

Seasonal variations in surface water nitrogen cycle in the western subarctic North Pacific revealed by nitrogen isotope ratios of amino acid from the settling particles

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The nitrogen isotopic composition ($\delta^{15}\text{N}$) of nutrients in the surface ocean transfer to the $\delta^{15}\text{N}$ of phytoplankton, settling particles, and eventually benthic sediment. The $\delta^{15}\text{N}$ of settling particles and sediment can therefore be used to trace the past nitrogenous nutrient environment. Previous observations have revealed that there is an inverse relationship between seasonal $\delta^{15}\text{N}$ and flux of settling particles. In winter at high latitudes, the settling particles have high $\delta^{15}\text{N}$ and low flux as compared with other seasons. In contrast, the surface water nitrate in winter has the lowest $\delta^{15}\text{N}$ in a year due to convective mixing. The winter settling particles should also have the lowest $\delta^{15}\text{N}$, if winter phytoplankton assimilates only nitrate. Previous studies pointed out three reasons why $\delta^{15}\text{N}$ of settling particles from autumn to winter increases despite the decrease in $\delta^{15}\text{N}$ of surface nitrate: (1) the increase in contribution of zooplankton, which have a $\delta^{15}\text{N}$ about 3 ‰ higher than that of phytoplankton; (2) the contribution of old particles most degraded with isotope fractionation in a year; and (3) the winter phytoplankton assimilates not only nitrate but also ammonium, which has higher $\delta^{15}\text{N}$ than nitrate due to nitrification. In this study, to clarify the reason we applied the compound-specific stable isotope analysis of amino acid and a marine nitrogen isotope model. Sediment trap experiment was conducted at 1000 m depth at station K2 (47°N, 160°E) from June 2014 to July 2015. The bulk $\delta^{15}\text{N}$ was determined by a sensitivity-improved EA/IRMS. The $\delta^{15}\text{N}$ of glutamic acid and phenylalanine were determined by GC/C/IRMS. The bulk $\delta^{15}\text{N}$ show relatively low values around 2 ‰ from July to August and increases to 5 ‰ from September to June, which is a typical seasonal variation observed at high latitudes. Surprisingly, the apparent trophic positions of settling particles estimated from the $\delta^{15}\text{N}$ of glutamic acid and phenylalanine are 2.0 ± 0.1 both in summer and winter. This is the first evidence that the winter high- $\delta^{15}\text{N}$ of settling particles does not reflect the increase in contribution of zooplankton. Our model result suggested that the winter high- $\delta^{15}\text{N}$ value of settling particles mainly reflects the winter high- $\delta^{15}\text{N}$ of ammonium due to nitrification, which was strongly supported by the nitrogen isotopic compositions of amino acids.

Keywords: Marine nitrogen cycle, Nitrogen isotope, Marine ecosystem model

Quantitative and qualitative distribution of fluorescent dissolved organic matter in surface waters throughout the Pacific

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Dissolved organic matter (DOM) in the ocean basically originates from marine organisms, i.e., phytoplankton and heterotrophic bacteria exudation, viral cell lysis, protozoan grazing and zooplankton sloppy feeding, and is mainly consumed by heterotrophic bacteria. It has also been well documented that ocean physics together with biological processes shape the basin scale distribution of dissolved organic carbon (DOC) concentration. Thus, distributional patterns of quantity and quality of DOM are possibly related to oceanic ecological provinces such as Longhurst's oceanic provinces that are divided based on the prevailing role of physical forcing as a regulator of phytoplankton distribution. Even though basin scale distribution of DOC concentrations throughout the open ocean has been clarified, qualitative (compositional) distribution of DOM in relation with oceanic ecological provinces has scarcely been reported. Thus, the knowledge regarding with factors controlling the oceanic DOM composition with basin scale is limited.

In this study, we determined quantity and quality of fluorescent DOM (FDOM) in surface waters throughout the Pacific using excitation and emission matrix (EEM) fluorescence spectroscopy combined with parallel factor analysis (PARAFAC). Surface water samples were collected from the North and South Pacific during four Hakuho-MarU cruises (KH-11-10, KH-12-3, KH-13-7, and KH-14-3 cruises). EEM analysis was performed using FluoroMax-4 (Horiba), and PARAFAC was conducted by the drEEM toolbox on MATLAB (MathWorks). EEM-PARAFAC identified two protein-like components and two humic-like components. We clarified spatial distributions regarding with abundance and composition (i.e., ratio of two components) of humic-like as well as protein-like components. In addition, we used cluster analysis for establishing oceanic provinces from FDOM composition. In the presentation, we will present (1) the meridional differences in FDOM abundance and composition throughout the Pacific, and (2) the similarity/difference between Longhurst's oceanic provinces and oceanic provinces determined by FDOM composition.

Keywords: Marine Dissolved Organic Matter, Fluorescent Dissolved Organic Matter, Oceanic Provinces

Influences of carbon and sulfur cycle inside the hypersaline microbial mat on the chemical composition of overlying brine water

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Salinity is one of the most important environmental factors limiting the habitability of the marine organisms. As the seawater evaporates and the salinity increases, unique ecosystem is formed by specific organisms tolerable to substantial fluctuations in osmotic pressure, pH, and redox condition. In particular, microbial mat often formed in shallow hypersaline aquatic environment is known to be densely inhabited by microorganisms such as cyanobacteria, phototrophic and chemotrophic sulfur bacteria, sulfate reducing bacteria, methanogens, and others (e.g. Ollivier et al., 1994). Intensive studies have been made to reveal the biogeochemical processes of these microorganisms and their mutual interactions (e.g. Des Marais, 2003), but only few studies have focused on its effect on the chemical composition of the overlying brine water. In this study, we analyzed brine water collected from the modern saline pan in Trapani, Sicily, to understand the influence of the microbial activity on the overlying brine water with different salinity. Major ion concentrations, DIC (dissolved inorganic carbon) concentration, and its carbon isotopic composition ($\delta^{13}\text{C}_{\text{DIC}}$) were measured on 9 brine water samples with different salinity (38-276). Although intensive carbon fixation by photosynthesis occurs in the ponds where microbial mat is formed (salinity 97-159), corresponding DIC concentration showed little decrease (1250-1000 $\mu\text{mol L}^{-1}$). This may be because mineralization of the fixed carbon by sulfate reduction occurs in the mat, releasing DIC in the brine water (e.g. Des Marais, 2003). This interpretation is supported by the low $\delta^{13}\text{C}_{\text{DIC}}$ value ($\sim -10\%$), because sulfate reduction supplies relatively ^{13}C -depleted DIC. Alternative explanation is the chemically enhanced atmospheric invasion of CO_2 , which can cause considerable depletion in $\delta^{13}\text{C}_{\text{DIC}}$ (Baertschi, 1952; Lazar et al., 1992). By contrast, increase in the $\delta^{13}\text{C}_{\text{DIC}}$ value ($\sim 7.2\%$) is observed in the ponds with higher salinity (>270) where no microbial mat is developing. This may be attributed to non-equilibrium escape of CO_2 due to higher salinity and lower pH (Stiller et al., 1985; Barkan et al., 2001). These results suggest that $\delta^{13}\text{C}_{\text{DIC}}$ of hypersaline environment varies substantially due to both biological and physical processes. Despite the intense sulfate reduction taking place in the mat, variation in SO_4^{2-} concentration follows the ideal seawater evaporation path (Timofeeff et al., 2001). This may be because sulfide originating from the sulfate reduction is re-oxidized biotically by sulfur oxidizing bacteria or abiotically by the oxygen produced by cyanobacteria inhabiting the upper layer (e.g. Oren et al., 2009). Taken together, although DIC and SO_4^{2-} are utilized intensively by the microorganisms in the mat, their content in the brine water are relatively unchanged due to efficient recycling in the mat.

Keywords: hypersaline environment, microbial mat, biogeochemical cycle

Nutrient uptake in river networks controls nitrogen and phosphorus transports along the river-to-ocean continuum

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Riverine transports of organic and inorganic matter from watersheds can be an important flux that supports the downstream and coastal food webs. Recent studies have identified that stream ecosystems uptake and/or mineralize the large amount of river-borne material leaking from terrestrial ecosystems, resulting in the decrease of material transports from land to the ocean. However, the uptake rates of nitrogen and phosphorus in the entire area of a river network from headwater streams to downstream rivers to estuary has remained unknown, especially in mountainous watersheds with high relief, such as watersheds in Japan.

We will present our recent empirical studies in the Fuji River watershed, which show the "basin metabolism" of nitrogen and phosphorus to identify the fate of river-borne material along the land-to-river-to-ocean continuum. Moreover, our study will show the relationship between fluvial geomorphology (e.g., channel size and river network structure) and the riverine transport of nitrogen and phosphorus. We emphasize that physical modifications of river network structure may affect the delivery of nutrients to coastal areas, resulting in change of the strength of land-ocean linkages through riverine nutrient flux.

Assessment of watershed scale nitrogen cycling by hydrochemical modeling

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Nitrogen cycling in terrestrial areas is affecting water quality and ecosystem of aquatic area such as lakes and oceans through rivers. Owing to the intensive researches on nitrogen cycling in each different type of ecosystem, we acquired rich knowledge on nitrogen cycling of each ecosystem. On the other hand, since watershed are composed of many different kinds of ecosystems, nitrogen cycling in a watershed as a complex of these ecosystems is not well quantified. Thus, comprehensive understanding of nitrogen cycling of watersheds by modelling efforts are required. In this study, we attempted to construct hydrochemical model of the Ise Bay watershed to reproduce discharge, TN, and NO₃ concentration. The model is based on SWAT (Soil and Water Assessment Tools) model. As anthropogenic impacts related to both hydrological cycling and nitrogen cycling, agricultural water intake/drainage, and domestic water intake/drainage were considered. In addition, fertilizer input to agricultural lands were also considered. Calibration period and validation period are 2004-2006, and 2007-2009, respectively. As a result of calibration using 2000 times LCS (Latin Cubic Sampling) method, discharge of rivers were reproduced fairly well with NS of 0.6-0.8. In contrast, the calibration result of TN and NO₃ concentration tended to show overestimate values in spite of considering parameter uncertainties. This implies that unimplemented denitrification processes in the model. Through exploring the results, it is indicated that riparian areas, and agricultural drainages might be important spots for denitrification.

Keywords: SWAT, denitrification

Geochemical characteristics of the groundwater in Toyooka basin

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The pH, EC, ORP and major ionic compositions of groundwater at 11 sites in Toyooka basin, Toyooka city of Hyogo prefecture, were determined in order to elucidate their regional and seasonal variations.

The ionic compositions of groundwater in southwestern part of Toyooka basin were same to those of steam water in the Izushi river and other tributaries of the Maruyama river. The depth of wells are shallow, 10-25 m. Their pH and ORP values showed slightly alkaline and oxic environment. EC and ion concentrations, except NO_3^- , were lower than other groundwater. These results indicate that groundwater in the southwestern part of the basin are originated from steam water.

On the other hand, the ionic compositions of groundwater in northeastern part of the basin were enriched in Na^+ and HCO_3^- . The change of ionic compositions of groundwater are ascribed to groundwater flow from south to north.

The groundwater in southeastern part of the basin had high EC and low ORP values. The depth of the well is shallow, 8 m, however, the groundwater sample contained red precipitation, such as Fe oxide, indicating that the environment of the aquifer are anoxic. The concentrations of K^+ , HCO_3^- and Si were higher than another groundwater, suggesting the input of ions during weathering process.

The ionic compositions of groundwater in central part of the basin were enriched in Na^+ , Cl^- and HCO_3^- , and showed the seasonal variations. In this area, land subsidence and lowering of groundwater level occur with the increasing of use for melting snow in winter. These results suggest that the geochemistry of groundwater may show seasonal variation and the saline contamination of groundwater occur in the right bank of the Maruyama river depending on the changing of level of groundwater, although there are some saline spring water leaking along the fault in the left bank of the Maruyama river in previous study.

The ionic composition of groundwater in northern part of the basin was enriched in Na^+ and Cl^- . EC and ion concentrations, except NO_3^- , were higher than other groundwater. These results indicate that the groundwater in this area is derived from the Maruyama river water effected by tidal. In eastern part of the basin, the ionic composition of groundwater was also enriched in Na^+ and Cl^- and their EC and ion concentrations, except NO_3^- , were also high. These results show the existence of fossil seawater in the aquifer in eastern part of the basin.

Gentle landform like hilly area is the spot to produce dissolved Fe

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[Introduction]

Iron is an essential element for plants, and is also a factor limiting primary productivity in some oceanic area. Moreover, Fe can be too short for phytoplankton's growth in some coastal zone (e.g. Hutchin et al., 1994). River is thought to be a main source of Fe to ocean, but there are few researches studying where dissolved Fe is produced in a river basin. The present research aims to examine geographic factors that control the concentration of dissolved Fe in stream with a special focus on reductive environments in a river basin.

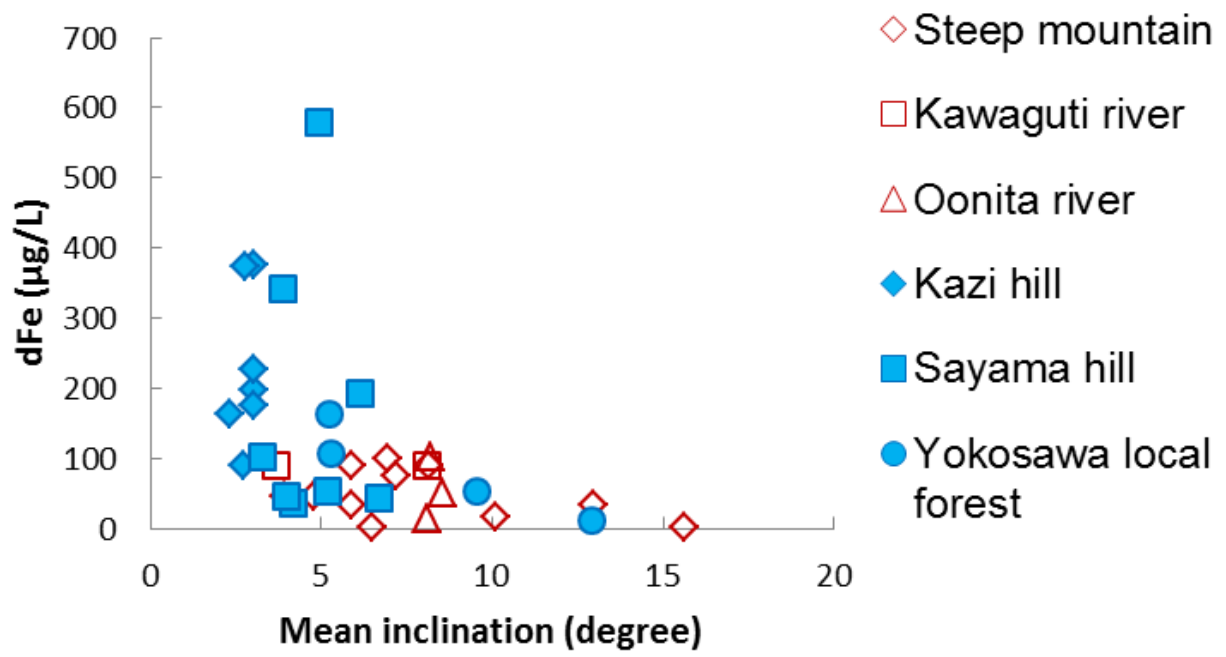
[Methods]

Streams from various landform types including steep mountain and gentle hill were studied, which were located in Hachiouzi-city, Akiruno-city, and Oume-city, Tokyo. In the research here, regions higher than 200m ASL were regarded as mountain and at lower than 200m as hill. Dissolved Fe and dissolved Mn were measured with ICP-AES (Thermo-Fisher iCAP6000). NO_3^- and SO_4^{2-} were measured with ion chromatography (DIONEX DX-120). To examine the influence of geographic factor in catchment area for the dFe concentration, mean inclination of the valley from the sampling spot to 200m upper was calculated with GIS software named QGIS.

[Results and Discussions]

Most of dissolved iron (dFe) concentrations sampled from mountainous area were below 100 $\mu\text{g/L}$. On the other hand those from hilly area were comparatively higher; 200 $\mu\text{g/L}$ and more. Considering the relationship between the mean inclination and dFe concentrations, dFe concentrations tended to be higher with the decrease in the inclination of valley. dMn concentrations also tended to increase in hilly area. NO_3^- concentrations and SO_4^{2-} concentrations were lower at the site high dFe concentrations suggesting denitrification and sulphate reduction in reductive conditions. In short, gentle landform like hilly area creates the reductive environment with a function of producing dFe.

Keywords: Dissolved Iron, Reductive environment



Accurate quantification of atmospheric nitrate in stream water eluted from a small forested watershed using triple oxygen isotopic composition

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Forest ecosystems are deficient in nitrogen in general. Excess loading of nitrogen, however, often leads to "nitrogen saturation" (Aber et al., 1989) in forest ecosystems from which significant quantity of nitrogen is eluted as nitrate. Enrichment of nitrate often caused environmental problems such as degradation of water quality and eutrophication so that we should clarify the origin and behavior of nitrate in stream water, especially for the mixing ratio of unprocessed atmospheric nitrate within total nitrate. The natural stable isotopic compositions of nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) have been widely used to determine the origin and behavior of nitrate in stream water (Durka et al., 1994). Besides to these isotopes, the triple oxygen isotopic compositions of nitrate have been available as an additional, more robust tracer for the unprocessed atmospheric nitrate (e.g. Michalski et al., 2004) in recent years, due to the stability during biological processings on nitrate. In this study, we measured stable isotopic compositions of nitrate in a stream eluted from the Kajikawa experimental forest in Niigata Prefecture. Besides, those in soil solutions were determined as well for comparison. The Kajikawa experimental forest have been characterized by high loading rate of atmospheric nitrogen and the stream water had been enriched in nitrate more than $50 \mu\text{mol L}^{-1}$, so that the forest might be under the nitrogen saturation.

The samples of rainfall, soil solution, and stream water in the study site were collected about once a month since December, 2012 to December, 2014. Nitrate concentrations were measured by ion chromatography. The stable isotopic compositions including the triple oxygen isotopic compositions of dissolved nitrate were determined using Continuous-Flow Isotope Ratio Mass Spectrometry (CF-IRMS) system in Nagoya University (Tsunogai et al., 2010).

Although the triple oxygen isotopic compositions of nitrate in soil solutions showed significant seasonal variation from +0‰ to +6‰, these in stream water samples showed small variation. On the other hand, the concentration-weighted mean of the soil solutions (+0.8‰) was consistent with that of stream water samples (+1.3‰). We conducted that the major source of the stream water was groundwater in the forest, in which seasonal variation in soil solutions had been smoothed. The estimated annual export flux of atmospheric nitrate occupied $9.2 \pm 4.4\%$ of the annual deposition flux of atmospheric nitrate in the study site. Previous study showed that the ratio (i.e. direct elution ratio of atmospheric nitrate within total nitrate) increased in proportion to the forest declined (Durka et al., 1994; Tsunogai et al., 2014; Rose et al., 2015). In particular, the ratio obtained in Kajikawa site coincided with those eluted from the nitrogen saturated forest in West Virginia under the Stage 3. We concluded that the ratio likely reflected the turnover time of nitrate with in the forest soil and thus we can apply the ratio in each forest ecosystem. As a result, we conducted that the triple oxygen isotopic composition can be applicable as the indicator of nitrogen saturation.

Stoddard (1994) proposed that the disappearance of seasonality in the nitrate concentrations in stream water as the indication of nitrogen saturation in forest ecosystems. Mitchell et al. (1997), however, reported that the seasonality in stream nitrate concentrations was already lost in those eluted from normal forest in Japan, so that the seasonality was not a reliable index of nitrogen saturation in Japanese forests. Present study implied that the direct elution ratio of atmospheric

estimated from the triple oxygen isotopic composition can be an alternative index of nitrogen saturation.

Keywords: nitrogen saturation, triple oxygen isotopic composition, forest ecosystem

Nitrogen isotope patterns of trees and soils in two different nitrogen deposition forests

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Anthropogenic nitrogen (N) deposition on forest site is concerning to modify plant species diversity and soil-to-plant N uptake. The N isotope ratio ($\delta^{15}\text{N}$) of soil and foliage reflects nitrogen cycle in the ecosystem and distinct plant N source. To better understand the effects of N deposition to soil N status and plant N uptake, we analyzed N content and $\delta^{15}\text{N}$ of soils and foliage in two different N deposition forests (Mt. Tsukuba: $11.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$, Katsura: $7.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$) in Kanto region. We sampled soil from upper and lower position of the two forest site respectively, and measured extracted inorganic N content and isotope ratio. We also analyzed leaf N content (N%) and $\delta^{15}\text{N}$ values of 30 woody species with different life forms (canopy and understory species). The soil nitrate concentration in Mt. Tsukuba was 25 fold higher than Katsura, and the $\delta^{15}\text{N}$ value was constant through the site ($-2.6 \pm 0.1\%$). While in Katsura, ammonium concentration in soil was high especially in upper slope, but in lower slope dominated nitrate. The foliage N% was high in Mt. Tsukuba than Katsura. The foliage $\delta^{15}\text{N}$ value differed significantly among species in Katsura but in Mt. Tsukuba foliage $\delta^{15}\text{N}$ value showed steady through species and the value corresponded with soil nitrate $\delta^{15}\text{N}$. From these results, N deposition may lead changing soil N status and alter plant N source and uptake.

Keywords: Nitrogen isotope ratio, Nitrogen deposition , Inorganic nitrogen

Long-term nitrogen dynamics in pine forest using ^{15}N tracer

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We investigated the retention of applied nitrogen(N) to vegetation and soil after application of ^{15}N tracer to determine the effects of atmospheric N deposition on the N dynamics in forest ecosystem. Most of previous studies using ^{15}N focused on relatively short duration effect, and it has been reported that microbes in organic layer is the major sink of the ^{15}N . However, it is not clear the long-term effects on N dynamics. This study clarified the ^{15}N retention to vegetation and soil ten years after the ^{15}N application.

We conducted survey in pine (*Pinus densiflora*) forest in Akagi field of Central Research Institute of Electric Power Industry (CRIEPI) in Gunma prefecture, Japan. We established the six plots (4x5m) surrounding each mature pine tree, and applied NH_4Cl solution (50mgN m^{-2}) in added plots (three plots) in 2002. Other three plots were control plots to compare with added plots. We collected boles, branches, leaves, roots 0 layer and soils (0-10, 10-20, 20-40 cm depth) in January 2013. Disks of boles were sampled at a height of 7-15 m and three radical replications were set. Furthermore, we sampled latest 15 years part and divided every five years. We determined delta- ^{15}N by using mass spectrometer.

Delta- ^{15}N of the bole were from -2.0 to -3.3‰ and from -4.7 to -5.3‰ in added and control plots, respectively. Delta- ^{15}N values of the branches, leaves, and roots were also high in added plots. Especially, in roots, delta- ^{15}N value was high (from 9.7 to 10.0‰) compared with from -5.7 to -5.1‰ in control. In the soil, the difference was large in organic layer and surface 10 cm layer. These results suggest applied N was retained in forest ecosystem even ten years after application. We will also discuss the changes of ^{15}N distribution and ^{15}N recovery during ten years.

Keywords: ^{15}N tracer, pine forest, nitrogen deposition

Nitrogen utilization of hinoki cypress at high and low altitude in Kochi

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Hinoki cypress is one of major tree species for timber in Japan. Hinoki cypress is an evergreen conifer which attains leaves in the crown for several years. Leaf longevity of hinoki cypress has shown to be longer in cooler areas. By contrast, evergreen tree species has been dominant in nutrient-poor soil condition and leaf longevity of a single species can vary with soil nutrient condition. We investigated nitrogen utilization of hinoki cypress in relation to soil condition at high and low elevation sites in Kochi prefecture, southern Japan. Nitrogen concentration in fresh leaves or leaf litter was negatively correlated with soil C/N ratio in each area but these relationships were different between two areas. Mean residence time of leaf nitrogen, leaf longevity and nitrogen resorption efficiency was different between two areas but was not related with soil C/N ratio. Leaf nitrogen content per area was related with soil CN ratio and common regression line was obtained for two areas. Because there is a tradeoff between leaf longevity and nitrogen concentration in fresh leaves between two areas, leaf nitrogen content was not different between two areas. Leaf nitrogen content was positively correlated with tree height growth and common regression was obtained for two areas. Therefore leaf nitrogen content is a useful index of nitrogen use by hinoki cypress in wide range of climate condition because it is less affected by mean temperature of the area.

Keywords: hinoki cypress, nitrogen, leaf longevity, altitude

Environmental controls on patterns of plant nitrogen uptake in Canadian permafrost soils

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Plants develop different strategies of nitrogen (N) uptake in response to N limitation. This may explain N supply to plants from N-limited soils and niche differentiation due to soil N levels. To analyze the relationships between N availability and patterns of plant N uptake, plant uptake rates of different N sources (¹³C, ¹⁵N-glutamic acid, ¹⁵N-urea, ¹⁵N-ammonium, ¹⁵N-nitrate) were measured in the field condition. To assess N availability, the concentrations of amino acids, ammonium, and nitrate in soil solution and the mineralization rates of glutamic acid, arginine, ornithine, and urea were studied. We compared four sites in Northwest Territories, Canada; white spruce forest (WSF) at upper slope and black spruce forest (BSS) at lower slope on foothill of glaciofluvial sands, black spruce forest (BSF) and shrub birch tundra (TND) on fluvial sediments. In soil solution, DON was abundant at all sites, but inorganic N was abundant only in TND and BSS. Urea mineralization potentials were consistently high at all sites, except for BSF. This suggests microbial N mineralization is highly limited in N-limited BSF soil. Birch and grass preferentially absorbed inorganic N, while white spruce and black spruce can utilize amino acid-N under N-limited soil to bypass N flow between soil and plants.

Keywords: Soil, Permafrost soil, Amino acid

Damages of the world trees caused by sulfuric acid of the air pollutant

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Air pollutants discharge sulfur oxides in proportion to the emissions of carbon dioxide resulting from combustion of fossil fuels. Sulfur oxides become sulfuric acid and are accumulated in the air unless they fall on the ground with the rain or snow. Sulfate ion was found in the ice core of 1785 in Greenland¹⁾, and the fossil fuel has been burning for 230 years. Sulfuric acid in the air sticks to the trees that stand in the areas where the polar vortex in the Southern Hemisphere and the westerlies in the Northern Hemisphere pass through, and then it is dropped to the ground with the rain. Sulfuric acid transforms the metal component of the soil (Al, Fe) to a soluble compound of sulfate, and the metal ions dissolved in rainwater are absorbed by the trees. Following the principle that coexisting substances become the compound with the strongest bonding power, the metal ions take the phosphoric acid from the phosphate compound in the trees and become an insoluble metal phosphate compound. Trees become the same phenomenon as the shortage of phosphoric acid and decline. Declined trees lose the resistance over damage by blight and harmful insects.

Beech and eucalyptus in Fuego Island in Argentina, at the southern tip of South Island of New Zealand, in Perth in Australia near the polar vortex in the Southern Hemisphere are completely destroyed. The westerlies in the Northern Hemisphere pass Japan and withered conifer and broad leaf trees, then travel beyond the Pacific Ocean and withered conifer trees in the southwest of British Columbia, Canada²⁾. Westerlies that pass through the United States absorb additional sulfuric acid from the thermal power plant near the Great Lakes and withered conifer trees in the Adirondack district in the state of New York and go across the Atlantic Ocean and withered trees in Europe.

When charcoal is sprayed, the acid soil is neutralized with potassium compounds contained in charcoal and metal ions become hydroxides which can no longer be absorbed by trees and the phosphoric acid is protected. Potassium is an essential element of trees and it helps the growing of trees and the weakened trees recover. From this fact, we can prove that the damage of trees is due to the acidification of the soil with sulfuric acid of air pollutants³⁾.

When pines weaken, the amount of pine resin decreases and tannin loses an insect repellent ability when it is combined with metal ions. As a result, it becomes easier for insects to get into trees and increase explosively.³⁾

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Keywords: air pollutant, sulfuric acid, charcoal

Effects of vegetation on soil microbial dynamics in a tropical forest and savanna of eastern Cameroon

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The forest-savanna transition zone is widely distributed on nutrient-poor Oxisols in central Africa. Our previous studies of soil nutrient stock in this area showed that forest is likely N rich and P limited ecosystems, due to the N-fixation tree, though savanna is likely N limited ecosystems. To reveal and compare the nutrient flow in relation to soil microbes for forest and savanna vegetation in this area, we evaluated seasonal fluctuations in microbial biomass carbon (MBC), nitrogen (MBN), and phosphorus (MBP) for 1 year as well as soil moisture, temperature, soil pH, and extractable soil nutrients for both vegetation types in eastern Cameroon. Soil pH was significantly lower in forest (4.3) than in savanna (5.6), and soil extractable N was larger in forest (87.1 mg N kg⁻¹ soil) than in savanna (32.9 mg N kg⁻¹ soil). We found a significant positive correlation between soil moisture and MBP in forest, indicating the importance of organic P mineralization for MBP, whereas in savanna, we found a significant positive correlation between soil N availability and MBP, indicating N limitation for MBP. These results indicate that forest is an N-saturated and P-limited ecosystem, whereas savanna is an N-limited ecosystem for soil microbes. Interestingly, we observed a significantly lower MBN and larger MB C:N ratio in forest (50.7 mg N kg⁻¹ soil and 8.6, respectively) than in savanna (60.0 mg N kg⁻¹ soil and 6.5, respectively) during the experimental period, despite the rich soil N condition in forest. This may be due to the significantly lower soil pH in forest, which influences the different soil microbial communities (fungi-to-bacteria ratio) in forest versus savanna, and therefore, our results indicate that, in terms of microbial N dynamics, soil pH rather than soil substrate conditions controls the soil microbial communities in this area.

Keywords: Soil N and P dynamics, Soil microbial dynamics, Forest-savanna transition zone, Tropical africa

Can we comprehend organo-mineral associations occurring at different levels of soil aggregate hierarchy? A case study using a volcanic-ash soil (Andisol)

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Organic matter (OM) in soil is subject to both microbial transformation and interaction with soil minerals, during which soil aggregates are formed at the spatial scales of nano to mili meters. Due to the variations in mineral and OM compositions as well as the nature of the interaction between the two, organo-mineral particles or aggregates have a range of size and density. Physical fractionation is an effective approach to study organo-mineral interaction and the factors controlling the storage and turnover of soil OM. However, it remains unclear how the findings from fractionation studies are related to the concept of aggregate hierarchy (e.g., larger aggregates are maintained by transient binding agents while smaller ones are held together by more persistent binders). Here we present three studies that use the fractionation approach to examine how short- and long-term soil OM dynamics are linked to the hierarchy concept using Japanese volcanic-ash soils that is known for strong aggregation and OM stabilization capacity.

First, we demonstrated that the isolation of low-density fraction, a readily accessible OM outside of aggregates, was necessary to examine the factors controlling decomposition temperature sensitivity. Second, using sequential density fractionation, we isolated soil aggregates that are resistant to mechanical shaking and showed density-dependent changes in the chemistry of OM ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{14}\text{C}$ as well as C:N ratio) and that of mineral phases (organically complexed metals and short-range-ordered minerals). Third, we found the particle size dependent changes in organo-mineral chemistry in the same soil only after achieving maximum dispersion of these aggregates by sodium saturation followed by sonication. Clay-sized particles after the dispersion, however, still showed aggregated features by SEM and TEM. We will discuss possible factors controlling OM stabilization in these fractions and the presumed relationship between the fractions obtained from different levels of aggregate hierarchy (sonication-resistant particles vs. shaking-resistant aggregates).

Keywords: soil carbon, microstructure, organo-mineral interaction

Nature of organo-mineral particles at a lower level of aggregate hierarchy among contrasting soil types

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Soil organic matter (SOM) accounts for a major portion of terrestrial C and is considered to be stabilized against microbial degradation due partly to its interaction with soil minerals. Particle-size fractionation is an effective approach to distinguish different types of organo-mineral particles. Many early studies showed hierarchical structure of organo-mineral particles that are bound together by various binding agents. Yet how organic compounds of microbial and plant origins interact with mineral phases and how such interaction contributes to the hierarchical structure remain unclear. Facing climate change induced by C imbalance, it is particularly important to better understand the factors controlling C concentration and its mean residence time among particle size fraction in different soil types. Here we focused on the sonication-resistant organo-mineral particles collected by particle size fractionation from four soil types of contrasting minerology. We hypothesize that the distribution of percent of modern carbon among particle size fractions differ among the soil types due to the difference in the major forms of organo-mineral associations. We compare top soils (A horizon) from four soil types: allophanic Andisol, non-allophanic Andisol, Mollisol, Ultisol. The recovered particle size fractions are characterized by selective dissolution (pyrophosphate, oxalate, and dithionite), isotopic contents (¹⁵N, ¹³C, ¹⁴C), and ¹³C solid state NMR. We will discuss common patterns and differences among the four soils.

Keywords: soil organic matter, organo-mineral interaction, advanced microscopy, soil aggregate hierarchy

What physicochemical properties better explain the long-term biodegradability of burning-derived char?

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Fires and field burnings produce char, which represents an important carbon (C) sink due to its high stability against biodegradation. Yet its potential for long-term C sequestration remains elusive as char has large variation in terms of physical and chemical properties depending on source material type and burning conditions. We thus need biodegradability indices that are applicable for the range of chars. The O/C molar ratio has often been used in the literature. On the other hand, H/C molar ratio better correlates with char's chemical composition which is likely to control biological stability against microbial degradation. We thus tested if H/C ratio serves as a better index of the biodegradability than O/C ratio by comparing the chars prepared under different conditions (200-600 °C, with/without heating temperature duration, low and ambient O₂ levels) from rice straw and husk. We assessed their physicochemical characteristics and chemical composition using solid-state CP/MAS ¹³C-NMR. Based on 295-day laboratory incubation, we obtained biodegradability at three time scales: short (<100 d), intermediate (295 d), and long (>500 d) using inter- and extrapolation of decay curves. The short-term biodegradability was better explained by O/C ratio whereas the long-term biodegradability was better explained by H/C ratio. The H/C strongly correlated with aromatic and O-alkyl C, while O/C correlated with carboxylic C as well, suggesting that O/C reflected the amount of labile organic matters such as organic acids. Our findings suggest that long-term C fate of burning products is better estimated by H/C ratio rather than O/C ratio at least for the rice residues.

Keywords: char, carbon sequestration, burning

Molecular level characterization of soil organic matter by using XRD and FTICR-MS

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Soil organic matter (SOM) includes metabolites and decomposed products of plants/organism and those products having different degrees of humification (or darkness). The SOM plays important roles associated with crop productivity and carbon sequestration. To understand the dynamics/functions of SOM, chemical structure of SOM is to be clarified. The molecular recalcitrance of SOM is one of their stabilization mechanisms in soils. Condensed aromatic components that could derive from char have been considered as the recalcitrant components. Here, we highlight our studies on the chemical characterization of soil humic acids (HAs), especially for condensed aromatic components.

Materials and methods

Humic acids (HAs) were prepared from ten Japanese soils to cover varying degrees of humification according to NAGOYA method. The degree of humification of HAs was evaluated with the absorbance at 600 nm per mg C mL⁻¹ (A_{600}/C) and the ratio of absorbances at 400 and 600 nm on a logarithmic scale [$\log(A_{400}/A_{600})$]. Based on these two variables, HAs were classified into four types: Rp < P < B < A, with the degree of humification increasing in this order.

The XRD profile was measured following to Fujimoto and Shiraishi (2004). The XRD profiles were analyzed by using Carbon Analyzer DiHiGa Series 2007 software (Ryoka Systems Inc., Tokyo). The composition of carbon layer planes on a weight basis was obtained by fitting the XRD profile to theoretical profiles. The FTICR-MS was performed according to Sleighter and Hatcher (2008). The molecular formulas assigned were examined using the van Krevelen diagram and Kendrick mass defect (KMD) analysis that focusing on condensed aromatic structure.

Results

- 1) The 11 band analysis indicated that the radius size of the carbon layer planes in HAs ranged from 0.48–1.68 nm, corresponding to 4- to 37-ring condensed aromatics.
- 2) The contents of the total and larger carbon layer planes were larger in HAs with both darker color and larger aromatic carbon content.
- 3) The number of molecular formulas in the condensed aromatic region increased with increasing degree of humification (from Type Rp to Type A HAs), as well as the sum of the peak magnitudes of those formulas.
- 4) The KMD analysis indicated that the largest number of the rings in potential condensed aromatic components increased in the order: Types Rp and P (7) < Type B (9) < Type A (10) HAs.

Keywords: soil organic matter, X-ray diffraction, condensed aromatics