Development of automatic analysis apparatus for triple oxygen isotopes of dissolved oxygen

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Oxygen molecules (O_2) consists of triple oxygen isotopes (mass numbers 16, 17 and 18) providing additional unique information such as triple oxygen isotopic compositions ($\Delta^{17}O = \ln(\delta^{17}O + 1) - 0.518\ln(\delta^{17}O + 1)$). In most of the terrestrial processes (e.g. photosynthesis and respiration) fractionate O isotopes in a mass-dependent way, such that ^{17}O enrichment is about half of the ^{18}O enrichment relative to ^{16}O. As a result, $\delta^{17}O$ and $\delta^{18}O$ in terrestrial materials plot along a single line with a mass-dependent slope of about 0.52. In contrast to these mass-dependent processes, ultraviolet-induced interactions among O_2, O_3, and CO_2 in the stratosphere cause mass-independent fractionation with equal lowering of $\delta^{17}O$ and $\delta^{18}O$ in atmospheric O_2. Therefore, $\Delta^{17}O$ of photosynthetically-produced O_2 in the hydrosphere shows higher values of about +150 - 250 per meg compared to atmospheric O_2. Since the $\delta^{17}O$ and $\delta^{18}O$ of O_2 fractionated by respiration vary along a line with a mass-dependent slope, which means the $\Delta^{17}O$ will not change, we can estimate a mixing ratio of O_2 produced from photosynthesis in the hydrosphere ($\Delta^{17}O$ = ca. +150 ~ 250 per meg) and atmospheric O_2 ($\Delta^{17}O$ = ca. +150 ~ 250 per meg) dissolved in water. This will make it possible to estimate gross primary production in the lake and ocean or the air-water gas exchange coefficient by measuring the $\Delta^{17}O$ of dissolved O_2. In this study, we constructed the new purge and trap system to measure $\Delta^{17}O$ of dissolved O_2. The system is fully automated, extracting dissolved gases from the water samples, separate O_2 from all the other gases including Ar, and collecting pure O_2 using a cryogenic temperature cooling sampling device (ca. 10K). We will report $\Delta^{17}O$ values of dissolved O_2 in Lake Biwa where remarkable eutrophication and hypoxia have been observed in recent years.

Keywords: dissolved oxygen, triple oxygen isotopes, vertical profile

Monitoring on atmospneric mercury concentration by Carbonized passive sampler
-Comparison of the Tokyo metropolitan area and Hokkaidou-

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[Introduction]
Mercury in atmosphere is typically measured as three fractions : Hg^0(Gaseous elemental mercury), Hg^{2+}(gaseous oxidized mercur) and Hg-p (particulate bound mercury). Hg^0 is the prevalent from in the atmosphere, consisting of >95% of the total mercury. Due to its volatility and chemical sability Hg0 can circulate in the atmosphere for 1~2 years, allowing its wide dispersion and long distance transportation. Monitoring on atmospheric mercury in Japan has started since 1997 year and at the moment, >300points monitoring stations research atmospheric mercury by active sampler (gold amalgam method). But measuring frequency is once monthly and different sampling day. And It's difficult for active sampler research at remote point because needs electric power.
In this research, We developed carbonized passive sampler and research atmospheric mercury at Hokkaidou, Gunma, Saitama and Yamanashi.
[Method]
Developed carbonized passive sampler was set at Horikawauchi, Hokkaidou (Uryuu experimental forest), Sapporo, Hokkaidou (Hokkaidou Univ), Kumagaya, Saitama (Risshou Univ), Kazo, Saitama (Center for environmental Science, Saitama), Nakanojou, Gunma and Nirasaki, Yamanashi. Sampling period was Jur/2014~Aug/2015. Moreover, Active sampler was set at Kumagaya and Kazo at the same time carbonized passive sampler sampling period.
[Result]
Relation between integrate atmospheric mercury concentration (M) and Carbonized passive sampler (P) was M=0.003P+0.06 (r=0.09, n=20). We used it equation to convert quantity of mercury adsorption in the carbonized passive sampler to atmospheric mercury concentration. Every points mercury concentration were 0.1~1.3ng/m^3 at the Horikawauchi, 0.6~1.5ng/m^3 at the Sapporo, 0.2~1.4ng/m^3 at the Nakanojou, 1.7~3.1ng/m^3 at the Kumagaya, 1.9~2.9ng/m^3 at the Kazo and 0.4~1.8ng/m^3 at the Nirasaki. Kumagaya and Kazo were same level as Japanese average of atmospheric mercury concentration (about 2.3ng/m^3) and, Other points were little lower than North American and European remote area (1.5~1.7ng/m^3).

Keywords: Monitoring on atmospnere, Cabonized passive sampler, mercury

Observation of O_3 flux in red pine forest

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The emission and absorption of trace gases at the biosphere affects to atmospheric chemistry, and thus it makes influence with potential indirect effects on carbon cycle and climate (Ollinger *et al.*, 2002). We constructed and tested O_3 and NO_x flux measurement system with the gradient method at a meteorological tower in red pine forest (Site Code: FJY) in the autumn of 2014 and 2015. We also measured CO_2 flux at the same meteorological tower for validation of the system by comparison with CO_2 flux determined by the eddy covariance method.

The heights of the forest canopy and the meteorological tower were about 25 m and 32 m. Concentrations of O_3, NO_x and CO_2 were measured at two heights (26 m and 32 m in 2014, 26 m and 34 m in 2015) above the canopy by an ultraviolet absorption O_3 analyzer (Thermo: 49C), a chemiluminescence NO_x analyzer (Thermo: 42iTL) and an infrared absorption CO_2 analyzer (Licor: LI-820). The O_3 instrument was calibrated before the observation, and the NO_x and the CO_2 instruments were calibrated every three weeks at the observation site. The air was sampled every 300 seconds from each two vertical heights and supplied to the analytical instruments through PFA tube. Concentration of CO_2 was also measured by an infrared absorption CO_2 analyzer (Licor: LI-6262) at 26.5 m to determine CO_2 fluxes by the eddy covariance method. Wind speed and wind direction were measured at 26.5 m and they were used to obtain fluxes by the gradient and eddy covariance methods.

The CO_2 fluxes in the day time (9:00-16:00) in the autumn of 2014 were observed with the gradient and the eddy covariance method as -9.0±7.3 mmol m^{-2} s^{-1} and -8.6±6.5 mmol m^{-2} s^{-1}, respectively. The CO_2 flux obtained by the gradient method was slightly lower and more scattered than CO_2 flux obtained by the eddy covariance method; however these values reasonably agreed. We made sure the flux observation system with gradient method worked properly.

The observed O_3 concentrations at the two heights differed significantly; however the observed NO_x concentrations at the two heights were similar and there were no significant differences, which indicated that it was difficult to obtain NOx fluxes with gradient method in the red pine forest.

The primary result indicated that O_3 deposition in the red pine forest in the day time (9:00-16:00) were -1.1±1.5 nmol m^{-2} s^{-1} in autumn 2014, and -1.9±2.5 nmol m^{-2} s^{-1} and 0.9±2.6 nmol m^{-2} s^{-1} in autumn and winter 2015. The O_3 deposition in winter was smaller than in autumn, which was a similar trend with literature (Fares et al., 2010).

References:

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Keywords: ozone, flux, forest

Mean residence time of leaf nitrogen and leaf longevity of hinoki cypress (*Chamaecyparis obtusa*) under nutrient-poor soil

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Mean nitrogen residence time of plants is decided by nitrogen resorption and leaf longevity. However, there is little knowledge about intra-specific variation in leaf longevity and mean nitrogen residence time along a soil nitrogen gradient. We evaluated the effects of nitrogen resorption and leaf longevity on mean residence time of leaf nitrogen (leaf-N MRT) of hinoki cypress under different soil nutrient status.
Mean residence time of nitrogen in organic horizon (A_0N-MRT) was used as the index of soil nutrient status. A_0N-MRTs ranged 5.4 to 38.3 years that were longer than those in other stands of hinoki cypress. Leaf longevity and leaf-N MRT increased as A_0N-MRT increased. Leaf production and leaf-fall nitrogen mass decreased with increasing A_0N-MRT. There were no significant relationships between A_0N-MRT and nitrogen resorption, leaf biomass, leaf nitrogen mass, nitrogen concentrations of fresh-leaf and leaf-fall. Nitrogen resorption was higher than that in other stands of hinoki cypress. It was suggested that nitrogen resorption did not significantly correlated with A_0N-MRT because of high resorption rate in all plots. These findings indicated that hinoki cypress under nutrient-poor soil to maximize mean residence time of leaf nitrogen increased nitrogen resorption before leaf-fall first, and additionally, altered leaf longevity by changing leaf production along a soil nitrogen gradient.

Keywords: mean residence time of leaf nitrogen, leaf longevity, leaf production, hinoki cypress, organic horizon

Investigation of streamwater chemistry in forest with heavy snowfall in northern part of Shiga prefecture

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Nitrogen exported from forest is considered to affect environment of downstream ecosystem, means that the understanding the processes of nitrogen export from forest is important. Particularly, many study reported that snow accumulation and snowmelt has important role in nitrogen export from forest with heavy snowfall region. The northern part of Shiga prefecture is specified as Special Heavy Snowfall Area under the Act on Special Countermeasures for Heavy Snowfall Area. However, temperature in the forest is relatively high, because the forest is located in the southernmost area of Special Heavy Snowfall Area. Therefore, during snow accumulation, snowmelt is often caused by high temperature in northern part of Shiga Prefecture. However, observation of nitrogen export during snow accumulation and snowmelt in such forest is very few. Therefore, we observed nitrogen export from the forest during snow accumulation and snowmelt in northern part of Shiga Prefecture. We conducted the experiment in the Surumi catchment located in the northern part of Shiga prefecture. We collected streamwater sample by automatic water sampler (ISCO, 3700) in the snow fall in 6 to 24 hour interval in a day. Samples were analyzed for total nitrogen, dissolved nitrogen, nitrate and ammonium. We also analyzed oxygen and nitrogen isotope of nitrate for examining the nitrate source. Chemical analysis for ion concentration were conducted in the University of Siga Prefecture, and isotope analysis was conducted at ICRE in University of Yamanashi.

Keywords: nitrogen export, forest, snowmelt, streamwater, isotope

Hydro-geomorphological factors which control reduction processes in a forested watershed.

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Many studies have reported that denitrification may occur in riparian zone(e.g., Hill et al (2000) where topographic gradient is small. The relationship between topography and reduction processes such as denitrification attracts researcher’s attention these days (Gold et al., 2000; Hill et al., 2000). Past studies (Ogawa et al., 2006; Shibata et al., 2010) have reported that the nitrate concentration of stream water is small in catchments of small topographic gradients. The cause of it is probably due to denitrification. But concrete and systematic knowledge is limited where the reduction processes such as denitrification occur in forested catchment.

The purpose of this study is to know hydro-geomorphologial conditions in which denitrification, manganese, iron and sulfate reduction processes occur.

The study site is a small forest catchment located in Hachioji Tokyo. We measured the topographic gradient and the concentration of nitrate, dissolved manganese, dissolved iron and sulfate in water extract from soil and ground water.

The nitrate concentrations of upper sampling points in steep slope are higher than 0.05mmol/kg from surface soils to deep soils (Fig.1). On the other hand, the nitrate concentrations have become lower than 0.05mmol/kg or nitrate was not detected at the saturated zone of middle and lower sampling points in gentle slope (Fig.1). So denitrification occurred in underground of gentle slope area.

The dissolved manganese concentrations have become higher than 1.0μg/kg at the saturated zone of middle and lower sampling points in gentle slope (Fig.1). Therefore, manganese reduction occurred in underground of gentle slope area.

The dissolved iron concentrations have become higher than 4.0mg/kg at the saturated zone of middle and lower sampling points in gentle slope (Fig.1). Therefore, iron reduction occurred in underground of gentle slope area.

The sulfate concentrations have become lower than 0.05mmol/kg at the saturated zone of middle and lower sampling points in gentle slope (Fig.1). The sulfate concentrations of other area were much higher than 0.05mmol/kg (Fig.1). Therefore sulfate reduction occurred in underground of gentle slope area.

The ground water concentration of nitrate gradually deceased along the ground water flow (Fig.2). And the ground water concentration of sulfate from the well E was very low (Fig.3). These changes of nitrate and sulfate concentration from well A to well E mean that these substances may have been reduced when the ground water flowed through this reduction zone (Fig.1) located at the bottom of this forested watershed.

This study demonstrated where nitrate, manganese, iron and sulfate reduction processes occur in forested watershed. The reduction zone was located at the underground in gentle slope. It is likely that gentle slope which makes shallow soils saturated by ground water is the hydro-geomorphologial factor and it causes the reduction processes. This result suggests that such reduction zone has a great influence on ground water and stream water chemistry.

Keywords: a forested watershed, hydro-geomorphological, reduction process

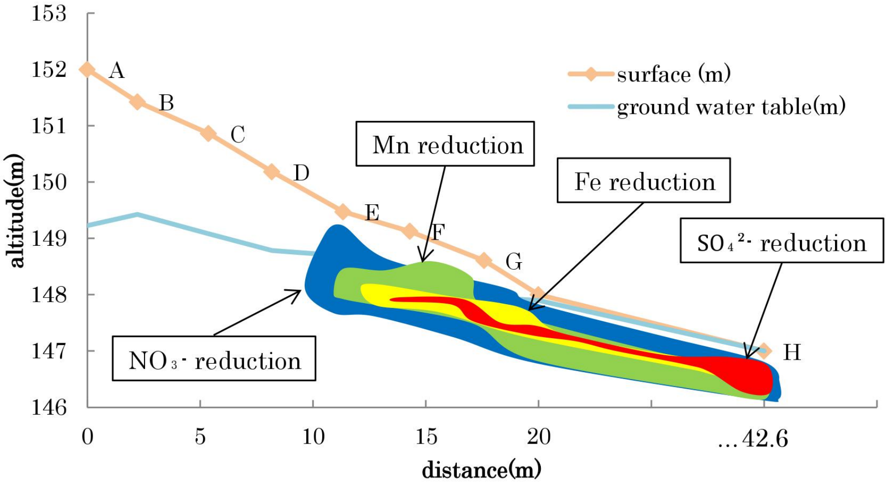

Fig.1 The distribution of reduction zone in forested watershed.

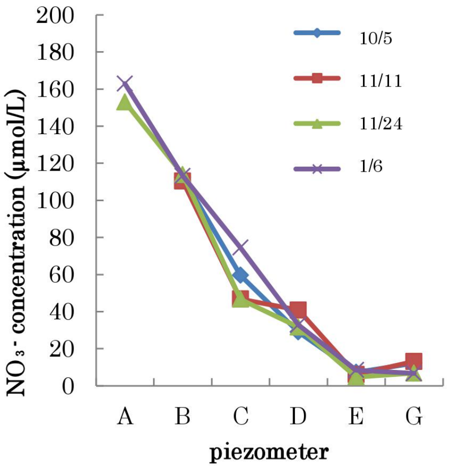

Fig.2 NO_3^- concentration of ground water

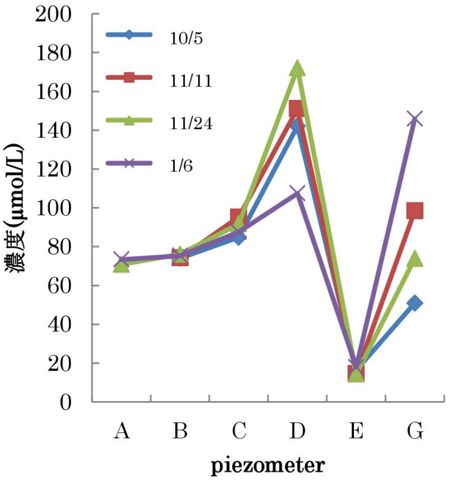

Fig.3 SO_4^{2-}concentration of ground water

Topographic influence on leaf nitrogen and phosphorus stoichiometry of Japanese cypress in a temerate forested watershed

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Plant stoichiometory has been potentially used to diagnose phosphorus (P) limitation caused by increased atmospheric nitrogen (N) deposition. However, spatial variability of N:P stoichiometry within an forested watershed has not been evaluated. This study conducted synoptic sampling of leaf in 27 plots within a temperate forested watershed on low P availability rock (serpentine bedrock) with a moderately high atmospheric N deposition (16 kg N ha^{-1} yr^{-1}) to assess the effects of spatial topographical variation on N:P stoichiometry. Leaf N and P concentrations and N:P ratio of Japanese cypress were assessed and their spatial variations were evaluated across a catchment. The results showed that average leaf P concentration was low (0.66 ±0.16 mg g^{-1}) across the sites, while leaf N concentration was high (13.0 ±1.5 mg g^{-1}), and subsequently N:P ratio was high (21 ±5). In addition, aboveground biomass increment of Japanese cypress was positively correlated to litter P, implying the P limitation of Japanese cypress at the study site. However, in 7 plots out of 27 N:P ratio was close to or below 16, the proposed indicator of P limitation. Leaf P concentrations responded to the index of convexity (IC) values more than N. Subsequently N:P ratio correlated with IC, suggesting N:P ratio are susceptive to topologic features. This could be partly caused by smaller spatial variability of N availability than P owing to increased atmospheric N deposition. This study concluded that topography should be taken into consideration when diagnosing P limitation caused by N deposition.

Keywords: P limitation, N saturation, Atmospheric deposition, Serpentine bedrock

Conservation of Soil Physical Properties by No-tillage Management in Tropical Sugarcane -Evaluation of Infiltration Characteristics with Artificial Aggregates-

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Artificial maropores were installed at subtropical red soils to reduce surface flow at sugarcane fields. The fields were suffering from heavy rain which is increasing these days because of climate change. Surface flow causes soil erosion which soil particles were directly delivered into sea with coral leaf. Soil particles would shade the sun and also nutrient rich water damage the coral leaf. Therefore, reducing surface flow with soil particles is crucial for protecting subtropical natural environment. However, conventional sugarcane employs cultivation and fresh planting every year. Agriculture soils are soft with cultivation and fresh planting needs bare soils. In that situation bare soil easily causes surface flow and soil particle loss. Non tillage or reduced tillage are strong countermeasures for those situation, however, agricultural farmers shows little appreciation for non-tillage management probably because it seems like uncontrolled or abandoned.

Therefore in this research, we installed artificial macropores into the fields as an option for these situation. Artificial macropores with bamboo fibers were installed 1-m interval for conventional tillage field and non-tillage field. Soil moisture sensors were also installed at 10 and 30-cm deep soil. Rainfall was measured with tipping bucket and surface flow was measured with partial flume.

Results showed that at conventional tillage field, soil moisture sensors at 30cm showed higher water content than 10cm after heavy rain. Surface flow was reduced after macropore installation at tillage field, while non tillage field did not show the effect. This results show that installation of macropore to tillage field reduce the surface flow while enhancing vertical infiltration. However, tubular macropore installation was tedious and time consuming. Here we installed another artificial macropore, namely “linear macropore ”for which macropores were created by subsoiler and fibrous materials were filled to reinforce the structure. The first result with heavy rain showed surface flow was reduced compare with bare soil. Its structure was also resistible for clogging when compared with liner macropore without fillings. We are planning to observe field condition next several months to evaluate this technique.

Keywords: No tillage, Soil structure, Sugarcane