played an important role in the variation of pH in both alkaline and acidified lakes. In alkaline lakes, nutrients enhance the activity of photosynthesis and as a result elevate pH of surrounding water. In the acidified lake, precipitation of $\text{Fe}(\text{OH})_3$ during the mixing of acidified river water and lake water removes phosphorus and limits photosynthesis, remaining the low pH in the lake water. In continental rivers which have longer residence time, nutrients may also affect pH and carbon cycle in river water as found in this study.

Keywords: nutrient, pH, lake, river, limnology, biogeochemical cycle

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AHW023-09

Room:102

Time:May 25 11:15-11:30

Chemical properties of spring water from different lithology and the related carbon cycle

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The earth's surface environment is determined by the interaction of the atmosphere, the ocean and the land. The river plays an important role on controlling ocean chemistry by chemical weathering. The transportation of dissolved material and particles chemical by the river is one of essential components to the ocean chemistry through the geological time scale. The research field in this study is Fukushima Prefecture, Ibaraki Prefecture, and Shizuoka Prefecture. According to surface geological map, I got spring water samples from the catchment of several lithologies, andesite, basalt, granite, granodiorite, gabbro, mafic metamorphic rock, limestone, and the sedimentary rock. 25 samples were collected. This water quality characteristic of 25 samples could be divided into three groups: Ca-HCO₃ type, Na-HCO₃ type, and Ca-(SO₄+NO₃) type. The alkalinity in ground water is an index that shows the level of the progress of chemical weathering. High alkalinity provides a good proxy for the degree of the reaction with more minerals. The alkalinity was associated with high concentration of calcium ion.

AHW023-10

Room:102

Time:May 25 11:30-11:45

Soil organic carbon redistribution in Japanese cypress (Hinoki) using radionuclides

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The forest cover of Japan (68%) is ranked among the highest of all nations, and its plantations, among the largest, are composed mainly of conifers (41%) dominated by hinoki and sugi tree species located in steep mountainous area. Given the huge carbon stores in this considerable land cover and the significance of the forest soil as a path in global carbon networks, understanding soil organic carbon (SOC) flux in forested areas is essential. We evaluated the potential of $\{^{210}\text{Pb}_{ex}\}$ and $\{^{137}\text{Cs}\}$ to assess SOC and soil erosion in hillslope forested area. Consequently, findings demonstrated a strong correlation between SOC and both radionuclides. But $\{^{210}\text{Pb}_{ex}\}$ showed a superior relation due to its chemical advantage to the cation exchanging site of the soil fabric. Using DM model, net soil and SOC loss of 0.7 ± 0.8 (SOC loss: 0.13 ± 0.16) and 1 ± 0.4 (SOC loss: 0.2 ± 0.08) $\text{t ha}^{-1}\text{y}^{-1}$ have been estimated based on $\{^{137}\text{Cs}\}$ and $\{^{210}\text{Pb}_{ex}\}$, respectively. In conclusion, due to strong relationship with SOC, natural and continues fallout nature and the presence of considerable concentration in the litter, $\{^{210}\text{Pb}_{ex}\}$ could be an alternative independent tracer to study SOC redistribution rate in forested hillslope starting from the very beginning of litter fall than $\{^{137}\text{Cs}\}$. This study contributes to efforts in developing a model to quantify water induced soil and SOC redistribution using $\{^{210}\text{Pb}_{ex}\}$ in forested area as a part of endeavor to credit and mitigate carbon-induced climate tribulations.

Keywords: Soil, SOC, radionuclide, redistribution, $\{^{137}\text{Cs}\}$, $\{^{210}\text{Pb}_{ex}\}$

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AHW023-11

Room:102

Time:May 25 11:45-12:00

Spatial distribution of atmospheric SF₆ mixing ratios in Japan: Implications for ground-water dating

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Sulfur hexafluoride (SF₆) is a promising transient tracer for young groundwater dating, but elevated levels of atmospheric SF₆ may limit application of this dating method in urban areas. To determine the magnitude of this limitation within Japan, we measured the atmospheric SF₆ mixing ratios around Nagoya and Tokyo.

Keywords: Sulfur hexafluoride, atmospheric mixing ratio, urban area, Japan, groundwater age

AHW023-12

Room:102

Time:May 25 12:00-12:15

Study on the origin of He and non-anthropogenic sulfur hexafluoride in groundwater in the Nakano-shima Island, Oki Dozen

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1. Introduction

Sulfur hexafluoride (SF₆) has been produced industrially since 1950s, and used as a tracer for dating young groundwater. In addition, SF₆ is known to be trapped in silicic igneous rocks with high concentration, and is also estimated to be contained in deep fluid (Busenberg and Plummer, 2000). High concentrations of SF₆ in groundwater in the Nakano-shima Island, Oki-dozen, were observed, and it was suggested that the geogenic SF₆ could be the reason for the high SF₆ concentration. In this paper, we discuss the origin of water, dissolved ³He and SF₆ in groundwater.

2. Method

Water samples were collected from twelve wellsprings and a hot spring well in June 2009, February and September 2010. All samples were analyzed for major dissolved components (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻), CFCs, ³H, SF₆, and stable isotopic ratios of water. Samples from four wellsprings and the hot spring were analyzed for isotopic ratios of He.

3. Results and discussion

3-1. Concentrations of CFCs, ³H, and SF₆

Concentrations of major dissolved components of water samples from deep wells tend to increase, and those of CFCs and ³H tend to decrease. These trends suggest that groundwater of deeper part has longer residence times. CFCs and ³H concentrations of groundwater from two wellsprings, W4 and W7, were much lower than those of other samples. SF₆ concentrations of these samples were higher than that of pond water which is assumed to be saturated with modern air. Considering that CFCs concentrations of these samples were lower, high SF₆ concentrations should be geogenic. It should be noted that the sample obtained from the hot spring showed lower concentrations of both CFCs and SF₆.

3-2. Stable isotopic ratios of water

Delta D and delta ¹⁸O values of groundwater were plotted parallel to the meteoric water line. These of the hot spring and W7 were smaller than other groundwater samples.

3-3. Isotopic ratio of He

Groundwater samples from W4 and W7, containing high concentrations of SF₆, and those from two wellsprings and the hot spring, containing low concentrations of SF₆, were analyzed for He isotopic ratios. ³He/⁴He values of the hot spring and W7 were higher than that of air, suggesting that mantle-derived ³He is added. Other three samples showed ³He/⁴He values close to that of air.

3-4. Origin of groundwater and dissolved gases

Because delta D and delta ¹⁸O values of groundwater were plotted parallel to the meteoric water line, groundwater is considered to be mainly meteoric water origin. Higher ³He/⁴He values of the hot spring and W7 samples indicated that the mantle-derived ³He are added to these samples. delta D and delta ¹⁸O values of magmatic water are estimated to be in the range between -80 and -50 per mill, and +6 and +10 per mill, respectively (Hoefs, 2007). These values are much different from those of groundwater in the island. Therefore, the contribution of magmatic water is considered to be quite small. The hot spring water contains little SF₆ and shows higher ³He/⁴He value than that of air, while groundwater at W4 contains higher concentrations of SF₆ and shows ³He/⁴He value close to that of air. These results suggest that SF₆ added to groundwater of W4 and W7 are not originated from mantle.

4. Summary

Delta D and delta ¹⁸O values of groundwater suggest that groundwater is mainly originated from meteoric water. Higher ³He/⁴He values of the hot spring and W7 indicated that mantle-derived ³He is added to groundwater. As the hot spring water

contains low concentration of SF₆, and W4 shows low ³He/⁴He value and high concentrations of SF₆. SF₆ added to groundwater in W4 and W7 is considered not to be originated from mantle. Identifying the origin of added SF₆ also needs further consideration by analyzing concentration of SF₆ trapped in rocks in the island.

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AHW023-13

Room:102

Time:May 25 12:15-12:30

Using tritium (^3H) and sulfur hexafluoride (SF_6) to estimate groundwater residence times around the Angkor's ruins

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Tritium (^3H) and sulfur hexafluoride (SF_6) provide a technique for dating young groundwater with a residence times less than 60 y. We applied these traces to estimate groundwater dating around the Angkor ruins. The tritium and SF_6 based groundwater ages showed clear areal variations in which residence times are relatively short (<20 y) in north area (Angkor ruins area) and long (20 to 40 y) in south area (Tonle Sap area). The increase of groundwater age from the north to the south is congruent with the distribution of the water table. However, the water chemistry of groundwater was quite different between the north and the south areas, suggesting that the groundwaters of both areas are maintained from the different groundwater flow system.

Keywords: Tritium, Sulfur hexafluoride, Groundwater age, Angkor's ruins

AHW023-14

Room:102

Time:May 25 12:30-12:45

Age dating of spring and groundwater and its modeling in Mt. Tsukuba, central Japan

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To estimate the spring and groundwater residence time and to understand the surrounding groundwater flow system, the multi-tracer approaches using CFCs and stable isotope, and numerical modeling were applied to Mt. Tsukuba. From September 2009 to June 2010, field survey was conducted every 3 months, for spring and groundwater. Residence time and recharge elevation were respectively estimated from dissolved CFCs concentration and oxygen stable isotope. Using Visual MODFLOW, distribution of groundwater potential was estimated and particle tracing method computed the flow line and residence time. These values were compared with the estimated results derived from tracers. Parameters such as hydraulic conductivity were calibrated by trial and error, thus we tried to make clear the groundwater flow system.

Water chemistry was almost constant during one year: it means that there is no seasonal change of flow path and residence time. Modeling results show that groundwater level is up to 500 m and altitude where topography intersects the water table is between 300 m and 400 m. The springs located at an altitude more than 300 m show a residence time ranging from 1 to 10 years, whereas springs and groundwater located at the altitude less than 300 m show an estimated residence time, ranging from 20 to 40 years. In the gabbro catchment at the upper part of the mountain, groundwater is characterized by an almost vertical flow type. However, in granite catchment at the lower part of the mountain, groundwater is characterized by a horizontal flow type; that may explain its longer residence time. In the foot of the hillslope, an upward flow is dominant.

Keywords: Mt. Tsukuba, groundwater flow system, residence time, CFCs, numerical model

AHW023-15

Room:102

Time:May 25 14:15-14:30

The characteristics of stable isotopes in precipitation at Japan

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Characteristics of Stable Isotopes in Precipitation over Japan

Spatial distribution and seasonal variabilities of stable isotopes in precipitation over Japan were considered.

The distribution of annual weighted average Oxygen-18 was considered. The Pacific Ocean side (Hachijo, Miyake, Tsukuba, Ryori) were recognized latitude effect. These of d-excess was also considered. D-excess of the Japanese sea side (Toyama, Tottori) were larger than those of Pacific sea side (Ryori, Kanto Plain, Kumamoto etc). This trend is same as previous studies. It is interesting that d-excess of Hachijo and Miyake (located in the Pacific Ocean) were almost same values in the Japanese sea side (Toyama, Tottori).

Seasonal variabilities of Oxygen-18 over Japan were recognized (increasing April and decreasing June). Seasonal variabilities of Oxygen-18 were classified into three types. The first type is summer type; high in summer (from July to August) and low in winter (from December to February). The distribution of summer type was in the Pacific Ocean side (Ryori, Kanto Plain, Kagoshima) and slope and intercept of Local Meteoric Water Line (LMWL) were less than 8 and less than 13, respectively. The second type is winter type; high in winter (from December to February) and low in summer (from June to August). The distribution of winter type was in the Japanese sea side (Toyama, Tottori). Slope and intercept of LMWL in winter type were more than 8, and more than 13, respectively. The third type is unclear seasonal variabilities. Seasonal variabilities of d-excess over Japan were recognized high in winter (from December to January), low in summer (from June to August).

Further study, the distribution of stable isotopes in precipitation will be compared with in shallow groundwater.

Keywords: stable isotopes in precipitation, seasonal variabilities, annual weighted average, LMWL

AHW023-16

Room:102

Time:May 25 14:30-14:45

Proposal method for estimating evaporation rates of water using characteristic of change of oxygen isotopic ratio

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Recently, water shortage is caused by climate change such as Global warming. Therefore, estimation of amount of evaporation for dam, reservoir and irrigation water is important for preservation of water resources.

There are various methods to calculation of the amount of evaporation such as Thornthwaite method (Thornthwaite, 1948), the Penman method (Penman, 1948), etc. The estimation method of evaporation rate using isotopic ratio was made by Allison et al.¹⁾ or Gibson et al.²⁾, etc. from before. However the method included many parameters such as humidity, partition coefficient, oxygen isotopic ratio of vapor, kinetic isotope effect, resistance of diffusion, and so on and then the some parameter is very difficult to estimate. Therefore, estimation method of evaporation rate to calculate from isotope is very difficult because evaporation rate is controlled by many parameters.

The purpose of this study is to develop simple method for estimating evaporation rates of water using oxygen isotopic ratio and to verify which parameter affects isotope ratio change and isotopic separation effectively. Then, we can estimate the isotopic ratio of the residual water when the evaporation rate of water reaches 1%.

In laboratory test, amount of average evaporation of day, temperature, humidity, and saturation deficit were measured and then the relation of isotopic ratio of water and their parameters was analyzed. From the test, negative correlation ($R = -0.84$) between the average humidity and the amount of change of the $\delta^{18}\text{O}$ per rate of unit evaporation was clarified and then the humidity change accompanying seasonal change was clarified to affect apparently the $\delta^{18}\text{O}$ per rate of unit evaporation. With the increase in an evaporation rate, the amount of change of the $\delta^{18}\text{O}$ per rate of unit evaporation with humid change was clarified to decrease.

The amount of evaporation in the Inawashiro lake in Fukushima was estimated from the relation of the amount of change of the $\delta^{18}\text{O}$ per rate of unit evaporation and humidity and the estimated values, 595 mm/year was good agreement with the calculation result of previous research. Therefore, the simple estimation method of this research is effective for estimation of evaporation rate of an actual lake or a pond.

Keywords: water resources, evaporation rates, oxygen isotopic ratio, humidity, lake

AHW023-17

Room:102

Time:May 25 14:45-15:00

Estimation of the springwater origin of Kushiro-moor using oxygen and hydrogen stable isotopic ratios

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Kushiro-moor is the greatest important moor in Japan with a valuable living thing such as endangered plant and inhabits. The Kushiro-moor has some springs, and then even cold winter, river water does not freeze around the spring and *Grus japonensis* can pass the winter. It is reported that the great portion of moor water derived from spring water. Therefore, in order to preserve moor, a wide water cycle including the catchment of spring was necessary.

The purpose of this study was grasping the water cycle of the Kushiro-moor using oxygen and a hydrogen stable isotope ratio. Flow analysis of the groundwater at the Kushiro area was performed using the 3-dimensional advection diffusion analysis software, G-TRAN/3D for Dtransu-3D.

There are some catchment areas for springs in the Kushiro-moor from the analyzed results. The springs with -10.0 permil for $\delta^{18}\text{O}$ along the upper stream of Chiruwatunai river was thought to be derived from areas at the north of 10~20km of the Kushiro-moor estimating from the $\delta^{18}\text{O}$ distribution. The springs with -8.0 permil for $\delta^{18}\text{O}$ along the upper stream of Chiruwatunai river was thought to be derived from areas at the southeast of the Kushiro-moor estimating from the $\delta^{18}\text{O}$ distribution. The springs with -8.5 permil for $\delta^{18}\text{O}$ near the Kirakotan cape was thought to be derived from the Taro lake area at the east of the Kushiro-moor estimating from the $\delta^{18}\text{O}$ distribution.

On the other hand, the spring with -7.0 permil for $\delta^{18}\text{O}$ along the down stream of Chiruwatunai river was found but water with -7.0 permil for $\delta^{18}\text{O}$ outside of the Kushiro-moor was not found. However, river water at the south area of the Kushiro-moor does not reach -7.0 permil but show high $\delta^{18}\text{O}$ values. The groundwater around the Kushiro-moor was estimated to flow into the center of the Kushiro-moor by flow analysis and then west, north and east areas surrounding the Kushiro-moor were thought to be all catchment area for springs. Therefore, the high $\delta^{18}\text{O}$ spring in the Kushiro-moor also was thought to be derived from area at the south of the Kushiro-moor.

Keywords: Oxygen isotopic ratio, Kushiro-moor, Springwater, Flow analysis

AHW023-18

Room:102

Time:May 25 15:00-15:15

Characteristics of water quality at Shiojiri Area, southern part of Matsumoto basin

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Matsumoto basin is located to slightly northward from the center of the Nagano Prefecture and surrounded the mountains (Hida-mountains and Tsukuma mountains). The complex alluvial fan is formed by the Metoba and Susuki river in the east part of the Matsumoto basin. The Matsumoto basin is from 500 to 700 m above sea level. There is some aquifer in the Matsumoto basin and large quantity of groundwater is stored in the basin. The people who live in Matsumoto city have been used the groundwater water or spring water for long period, and now that the water supply facilities is completed people use the groundwater or spring water for drinking water. In this presentation, the objective of this study is make clear the characteristics of water quality and stable isotopes in groundwater and spring water at Shiojiri City which is located to southern part of Matsumoto basin.

The water samples of groundwater and spring water have been samples at 14 sites. The EC value is from 30 to 413 $\mu\text{S}/\text{cm}$. The EC value is relatively low in the mountainous area and relatively high around the Shiojiri station (urban area). And the spring water of the limestone area also shows the high EC value. The pH is from 5.69 to 8.10. The pH is low in the urban area and high in the limestone area. The groundwater or spring water temperature is from 11 to 12 degree, this water temperature is almost corresponding to the annual air temperature in this area.

The water quality compositions of groundwater and spring water show mainly Ca-HCO_3 type. However, Na-HCO_3 type is also shown at deep groundwater samples, it is assumed that the residence time of this groundwater is relatively long. The NO_3 concentration is relatively high in the urban area, so it is considered that the water quality is affected by artificial influence. The stable isotope of oxygen ranges from -11.7 per mill to -11.4 per mill and hydrogen ranges from -84 per mill to -80 per mill. The isotope values in groundwater of Shiojiri area are almost corresponding to those of Matsumoto urban area (yabusaki, 2010). In the future, the investigation and sampling of groundwater and spring water at Shiojiri area will be continued, and finally the groundwater flow system of Matsumoto basin will be clarified.

Keywords: Matsumoto basin, Shiojiri area, water quality, stable isotope

AHW023-19

Room:102

Time:May 25 15:15-15:30

Fundamental study of Understanding the water cycle using oxygen and hydrogen isotopes in the region Shirahama Spring

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1.Introduction

The Shirahama Hot Spring is a famous hot spring at the west coast of the Kii Peninsula and there are many types of hot spring for water chemistry such as bicarbonic acid, chlorine and hydrogen sulfide. Hot springs temperature ranges 40 degrees to 80 degrees. Past, there were artesian flowing wells and at present, most of source of hot spring needs pumping. Although near the Shirahama Hot Spring there is neither volcano nor volcanic activity at present, the temperature of hot spring is high and heat source is not clarified.

A present problem of the Shirahama Hot Spring is decrease of flow rate and flowing pressure of the hot spring and water chemistry changes such as contamination of sea water caused by excess pumping up.

It is important to understand the source and migration of hot spring water in the Shirahama Hot Spring area in order to preserve stable supply of hot spring water. Therefore, in this study, the source and migration of hot spring water were analyzed by oxygen and hydrogen isotopes and water chemistry.

2.Experimental Methodology

Hot spring water was sampled from the Shirahama Hot Spring and the Tsubaki Hot Spring with the type of hydrogen sulfide next to the Shirahama Hot spring along the coast. River water, cold well water and sea water was sampled from the Shirahama area and the Tonda River in side of the Shirahama Hot Spring.

Oxygen and Hydrogen isotope ratios of the sampled water were analyzed by mass spectrometer with equilibrium method between sample water and hydrogen and carbon dioxide gas. In field, EC, pH, ORP and temperature were measured. Soluble substance such as Cl^- , Br^- , SO_4^{2-} , NO_3^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} was measured by ion exchange chromatograph. HCO_3^- concentration was titrated by acid.

3.Results

The relationship between the Oxygen and Hydrogen isotopes for the sampled water shows that all sampled waters were on the Meteoric Water Line.

Hydrogen and oxygen isotope ratios of hot spring water near the shoreline sites were slightly higher than those in the mountains at the Shirahama Hot Spring area.

Chloride ion concentrations in the Hot Spring water, sea water and cold well water increase with hydrogen and oxygen isotope ratios although under the condition of low chloride ion concentration, hydrogen and oxygen isotope ratios were variable. The relation between Chloride ion concentration and hydrogen and oxygen isotope ratios were as follows;

$$\delta D = 0.0019 \cdot \text{Cl}^- - 49.11$$

$$\delta^{18}\text{O} = 0.0003 \cdot \text{Cl}^- - 8.4634$$

As both end points were sea water and cold well water, hot spring water was thought to be mixed water by sea water and cold well water and sea water ratios for the hot spring water in the Shirahama Hot Spring were 1 to 50 %.

Reference list

- 1) URBAN KUBOTA NO.38, pp.42-56, 1999, 9

Keywords: oxygen and hydrogen isotopes, Spring

AHW023-20

Room:102

Time:May 25 15:30-15:45

Role of deep-seated fluid in formation of CO₂-rich springs in the central part of San'in district

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Many CO₂-rich springs are distributed in the central part of San'in district, southwest Japan. It has been assumed that they are affected by volcanic fluid owing to existence of a small-scale Quaternary active volcano (Sambe volcano) at the center of the distribution area. It is expected, however, that deep-seated fluid derived from lower crust contributes to the formation of CO₂-rich springs, because the discharge points of them exist more than 10km away from the Quaternary volcanos. For investigate of the above mentioned details, the geochemical feature and formation process of CO₂-rich (> 250mg/L) thermomineral spring and well waters were discussed.

From the chemical composition of major dissolved solids, CO₂-rich springs are divided into Na-Cl and Na-HCO₃ types. The former is located around the Quaternary volcanos (Mt. Sambe and Oe-Takayama volcanic group) and the latter is located in the Chugoku mountains composed of Paleozoic basement rocks and many granite intrusions. Isotopically, we could not find influence of deep-seated water except for Yodani hot spring (Na-Cl type) slightly shifted for magmatic water on delta-diagram.

To detect the deep-seated fluid contained in CO₂-rich spring waters, a ternary diagram (proposed by Ohsawa et. al., 2010) plotted on relative ratio of chlorine (Cl), lithium (Li) and boron (B), which are conservative components in fluid, were used in this study. All of Water samples were plotted along the B-Li axis between inter-layer dehydrated water of clay minerals (B-rich) and Arima-type brine (Li-rich), which is likely originated from dehydrated water from altered basalts in the Philippine Sea slab. Na-Cl type waters were clustered close to Arima-type brine, while Na-HCO₃ type waters were plotted nearer part of the B-enrichment inter layer water. Difference of Li/B ratio between Na-Cl and Na-HCO₃ types may be related to the originated depth of fluid (Hrajima et. al., 2010). Therefore, Na-Cl type waters with higher Li/B ratio are originated from deeper part of crust (probably lower crust).

Carbon isotope composition of dissolved inorganic carbon in water samples were ranging from -8.7 to -2.4 per mil indicating that deep source CO₂ play a important role for the formation of CO₂-rich springs. The contribution rate of deep source CO₂ in Na-Cl type waters was high compared with that in Na-HCO₃ type ones.

Deep low frequency earthquakes are occurring at about 30km depth beneath the Sambe volcano, where Na-Cl type waters are distributed, and northern part of the Miyoshi city, where Na-HCO₃ type waters are found, indicating that aqueous fluid exist in the lower crust. The fluid in lower crust might be dehydrated (degassed) from solidifying basaltic magma (Kazahaya, 2010). Difference of the geochemical feature of Na-Cl and Na-HCO₃ type waters may be related to the different geological structures which influence the rise of deep-seated fluid in both Quaternary volcanic and non-volcanic area.

Keywords: CO₂-rich spring, isotopes, Cl-B-Li composition, deep source CO₂, deep-seated fluid

AHW023-21

Room:102

Time:May 25 15:45-16:00

Lithium isotopic variation of spring water in the vicinity of Suma fault after 1995 Kobe Earthquake in Japan

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It has been proposed that the island arc deep-crustal fluid has played important role in intra-arc earthquakes (e.g., Iio et al., 2002), although many things, including the relationships between the island arc deep-crustal fluid and slab-derived fluid, have been still unresolved. It has been difficult to identify the nature of deep-crustal fluid based on the geochemical researches using underground water recovered from spring and well, because the deep-crustal fluid is very diluted by surface water during ascending. Lithium (Li), the lightest alkali metal, is a fluid-mobile element having two stable isotopes, ⁷Li/⁶Li, with abundances of 92.5% and 7.5%, respectively. Amount of Li leached from rock to fluid drastically increases with the temperature, and once leached Li is kept in fluid while decreasing temperature (cooling). These features indicate that non-traditional Li isotopic tracer has a great potential to provide new insight on the origin of nature of island arc deep-crustal fluid.

The 1995 Kobe earthquake (M7.2) is one of destructive intra-arc earthquake in the past 100 years. Seismic tomography revealed that deep-crustal fluid was contributed to the initiation of this Kobe earthquake (Zhao et al., 1996). The geochemical results have also demonstrated that chlorine contents of underground water in Kobe area increased from August 1994 to just before the earthquake, January 1995 (Tsunogai and Wakita, 1996). This means that the degree of discharge of the chlorine enriched deep-crustal fluid to the surface was increased with the time before the earthquake. The nature of the deep-crustal fluid involving the earthquake has never been revealed. Then, we have analyzed Li isotopic variation of spring water from Suma Reisen since March 1995. The spring, Suma Reisen, is located in the vicinity of Suma fault in the Rokko-Awaji fault zone, of which southern part moved in 1995 Kobe earthquake. We have also researched the Li isotopic compositions of spring water and river water that were recovered from the area around the Suma fault. Based on these results, we will present the nature of the deep-crustal fluid involving the 1995 Kobe earthquake.

References:

Iio et al., 2002, EPSL 203, 245-253.

Tsunogai and Wakita, 1995, Science 269, 61-63.

Zhao et al., 1996, Science 274, 1891-1894.

Keywords: lithium isotope, geofluid, deep-crustal fluid, Suma fault, Southern Hyogo Earthquake, fault-fluid

AHW023-22

Room:102

Time:May 25 16:00-16:15

Helium isotopes and ^{36}Cl in saline deep groundwater from the Osaka Basin, Southwest Japan

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Isotopic composition and concentration of helium and chlorine in groundwater are a useful indicator for identifying groundwater flow path and estimating a very old groundwater age. Morikawa et al. (2008) investigated the He isotopes in deep groundwater from the Osaka Basin, southwest Japan, in which unusual saline water containing upper mantle-like helium welled out (Especially in Arima and Ishibotoke area). Observed $^3\text{He}/^4\text{He}$ variation in deep groundwater was clearly related with the geological structure. The $^3\text{He}/^4\text{He}$ ratios decrease with increasing distance from the faults. It has been proposed a model that spatial distribution of $^3\text{He}/^4\text{He}$ ratio reflects the movement of fluids through the fault and following dissolution of crustal $^3\text{He}/^4\text{He}$ during groundwater flow. The amount of accumulated $^3\text{He}/^4\text{He}$ corresponds to the age for hundreds of thousands of years.

Chlorine-36 is a radioactive nuclide, which decays with a half-life of 301,000 years and is thus applicable to dating very old groundwater. Another possible application of this isotope is a method using subsurface produced ^{36}Cl to investigate the origin and evolution of saline water.

In this study, we investigated the distribution of $^{36}\text{Cl}/\text{Cl}$ ratio to examine the saline groundwater flow model inferred from the He results. Most of $^{36}\text{Cl}/\text{Cl}$ ratios in the deep groundwaters from the Osaka Basin ($4.1\text{-}25.6 \times 10^{-15}$) are higher than those in Arima-type thermal water and sea water. These high ratios are not due to mixing of modern surface water which contains bomb- ^{36}Cl , but an incorporation of subsurface products of nucleogenic ^{36}Cl during deep groundwater flow, since the data points are significantly plotted above the mixing line between modern meteoric water and Arima-type water. Spatial distribution of these data shows that the $^{36}\text{Cl}/\text{Cl}$ ratios increase straightforward towards the middle part of the basin. This trend is consistent with observed decreasing $^3\text{He}/^4\text{He}$ ratio toward the middle part of the basin. Considering a concurrent change in $^{36}\text{Cl}/\text{Cl}$ and He concentration, increasing $^{36}\text{Cl}/\text{Cl}$ ratio reflects increase of groundwater residence time towards the basin and thus shows groundwater flow direction.

Keywords: groundwater, helium, chlorine-36, groundwater age, Osaka Basin