Comparison of satellite observation of lower tropospheric ozone with model simulation over East Asia

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The lower tropospheric ozone enhancement over Central and Eastern China (CEC) was reported by Hayashida et al. (2015) by using the Ozone Monitoring Instrument (OMI) multiple-layer product retrieved by Liu et al. (2010). However, to clarify the enhancement in the concentration of the lowermost ozone using spaceborne measurements, it is necessary to understand the effect of ozone variation in the upper troposphere and lower stratosphere (UT/LS) because of large smoothing errors in the retrieval scheme. In this study, a scheme was developed to eliminate the artificial effect of UT/LS ozone enhancement on lower tropospheric ozone retrieval using OMI. By applying the UT/LS screening scheme for June 2006, we removed the effect of the UT/LS ozone enhancement on the artificial effect on the lower tropospheric ozone. Even after UT/LS screening, we were able to show a clear enhancement in the lower tropospheric ozone over CEC in June 2006 and confirmed the conclusion derived by Hayashida et al. (2015). After screening the UT/LS effect, we compared satellite measurements with model simulations for O_3 by using MRI-CCM2 (Deushi and Shibata, 2011). The observed O_3 enhancement over CEC in June 2006 was reproduced very well by the model simulations. The effects of emissions from the open crop residue burning (OCRB) in the North China Plain on lower tropospheric ozone were also examined by utilizing the emission inventory developled by K. Yamaji (Yamaji et al., 2010). In the scale of the vertical resolution of OMI observation, the difference between the O_3 with and without the OCRB effect was not very large (about 1 DU).

Acknowledgements
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Keywords: ozone, satellite, model simulation, pollution

Estimation and trend analysis of the tropospheric baseline ozone and carbon monoxide concentrations at Mt. Happo

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A large increase in tropospheric O_3 concentrations was observed during spring for the period from 1998 to 2006 at Mt. Happo Observatory (36.7°N, 137.8°E, 1840 m asl), which is one of the Acid Deposition Monitoring Network in East Asia (EANET) stations (Tanimoto, 2009). The increase in the springtime O_3 reproduced by a regional chemistry-transport model incorporating the updated anthropogenic emissions inventory in East Asia can only explain about half of the observed O_3 increase (Tanimoto et al., 2009). Observational datasets at mountain sites have been utilized for estimation of baseline levels of greenhouse gases and aerosols because remote mountainous sites are regarded as having little direct influence from local or regional sources/sinks (e.g., Parrish et al., 2012). However, observations at ground-based stations can often be influenced by local sources. Therefore, the data selection is often an essential part of the analysis for estimation of regional representative baseline levels.
In this study, we estimated baseline and polluted concentrations of O_3 (1998–2014) and CO (1996–2014 and 2013–2014) at Mt. Happo by using the statistical method “REBS (Robust Extraction of Baseline Signal)” (Ruckstul et al., 2012), which is based on the robust local regression. Then, we analyzed these long-term trends. CO concentration (2013–2014) is significantly lower than CO concentration (1996–2004), and the degree is larger in summer and autumn than in spring. Recent baseline CO concentrations are decreasing in all season except for spring. Spring baseline concentration is slightly increasing. Polluted CO concentrations are decreasing in all season, and the degrees are larger than those of baseline concentration. On the other hand, O_3 concentrations show decreasing trends with maximum in the mid-2000s in all season. The rate of decrease is characterized by a spring maximum and summer minimum. Both baseline and polluted O_3 concentrations show decreasing trends in all season and both rates of decrease are the same degree. Hence it is considered that the decrease of springtime CO concentration at Mt. Happo is mainly caused by the decrease of polluted CO concentration, and that the decrease of O_3 concentration is caused by the decreases of baseline and polluted O_3 concentrations.

Keywords: Ozone, Carbon monoxide, Baseline level

Long-term observations of black carbon at Fukue Island during 2009–2015: Rates of emissions from East Asia and removal

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Black carbon is a component of atmospheric fine aerosol particles contributing to global warming. However, its emission strengths and removal rates have not been sufficiently understood. We have conducted long-term observations of black carbon mass concentrations using a COSMOS instrument since 2009 at Fukue Island (32.75°N, 128.68°E), western Japan, to provide information on the emission strengths of important source regions in East Asia and on wet removal rate constraints. The annual average mass concentration was 0.36 μg m^{-3}, with distinct seasonality; high concentrations were recorded during autumn, winter, and spring, and were caused by Asian continental outflows, which reached Fukue Island. Statistical analysis of the observed ΔBC/ΔCO ratio was separately made for two classes of data with and without a wet removal effect, using the accumulated precipitation along a backward trajectory (APT) for the last 3 days as an index. The emission ratios estimated from observations with zero APT (5.2–6.9 ng m^{-3} ppb^{-1}) varied over the six air mass origin areas; the higher ratios for South Central East China and South China indicated the relative importance of domestic emissions and/or biomass burning sectors. The BC/CO emission ratios adopted in the bottom-up Regional Emission inventory in Asia (REAS) version 2 (6.5–23 ng m^{-3} ppb^{-1}) over the continent were significantly higher; the ratios needed to be reduced by 60% for China and by a factor of 3.5 for Korea, although the ratio for Japan was in an acceptable range. The wintertime enhancement of the BC emission from China, predicted by REAS2, was verified for air masses from South Central East China. Wet removal of BC was clearly identified as a decrease in the ΔBC/ΔCO ratio against APT. The transmission efficiency (TE), defined as the ratio of the ΔBC/ΔCO ratio with precipitation to that without precipitation, was fitted reasonably well by a stretched exponential decay curve against APT. The dependence on APT was almost similar among the air mass types. An accumulated precipitation of 15 mm halved the BC mass concentration. This expression of wet removal and the emission constraint for East Asia help to test and improve chemical transport and/or climate model simulations.

Keywords: aerosol particles, trans-boundary air pollution, climate Effect, budget analysis, process analysis

Budget analysis of aerosols in China: interannual variation in aerosol concentration and outflow

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Aerosols and their precursor emitted from polluted regions strongly influence climate and atmospheric environment not only at local areas but also in remote areas due to long-range transport. Therefore, it is needed to investigate temporal variations of aerosol concentration in source region and associated ouflow from the region in order to evaluate impacts of air pollutants on climate and atmospheric environment. In this study, we evaluate main factors of changes in aerosol concentrations in the China region (18°N-46°N, 104°E-123°E) and aerosol outflow there focusing on black carbon (BC) and sulfur oxides (SOx) by budget analysis of aerosols using a global chemical climate model CHASER. As a consequence, we found that aerosol outflow from the China region has a seasonal peak in winter and the outflow across the east boundary in the region and the inflow across the west boundary both have peaks on March. Our analysis also shows that variations of net zonal outflow largely contribute to the interannual variability of outflow from the China region. We also found that aerosol outflow largely controls the interannual variation of aerosol concentration in the China region (deposition in the region makes only a small contribution to it). Additionally, our sensitivity experiments with BC emission which has a positive radiative forcing and climate impacts, indicate that the domestic sources in the China region and long-range transport from India account for 75% and 12% of the tropospheric BC burden in the China region, respectively. About a half of the BC inflow across the west boundary in the China region is contributed from BC emitted from India. BC emitted from the China region and from India contribute by about 60% and 20% respectively to the total BC outflow across the east boundary. This study, therefore, suggests that BC transported from South Asia such as India influence variabilities of BC concentration in China, and this BC can be farther transported to Japan and the North Pacific regions.

Keywords: aerosol, long-range transport, black carbon, China

Return to the decade-ago level of tropospheric nitrogen dioxide pollution in East Asia

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Long-term (2005-2015) tropospheric nitrogen dioxide (NO_2) column data recorded by the satellite-borne Ozone Monitoring Instrument (OMI) in East Asia were analyzed to investigate annual trends quantitatively and their potential causes. We found an evident decrease in the NO2 level over China after 2011 and then a return to the 2005 level in 2015. The grid-basis trend analysis implies that the rapid decrease occurred on a provincial or larger spatial scale and was likely due to a nationwide action such as the widespread use of denitrification units. Other prominent features were seen in Japan. Despite a significant substitution from nuclear to thermal power after 2011 as a consequence of a massive earthquake off the Pacific coast of northern Japan, the NO_2 level continued to decrease for both periods (2005-2011 and 2011-2015). The decrease contributed to a return to the decade-ago level of tropospheric NO_2 pollution in East Asia.

Keywords: NO2, trend, East Asia, OMI

Rabi-crop CO_2 uptake inferred from CONTRAIL measurements over Delhi, India

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Recent studies propose that growing agriculture has altered atmospheric CO_2 variations and the global carbon cycle. In this study, we show a clear evidence of significant impact of Indian wintertime (*rabi*) agriculture (mainly wheat) on the regional carbon budget based on high-frequency atmospheric CO_2 measurements onboard commercial airliners over Delhi, India. While a general increasing gradient toward the ground was observed throughout December–April, we have frequently observed sharp decreases near the ground during January–March. In this period, CO_2 concentration at altitudes below 2 km was at seasonal stagnation. Meteorology in the season infers influence from neighboring croplands with patchy urban areas located upwind. We conclude that the observed CO_2 decrease is attributable to active uptake by *rabi*-crop growing in the season and that the uptake is comparable in magnitude to urban CO_2 emissions from the Delhi metropolitan area.

Keywords: CO2, rabi crop, aircraft measurements

Temporal variations of the atmospheric CO_2 concentration and $d^{13}C$ at Ny-Ålesund, Svalbard

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Long-term measurements of the atmospheric CO_2 concentration and its carbon isotope ratio ($d^{13}C$) have been used for partitioning CO_2 sinks into the terrestrial biosphere and the ocean. However, the CO_2 sinks estimated from $d^{13}C$ suffer with uncertainties in isotopic disequilibrium flux between the atmosphere and the ocean and between the atmosphere and the terrestrial biosphere (so-called isoflux). For a better understanding of the global carbon cycle, we have been carrying out the systematic observation of the atmospheric CO_2 concentration and $d^{13}C$ at Ny-Ålesund (78.93°N, 11.83° E), Svalbard since 1991 by weekly air sampling with subsequent analysis in NIPR. Here, we will present the observational results of CO_2 concentration and $d^{13}C$ for 1991–2013 and 1996–2013, respectively. The $d^{13}C$ data before 1996 were removed from our analysis due to experimental and sample quality problems (Morimoto et al., 2001).

The CO_2 concentrations show a clear seasonal cycle with peak-to-peak amplitude of about 17 ppmv, which reaches the maxima in late April to early May and the minima in late August, superimposed on a secular increase with an average rate of 2.0 ppmv/yr for the period of 1996–2013. On the other hand, the $d^{13}C$ decreases secularly at an average rate of −0.018 ‰/yr, and varies seasonally in opposite phase with the CO_2 concentration. We have also maintained atmospheric $d(O_2/N_2)$ measurements at Ny-Ålesund since 2001 (Ishidoya et al., 2012). Using the atmospheric $d(O_2/N_2)$ and CO_2 concentration records, the terrestrial and oceanic CO_2 sinks are estimated to be 1.7 ±0.8 GtC/yr and 2.2 ±0.7 GtC/yr, respectively, for the 13-year period (2001–2013). Using these values of CO_2 sinks and the $d^{13}C$ record, the average isofulx for the period of 2001–2013 is estimated to be 99 ± 28 Gt ‰/yr.

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Keywords: atmospheric CO2, carbon isotope ratio, O2/N2 ratio

Diffusive separation of the lower atmosphere suggested by Ar/N_2, delta^{15}N of N_2, delta^{18}O of O_2 observed at Ny-Ålesund, Svalbard.

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Recent technical advances has made it possible to observe a molecular diffusive separation of the atmosphere based on high precision measurements of the composition of atmospheric major components. In the middle to lower stratosphere, Ishidoya et al. (2013) reported the existence of observable gravitational separation based on the measurements of stratospheric air samples collected using a balloon-borne cryogenic air sampler. In the lower atmosphere, Adachi et al. (2006) reported the diffusive separation of Ar and N_2, mainly due to thermal diffusion, in the center of a wide desert during the nighttime when vertical temperature inversions are generated. To examine whether the diffusive separation of the atmosphere is also detectable near the surface in polar region, air samples collected at Ny-Ålesund, Svalbard (79°N, 12°E) have been analyzed for delta(Ar/N_2), delta(O_2/N_2), delta^{15}N of N_2, delta^{18}O of O_2 and delta^{40}Ar by using a mass spectrometer (Ishidoya and Murayama, 2014) since January 2013. It was found that delta^{15}N and delta^{18}O show small but significant seasonal cycles, with the seasonal maxima and minima in winter and summer, respectively. The peak-to-peak amplitudes of the respective seasonal cycles of delta^{15}N and delta^{18}O were about 2 and 4 per meg. On the other hand, no significant seasonal cycle was seen in delta(Ar/N_2). If we assume the seasonal cycles of delta^{15}N and delta^{18}O are attributed mainly to gravitational separation in a temperature inversion layer during polar night in winter and corrected the delta(Ar/N_2) for the separation by subtracting 12 x (delta^{15}N + delta$^{18}O/2)/2$ (delta$(Ar/N_2)_{cor}$), then the delta$(Ar/N_2)_{cor}$ show clear seasonal cycle with a maximum in August. The peak-to-peak amplitude of the seasonal delta$(Ar/N_2)_{cor}$ cycle is about 25 per meg, and the appearance time of seasonal maximum agrees with that of the sea surface temperature around Ny-Ålesund. These results suggest that gravitational separation is observable near the surface at Ny-Ålesund. Our suggestion would be supported by Keeling et al. (2004) who reported the delta(Ar/N_2) observed in the polar region may be detectably enriched near the ground by gravitational separation or thermal diffusion under condition of strong surface inversions.

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Keywords: diffusive separation of the atmosphere, Ar/N2 ratio, delta15N of N2, delta18O of O2, vertical temperature inversions

Seasonal cycle of aerosol size distribution at Syowa Station, Antarctica

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Atmospheric aerosols are related closely to the climate change through direct and indirect effects. Number concentrations and size distributions of aerosols are one of the most important properties. Recently, aerosol size distributions have been measured even in the Antarctic regions during summer (e.g., Virkkula et al., 2007; Asmi et al., 2010; Pant et al., 2011; Park et al., 2004). These studies focused on the respect of new particle formation. However, only a few wintering-measurements of aerosol size distributions in fine - ultrafine modes have been made in the Antarctic regions (Ito, 1993; Hansen et al., 2009; Järvinen et al., 2013). This study aims to understand seasonal cycle of aerosol size distribution and new particle formation at Syowa Station, Antarctica. For measurement of size distribution in ultrafine - fine modes (Dp: 5–168 nm), a scanning mobility particle sizer (SMPS: 3936-N-25; TSI Inc.) was used from February 2004 - December 2006 at Syowa Station, Antarctica. The scanning time for one scan was set to 5 min in SMPS measurement. Local contaminated data were filtered using CN data (aerosol monitoring data) and wind data (observed by JMA). Log-normal fitting was used to compare modal structure of aerosol size distributions in this study. All daily-mean aerosol size distributions were fitted using the following lognormal modes: fresh nucleation mode (Dp<10 nm), aged nucleation mode (Dp=10-25 nm), 1st Aitken mode (Dp=25-50 nm), 2nd Aitken mode (Dp=50-100 nm), and accumulation mode (Dp>100 nm). Aerosol size distribution showed 2 –4 modal structures from early September –end-March. Fresh nucleation mode appeared occasionally in March-April, and August-November, and rarely in December-February and May-July. The number concentrations in aged nucleation –2nd Aitken modes increased in summer. In contrast, most of size distribution showed 1 - 2 modal structures during April - August. Strong mono-modal distribution appeared in 2nd Aitken and/or accumulation modes under/after the storm conditions in the winter –early spring. This seasonal feature might be associated with seasonal cycles of (1) the concentrations of condensable vapors linked to photochemical reactions and biogenic activity, and (2) sea-salt particles released from sea-ice surface in the winter - spring. Here, we discuss and characterize seasonal cycle of aerosol size distribution in ultrafine –fine modes in the Antarctic coasts.

Keywords: aerosols, size distribution, Antarctica

Seasonal variation of the concentration of black carbon and the size distribution of the surface snow sampled in the Syowa station in the Antarctica

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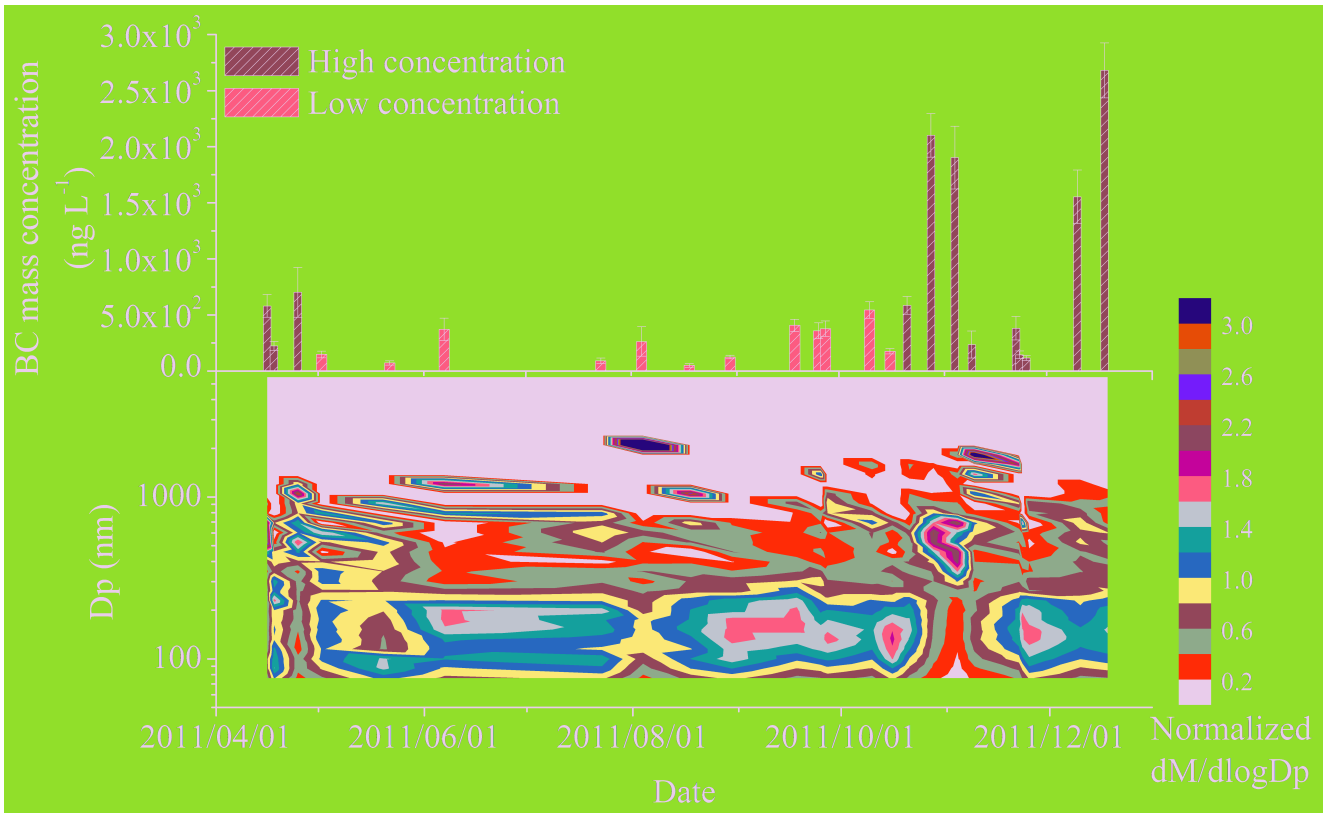
Black carbon (BC) strongly absorbs the radiation, leading to large climate effects. BC deposited on the snow/ice packs also leads to positive radiative forcing, reduces the snow/ice albedo. The snow albedo is estimated considering snow grain size and impurities, to clarify the size distribution of BC particles in snow is important. But the technique for measurement of the size distribution of BC in snow is developed in recent, the size distribution of BC is not understood sufficiently, especially Antarctica.
In this study, 29 snow samples were obtained at Antarctica, Syowa station, with the Japanese Antarctic Research Expedition 52 (JARE52, 2010-2012), measured for the BC concentration and its size distribution in snow and discussed. The BC concentration and its size distribution are measured by the Single Particle Soot Photometer (SP2) with an improved technique for measuring the size distribution wider (Mori et al., 2016), and ions and pH are measured at the each samples. The atmospheric BC concentration was measured by an Aethalometer during sampling period.
Snow samples were scooped from the surface of the snow to 250cc glass bottles directly, had been kept below -20 °C until the measurement. October 2011, relatively continent snows were sampled on the traverse route for the Mizuho station by JARE52. Based on reports of Kinase et al. (JpGU2015) and Kinase et al. (2016), snow samples were distributed to 3 of 20 cc glass bottles using a ceramic knife, melted in refrigerator, sonicated 15 minutes, and mixed to an 1 bottle. 30cc LDPE bottles were obtained for measurements of ions and the pH.
From results, the averaged BC concentration in snow samples were 591.6 ±714.1 (ng L^{-1}), and we found the seasonal variation, low in winter (May to September) and high in other seasons. Mizuho route samples were higher than Syowa. These results were little higher than previous studies which were obtained in other period, other locations and other method, but agreed on an order. Also we could find the seasonal variation of the size distribution, small particles were mainly in winter, but large particles were found in summer. But this measurement had not done in previous, we could not compare with other studies. Concentrations of ions and pH had no same variations.
For the atmospheric BC concentration, the sample air was heated to 300 ºC for decreasing effects by the volatile particles, but the effect of non-volatile particles remained. Hence, the measurement of the atmospheric BC had a large uncertain, it was high during winter and low during summer. Hara et al. (2008) showed that there are two processes of transporting atmospheric BC around Syowa, by the blizzard during winter and by the katabatic wind during summer. This result indicates that the dominant transporting/deposition process of atmospheric BC would change in each season.
Therefore, the atmospheric BC had the opposite trend to BC in snow, the atmospheric BC concentration would not effect to the BC in snow directly. The seasonal variation of BC in snow would depend on other process, such as the deposition process and others.

Moreover, the radiation had the same trend to the concentration and the size distribution of BC in snow, the radiation would effect for the seasonal variation of BC in snow. Heating and melt/refreeze cycle would change the size distribution (Kinase et al., (JpGU2015) ; Kinase et al., (2016)). The radiation would lead the heating of ice nuclei and surface snow, this indicates the seasonal variation of the concentration and the size distribution of BC would be related to the seasonal variation of the radiation. More studies of BC in snow are needed in the future, such as a long-term monitoring, the variation of the water cycle and deposition efficiency of BC to the snow, and the heating effect for the snow and ice nuclei.

Keywords: Antarctica, Syowa station, snow, Black carbon, size distribution, seasonal variation



Volatility measurements of SOA formed from α-pinene ozonolysis and data interpretation

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The volatility basis-set (VBS) model employs the secondary organic aerosol (SOA) volatilities evaluated from yield curve measurements. To verify the VBS model, we evaluated the volatilities of dry α-pinene ozonolysis SOA not only from yield curve measurements but also from thermodenuder-AMS measurements, LC-MS and PTR-MS chemical composition analysis, and external dilution chamber measurements. We evaluated also the uncertainty of volatility determined by each experimental metod. The results of thermodenuder-AMS measurements, chemical composition analysis, and external dilution chamber measurements showed that lower-volatility organic compounds are present in SOA particles compared with the results of yield curve measurements. The thermal and dilution properties of oligomers, produced in the particle phase by heterogenious reactions, will strongly affect the total properties of SOA particles under dry conditions.

Keywords: Secondary organic aerosol, Heterogeneous reaction, Oligomer formation

Experimental study on the heterogeneous reaction of gaseous OH radical with aqueous DMSO: Determination of the $CH_3SO_3^-$/ SO_4^{2-} production ratio

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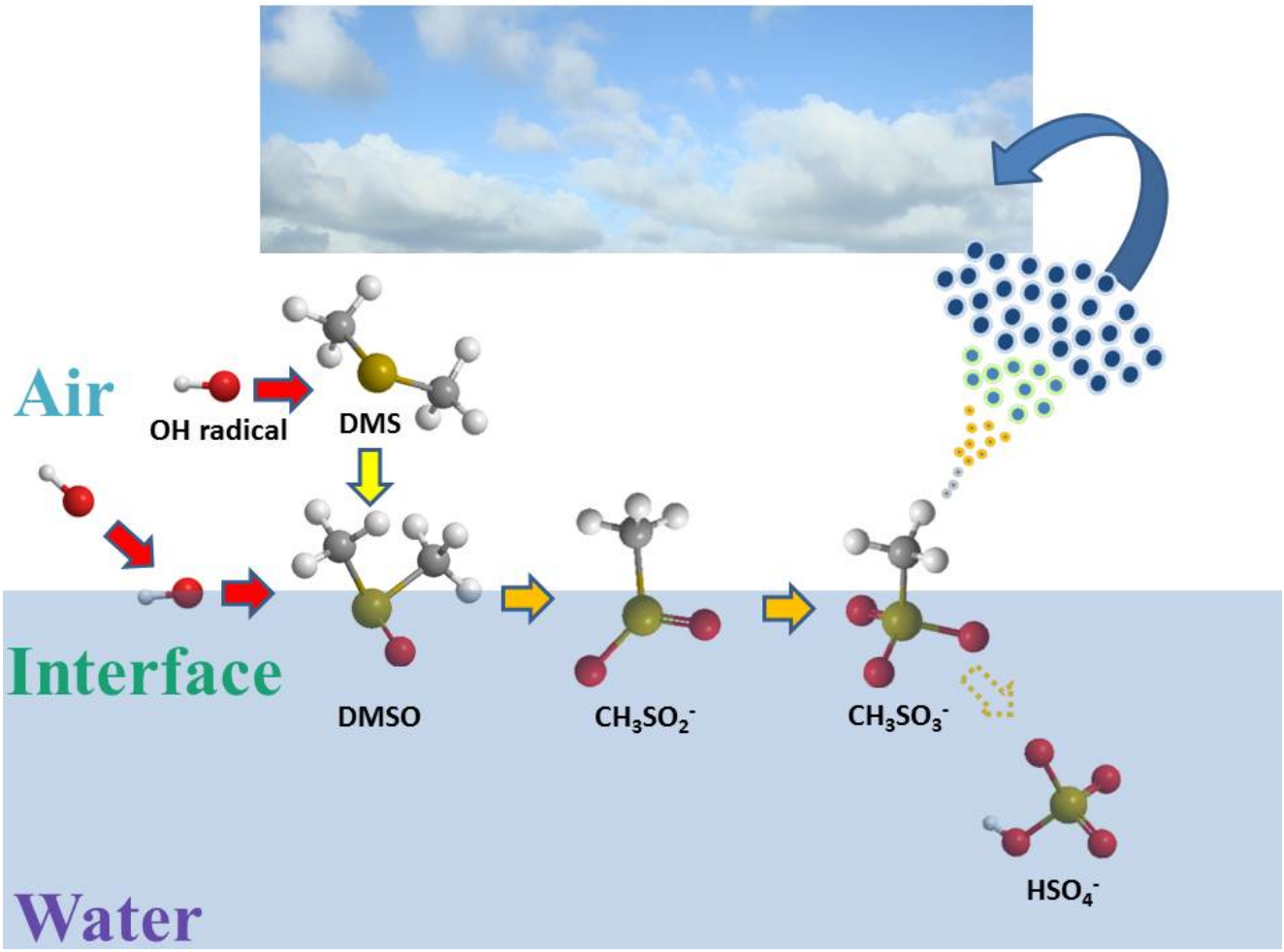
The oxidation of dimethyl sulfide (DMS) emitted from ocean (~ 45 Tg S per year) is a global source of cloud condensation nuclei. Hydrophobic DMS is mostly oxidized in the gas-phase into H_2SO_4(g) + DMSO(g) (dimethyl sulfoxide), whereas water-soluble DMSO is oxidized into SO_4^{2-} + $CH_3SO_3^-$ (methane sulfonate) on water surfaces. R = $CH_3SO_3^-/SO_4^{2-}$ ratios therefore indicate the extent of DMSO heterogeneous oxidation if R_{het} = $CH_3SO_3^-/SO_4^{2-}$ for DMSO(aq) + ·OH(g) were determined. Here, products and intermediates of the oxidation of aqueous DMSO initiated by gas-phase hydroxyl radicals, OH(g), at the air-water interface were directly detected by mass spectrometry in a novel setup under various experimental conditions. Exposure of millimolar DMSO aqueous microjets to ~ 10 ns OH(g) pulses from the 266 nm laser flash photolysis of O_3(g)/O_2(g)/H_2O(g)/N_2(g) mixtures yielded an array of interfacial intermediates/products, including $CH_3SO_3^-$ and HSO_4^-, that were unambiguously and simultaneously identified in situ by mass spectrometry. We determined R_{het} = 2.7 from the heterogeneous OH-oxidation of DMSO on aqueous aerosols for the first time. The nearly quantitative production of H_2SO_4(g) (that leads to SO_4^{2-}) in the oxidation of DMSO in the gas-phase versus the R_{het} ~ 2.7 value determined at the air-water interface means that R = $CH_3SO_3^-$/nss-SO_4^{2-} variations in the aerosol, particularly in remote locations, should arise from the competition between the gas-phase versus the heterogeneous DMSO oxidation pathways. The present study reveals that interfacial OH-oxidation processes play a more significant role in the generation and growth of atmospheric aerosol over ocean than previously envisioned.

Keywords: Aerosol, Photochemical aging, Climate change, heterogeneous reaction, marine chemistry



Development of a compact, simple and precise PM2.5 sensor and its applications

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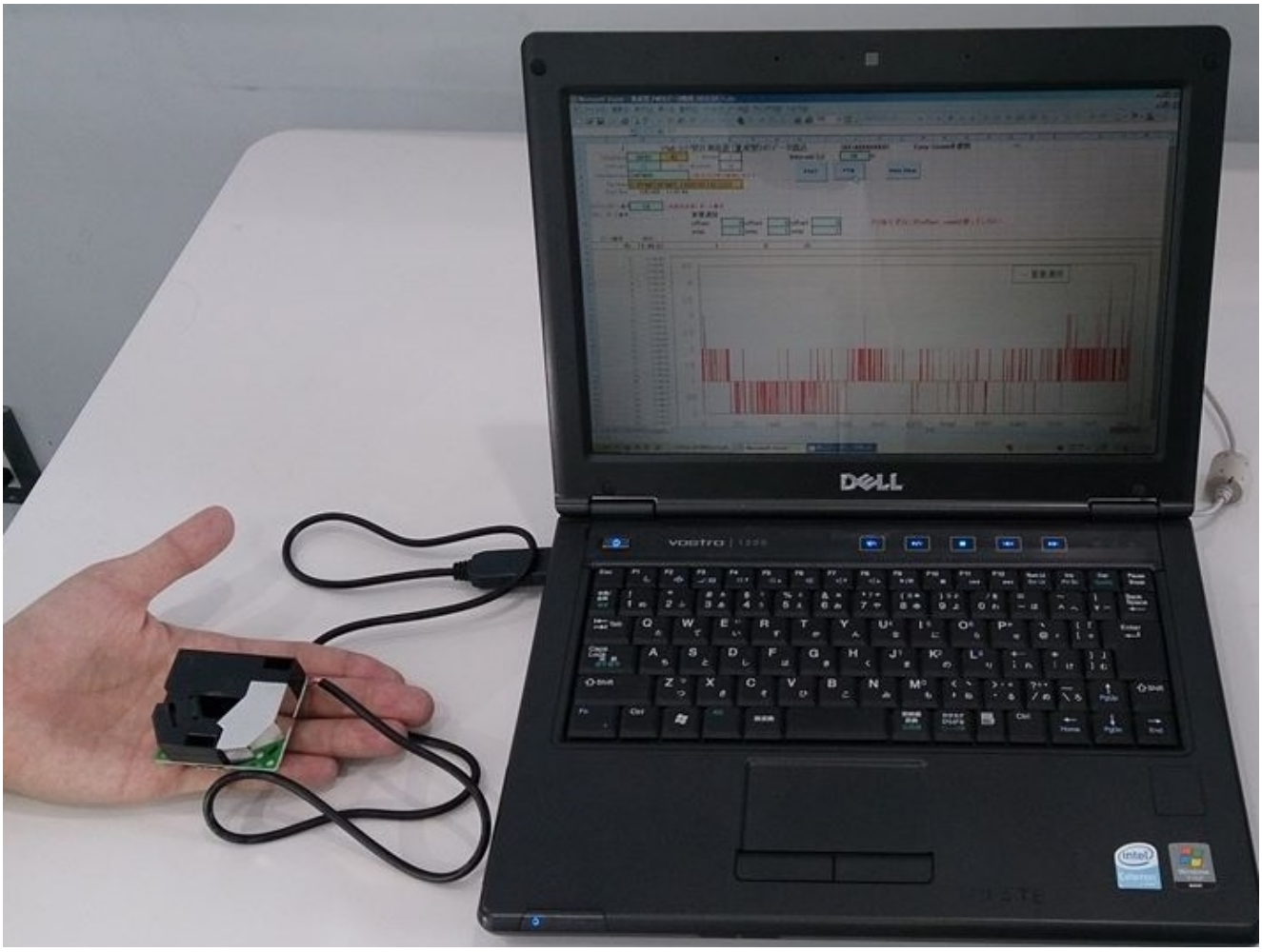
PM2.5 is the concentration of small particles floating in the air with the diameter size of less than 2.5 micrometer. The nation-wide interests about PM2.5 in Japan have increased since the PM2.5 concentration in Beijing, China became extra-ordinary high in 2013-2015. The high concentrations of PM2.5 in China influence not only the environmental conditions in China but also those in Japan through the long-range transportation across the border. The regulation for the PM2.5 concentration in Japan is defined in units of mass concentration. The upper limit values of the regulation are 15 microgram per cubic meter for one-year average and 35 microgram per cubic meter. For instruments for PM2.5 measurements, beta attenuation monitoring (BAM) and filter-based gravimetric method (TEOM) have been used in public observational stations and in environmental research stations. However, those instruments are very expensive and need accumulation time of about half a day for PM2.5 measurements. We have developed a compact and low-cost PM2.5 instrument in collaboration with Panasonic Corporation.
The new compact, palmtop PM2.5 instrument consists of a LED light source and photodiode detecting aerosol particle light scattering. To increase the precision of measurements, the sizes of individual aerosol particles are estimated from the intensities of the scattering light intensity and the PM2.5 mass concentrations are calculated. The PM2.5 measurement results for ambient air using the compact PM2.5 instrument indicated high correlation factor of > 0.8 with the results obtained by simultaneous measurement using a BAM instrument (Thermo, Sharp 5030).
Many applications of the compact, low-cost and simple PM2.5 instrument have been developed. In urban area, many instruments can be installed with high densities. Local PM2.5 sources in the urban areas can be detected with the PM2.5 instruments. 2D and 3D measurements in the atmosphere can be measured by installing the PM2.5 instruments on automobiles, drones (multicopters). Especially, the new PM2.5 instruments are suitable for the measurements in developing countries. Some of developing countries suffer from serious environmental problems of extremely high PM2.5 concentrations and their health effects. The PM2.5 observations in the developing countries have difficulty to install valuable and delicate PM2.5 instruments because of many serious difficulties about space, electric supply, dust, temperature, roof leaks, insects, safety, transportation, maintenance access, standard-gas supply and so on. The new PM2.5 instruments can be installed and operated in those conditions. The PM2.5 instruments widely distributed in high PM2.5 concentration area are suitable for epidemiological studies.
In this presentation, we will present the features of the compact PM2.5 instrument, and also present the new applications such as measurements on vehicles and in the developing countries. We have provided the measurement system which consist of a palmtop sensor and a computer with the USB cable connection. We have also provided the outdoor stand-alone system with small CPU and USB memory for year-long measurements. We will accept proposals of new applications of our compact PM2.5 instrument, and discuss the possibilities of collaborative work for the applications.

Keywords: Compact PM2.5 sensor, Instrument development, Atmospheric aerosol



Tar ball particles from biomass burning smoke

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Tar ball is a spherical organic particle emitted from biomass burning and is brown carbon that influences climate. Tar ball is abundant in ambient atmosphere and sometime dominates in aged biomass burning smoke. However, its effect on climate remains uncertain because both its composition and shape, which can be determined using microscopic technique, are necessary to identify tar ball. This study uses a transmission electron microscope with an energy-dispersive X-ray spectrometer (TEM-EDS) to analyze tar balls and aims to reveal its abundance in wild biomass-burning smoke and its micro-physical properties.
The samples were collected from wild fires in North America during Biomass Burning Observation Project (BBOP) 2013 aircraft campaign. BBOP campaign is an aircraft-based field campaign to study the near-field evolution of particulate emissions from biomass burning from July to October 2013. Aerosol particles from wildfires in the Western US (Idaho, Oregon, and Washington) and from agricultural burns in the Mississippi Embayment (Arkansas) were sampled. From these samples, number fractions of tar ball were measured from TEM images.
Tar balls primarily originated from wildfires and were lack in agricultural-burning smoke. They were abundant in relatively aged smoke (>several hours from emission), and the number fractions could reach more than half of all aerosol particles with aerodynamic diameter between 100 and 700 nm. Samples with relatively high tar ball fractions were focused, and the bulk optical and chemical compositions within the smoke with many tar balls will be discussed. Abundances and optical properties of tar balls shown in this study are useful to evaluate their effects on the global climate.

Keywords: aerosol, Transmission electron microscope, climate, tar ball, biomass burning

Observational study of wet removal process of black carbon particles

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Black carbon (BC) particles absorb visible solar radiation and heat the atmosphere. An improved understanding of wet removal process is important because it strongly influences temporal and spatial distribution of BC in atmosphere. There are two categories of removal mechanisms: nucleation scavenging and impaction scavenging. The former refers to the mechanisms that BC particles are incorporated into cloud droplets by serving as cloud condensation nuclei (CCN), while the latter refers to scavenging via impaction with cloud droplets or rain droplets. Theoretically, the efficiencies of these mechanisms depend on BC sizes. However, their relative contribution to the removal of BC has never tested by direct observation.
In this study, we observed relationships between size-dependent removal efficiency (RE) and size-dependent CCN activity in Tokyo during summer 2014 and 2015. The size-dependent RE was determined by measuring both size-resolved BC number concentrations in air and in rainwater. The size-dependent CCN activity was estimated by measuring coating thickness and hygroscopicity of BC particles.
Out of 32 rain events during observation period, the strong size-dependent RE was successfully explained by the size-dependent CCN activity for 29 rain events, indicating that nucleation scavenging was the dominant removal process of BC particles. For the other rain events, impaction scavenging might be also effective for larger BC particles.

Keywords: Black carbon, wet deposition

Aerosol single scattering albedo comparison between SKYNET and AERONET

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SKYNET and AERONET are two aerosol observing networks in the world. Though aerosol optical thickness (AOT) between them are reported to agree fairly well, their aerosol single scattering albedo (SSA) values have some difference. To explore the reasons behind inconsistent SSA between SKYNET and AERONET, we analyzed collocated observation data of SKYNET and AERONET of four sites, Chiba (Japan), Pune (India), Valencia (Spain), and Seoul (Korea). SKYNET and AERONET algorithms are found to produce nearly same SSAs for similarity in input data, suggesting that SSA differences between them are primarily due to quality of input data due to different calibration and/or observation protocols as well as difference in quality assurance criteria. The most plausible reason for systematically overestimated SKYNET SSAs is found to be underestimated calibration constant for sky radiances determined from the disk scan method in SKYNET, though the disk scan method is noted to produce stable wavelength dependent values in comparison to those determined from the integrating sphere used by AERONET. Aerosol optical thickness (AOT) difference between them can be the next important factor for their SSA difference, if AOTs between them are not consistent. Difference in surface albedos between SKYNET and AERONET while analyzing data can also bring SSA difference between them, but the effect of surface albedo is secondary. The aerosol non-sphericity effect is found to be less important for SSA difference between these two networks.

Keywords: aerosol, single scattering albedo, SKYNET

Analysis of individual aerosol particles collected at the top of Mt. Fuji in 2014 and 2015

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Atmospheric aerosol particles impact on climate effects by scattering and absorbing solar radiation directly, and by changing radiative properties of clouds indirectly as cloud condensation nuclei (CCN). Climate effects of atmospheric aerosol depend to a large extent on physicochemical properties of individual particles. Morphological features and mixing states of individual particles in the free troposphere are important to investigate aging of particles during long-range transport and its potential impacts on climate. To elucidate morphological features and chemical composition of individual particles according to their sources and weather conditions, we collected aerosol samples at the summit of Mt. Fuji (35.36°N, 138.73°E, 3776 m a.s.l) located in the free troposphere during summer in 2014 and 2015.
The aerosol samples were obtained using a cascade impactor (the 50 % cut-off diameters of the stages were 0.25 μm and 1.0 μm) on carbon-coated collodion films for 1 hour at flow rate of about 0.55 L/min. To measure the heights of individual particles, particles were coated with Pt / Pd alloy at a shadowing angle of arctan 0.5. Size and chemical composition of individual particles were analyzed using a transmission electron microscope (TEM) equipped with an energy-dispersive X-ray (EDX) analyzer. In this study, 11 samples were obtained and analyzed. The backward trajectories and the average relative humidity (RH) along the trajectories were computed using the HYSPLIT trajectory model (https://ready.arl.noaa.gov/HYSPLIT_traj.php).
In this study, the particles were classified into 9 types (Figure1) based on their morphological features (Ueda *et al.*, 2011). Most of particles were classified as *eroded, dome-like or cluster* particles. In this study, particles classified as the *cluster* particles were included in 6 samples. The *cluster* particles were comprised of some units of *spherical* or *coccoid* particles. It is reported that the *cluster* particles are formed under low RH and rich in sulfur (Ueda. *et al.*, 2011). In this study, however the *cluster* particles were formed under high RH condition. Analysis based on backward trajectories indicates that the sizes of individual particles that constituted *cluster* particles depend on sources and weather conditions. Therefore, the formation mechanism of cluster particles has to be investigated further.

Keywords: Atmospheric aerosol, TEM, Individual particles analyses

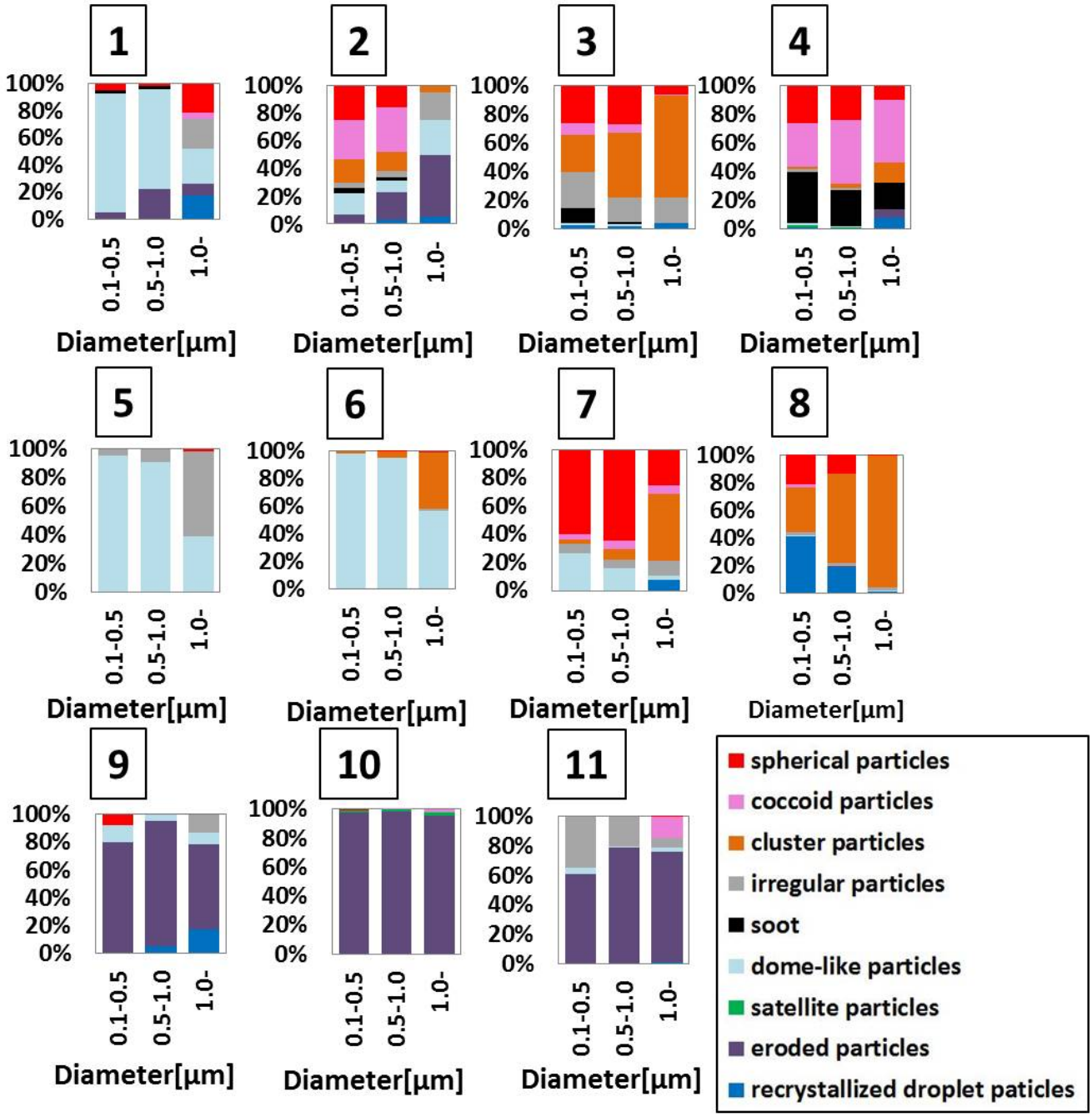

Figure. 1 Size-segregated number proportions of morphological types of particles for samples.

Off-Line Analysis of the Hygroscopicity of Water-Soluble Particulate Matter in the Urban Air of Nagoya

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Atmospheric aerosol particles are involved in the cloud formation process in the atmosphere by acting as cloud condensation nuclei (CCN). Whether the particles act as CCN are governed by the chemical composition as well as the size and the condition of the water-vapor supersaturation. The presence of water-soluble matter (WSM) in the particles is essential for the CCN activation. Because the composition of water-soluble fraction is complex in terms of the water-soluble organic matter (WSOM), it is difficult to understand the relationship between the composition of aerosol particles and their CCN activity. In this study, we investigated the hygroscopicity of the WSM and the WSOM in urban aerosols over Nagoya, based on the collection of aerosol samples on filters and the analysis of the CCN activity of the water soluble components in the laboratory. The relationship between the O/C ratio of the WSOM and their hygroscopicity was also examined.

Atmospheric aerosol particles with aerodynamic diameters smaller than 0.95 μm ($PM_{0.95}$) were collected on filters in the Higashiyama Campus, Nagoya University, Nagoya, Japan, from 11 to 31, August 2013. Ten aerosol samples were collected, and aerosol components on the filters were extracted with water. Particles were generated by atomizing an extract solution, and they were classified by size using a differential mobility analyzer (DMA). Whereas the classified particles were counted using a condensation particle counter (CPC), CCN-active particles among the classified particles were counted using a CCN counter (CCNC). Four different water-vapor supersaturation (SS) conditions of 0.13%, 0.27%, 0.47%, 0.90% were applied to investigate the CCN activity of the particles. Activation diameters were determined from size-resolved CCN fractions, and then the hygroscopicity parameter $\kappa$of WSM (κ_{WSM}) were calculated. The mass concentrations of WSOM in the sampled atmospheric aerosols were obtained from the analysis of WSOC using a total organic carbon analyzer and the OM/OC ratios derived from the mass spectra collected using a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). The hygroscopic parameter $\kappa$of the WSOM (κ_{WSOM}) was calculated using the κvalue of the generated particles and the chemical composition data. Two different methods, i.e., a regression-extrapolation method and a Zdanovskii, Stokes, and Robinson (ZSR) method for respective samples, were used to obtain the κ_{WSOM} values.

The κ_{WSM} ranged from 0.34 to 0.51 with a mean of 0.44. The κ_{WSOM} calculated from the regression-extrapolation method were in the range from 0.23 to 0.28 for four respective SS conditions. From the ZSR method for respective samples, the κ_{WSOM} were calculated to be on average 0.16 - 0.28. Whereas no clear relationship was observed for the κ_{WSOM} derived from the regression-extrapolation method and the SS conditions, the higher the SS condition was, the higher the κ_{WSOM} derived from the ZSR method for respective sample was. Further investigation about the cause of the difference of the κ_{WSOM} derived from these two methods is necessary. In the analysis of the studied ten aerosol samples, no clear relationship between the O/C ratio and the κ_{WSOM} was found (r: -0.21).

Individual particle analysis of marine aerosols collected over the Pacific Ocean and its marginal seas

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Sea-salt particles are produced by bubble bursting processes at the sea surface. Chemical compositions of sea-salt particles are modified when they react with acidic substances such as sulfuric acid (H_2SO_4), nitric acid (HNO_3) and methanesulfonic acid (MSA) in the atmosphere. The sources of acidic substances include anthropogenic pollutants, volcanic eruptions and dimethyl sulfide (DMS) from marine biota. If the acidic substances react with sea-salt particles, they are easily scavenged from the atmosphere. So the lifetime of acid substances in the atmosphere will be reduced and they are unlikely to be cloud condensation nuclei. Therefore cooling effect of clouds might be smaller than expected in the environment where sea-salt particles are abundant. In this study, difference in chemical compositions of sea-salt particles among ocean regions was revealed based on individual particles analyses of marine aerosols collected over the Pacific and its marginal seas. Additionally, source of acidic substances that modified sea-salt particles was discussed.

Sampling of marine atmospheric aerosol particles was carried out during KH-13-7 cruise (2013/12/11~2014/2/12) and KH-14-3 Leg2 cruise (2014/7/17~8/11) in the Pacific and its marginal seas. Individual particles were analysed using a transmission electron microscope and an energy dispersive X-ray spectrometer.

In most ocean regions, unmodified sea-salt particles accounted for more than 80% of the analysed particles. However, sulfate particles accounted for more than 85% in the sample collected around Guam islands. High concentrations of radon and number of aerosol particles, along with analysis of backward trajectories suggested that polluted air masses originated from the Asian continent came to the observation area. The aerosols collected around the Aleutian Islands included large number of sulfate and modified sea-salt particles. A Na-Cl-S ternary diagram indicates that sea-salt particles were modified with MSA produced from DMS oxidation or H_2SO_4. Air masses from a volcano transported from the Kamchatka were also the potential source of H_2SO_4 around the Aleutian island.

Keywords: marine atmospheric aerosol, sea-salt, sulfate, volcano, dimethyl sulfide, methanesulfonic acid

Evaluation of performance of simulated secondary air pollutants by using air quality models for the Kanto area in summer 2011

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Emissions and concentrations of primary atmospheric pollutants (eg. NOx and VOCs) have been decreased in the Kanto area owing to conduct their emission regulations. Nevertheless, atmospheric pollutants such as particulate matters (PM) with aerodynamic diameter less than 2.5 μm (PM2.5) and photochemical oxidants (Ox) have still remained high concentration levels and their air quality standards of Japan have not been attained at most monitoring stations (Ministry of the Environment of Japan (MOE), 2015). For forming effective air pollution control strategies, currently, we raise expectations for applying air quality models reproducing complicated physical and chemical processes of both of primary and secondary pollutants.
The urban air quality model inter comparison study in Japan (UMICS) was started to improve performances of air quality models (eg. Chatani et al., 2014, Shimadera et al., 2014). UMICS showed some critical problems immanent in the air quality models. For example, the models tended to overestimate NO_3^- but to underestimate OA, although simulated PM2.5 concentrations were reasonable with comparing to observations at Kanto area (Shimadera et al., 2014). In terms of O_3, the models reproduced well the diurnal and inter-diurnal variations in the O_3 concentrations at most observational stations in Kanto area but tended to overestimate nighttime O_3 and to underestimate daytime O_3 at several observational stations (Morino et al., 2010), therefore these models might have a risk failing to predict some of high pollution events.
In order to find the causes of discrepancies between the simulated and observed concentrations of secondary pollutants, constituents of PM2.5 and O_3, in this study, air quality simulations were performed using the Weather Research and Forecasting (WRF) model for a meteorological model and the Community Multi-scale Air Quality (CMAQ) model system for a chemical transport model under the following different model settings. Meteorological analysis data (FNL/NCEP and MSM/JMA) with both different temporal and spatial resolutions were used as for input data of meteorological simulations by the WRF model, respectively. Additionally, the updated JEI-DB (JATOP Emission Inventory Data Base) was used for input emission information for the CMAQ model. Performances of these models under different settings were evaluated by comparing with observed concentrations (O_3, PM2.5, and constituents of PM2.5) of secondary pollutants at Kanto area, which were provided by UMICS and MOE. These results are also compared with the previous studies (eg. Shimadera et al., 2014).

Keywords: Air quality model, secondary pollutants, Urban Air quality

Development of a global aerosol model using a two dimensional bin method

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Atmospheric aerosols play an important role in Earth's climate system through radiation and cloud/precipitation processes. Estimates of these aerosol impacts on climate remain highly uncertain, and they are one of the largest uncertainties in predicting climate change. Accurate estimations of these effects through a model require good representations of number concentration, size distribution, and mixing state of aerosols. However, many of existing three-dimensional aerosol models do not represent these aerosol parameters sufficiently. In our previous studies, we developed an aerosol model, the Aerosol Two-dimensional bin module for foRmation and Aging Simulation (ATRAS), that can explicitly calculate aerosol number concentration, size distribution, and mixing state with a two-dimensional bin representation. The ATRAS model was implemented into a regional three-dimensional model WRF-chem, and we have shown the importance of aerosol simulations using a model that can treat detailed aerosol processes and parameters [Matsui et al., 2014; Matsui, 2016a, 2016b]. In this study, we developed a new aerosol model based on the ATRAS model and implemented it to a global climate model CAM5.

The computational cost is one of the most important factors in the development of a global aerosol model using a two-dimensional bin representation because global and long-term simulations are necessary in a global modeling study. To reduce the computational cost, we developed a new aerosol box model by improving the source codes of all aerosol microphysical and chemical processes in the ATRAS model and by reducing the number of aerosol variables considerably. These changes reduced the computational cost of aerosol microphysical and chemical processes by 90% compared with the original ATRAS model with keeping the accuracy of simulations for aerosol number concentration, size distribution, and mixing state.

We implemented this new box model to CAM5 and conducted five-year test simulations. The model simulations were validated through the comparison with the original aerosol model in CAM5 (MAM) and various surface and aircraft measurements of aerosols. We also calculated global distributions of some aerosol parameters that can be estimated globally for the first time by using our detailed aerosol model.

In the presentation, we would like to show the concepts and results of the new box model and the results of global model simulations such as the comparison with MAM simulations and measurements and sensitivity simulations.

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Matsui, H. (2016b), J. Geophys. Res. Atmos., 121, doi:10.1002/2015JD023999.

Keywords: Aerosol, Global aerosol model, Two-dimensional bin model, Number concentration, Size distribution, Mixing state

Estimating global budget of formaldehyde and BVOCs emission using satellite observations and global chemistry transport model

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This study evaluates global distribution and budget of atmospheric formaldehyde using satellite measurements and global chemistry-transport model simulations, particularly focusing on the roles of global emission of biogenic VOCs (BVOCs) and methane oxidation. Formaldehyde (HCHO) is chemically produced by oxidation of methane (CH_4) and volatile organic compounds (VOCs) in the atmosphere, and hence its global budget can be used for deriving methane concentrations and VOCs emissions. For simulating global HCHO, this study uses a global chemistry-transport model CHASER (MIROC-ESM version) which considers detailed chemistry in the troposphere and stratosphere with an on-line aerosol simulation including production of particulate nitrate and SOA. We use the NCEP reanalysis data (FNL) for constraining the model's meteorology. Anthropogenic and biomass burning emissions are specified using the EDGAR-HTAP2 and MAC inventories, respectively. For a base emission of BVOCs, we employ calculation by the land ecosystem/trace gas emission model VISIT (Ito et al., 2008) and MEGAN (Guenther et al., 2006) for 2000-2012. In this study, global emission of BVOCs is first estimated employing a series of emission sensitivity simulations by CHASER in combination with the global and regional HCHO distributions derived from the OMI satellite observation. As a result, the global emission amount of isoprene (a major component of BVOCs) is estimated at 300 - 400 TgC yr^{-1}, suggesting that the current estimates as by the VISIT and MEGAN land-ecosystem models (> 500 TgC yr^{-1} for isoprene) are probably overestimated. For the global budget of HCHO, the model with global isoprene emission of 400 TgC yr^{-1} estimates a major contributions from the CH_4 oxidation (ca. 66%) to the global production of HCHO, which is followed by oxidation of BVOCs (ca. 21%) and anthropogenic and biomass burning related VOCs (ca. 13%). The CH_4 contribution to the global HCHO production, inferred from the OMI HCHO observation, is about 71%, significantly larger than the above-estimated value, suggesting that global isoprene emission may be less than 300 TgC yr^{-1} or that anthropogenic VOCs emissions in the current inventories may be overestimated.

Keywords: BVOCs, Isoprene, Formaldehyde, OMI satellite observation, Chemistry-transport model

Contribution of plant-associated microorganisms as global sinks of atmospheric hydrogen

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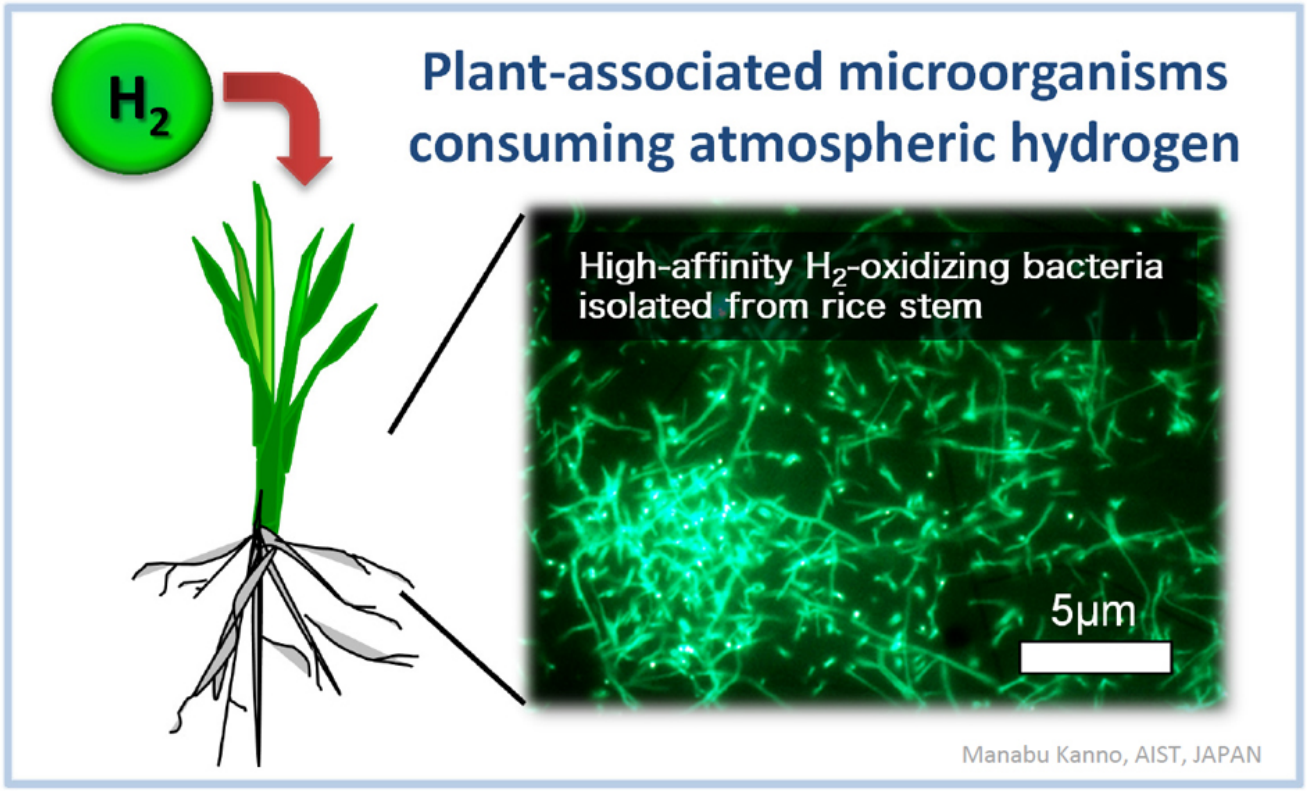
Hydrogen (H_2) is an important constituent of the atmosphere, with a typical mixing ratio of 0.530 parts per million by volume (ppmv). Rising H_2 emissions under a future H_2-based economy are concerned to increase the atmospheric burden of H_2, resulting to the indirect influence of the lifetime of greenhouse gas CH_4, an alteration of temperature and ozone loss in the stratosphere. Thus, mitigation of H_2 emission is of critical importance for atmospheric chemistry. The most part (~80%) of tropospheric H_2 is consumed by microorganisms in soil. A recent literature survey of H_2 flux measurements unveiled that soil H_2 uptake is responsible for the loss of 40 to 90 Tg yr^{-1}. Recently, high-affinity H_2-oxidizing bacteria possessing novel hydrogenase have been found as important contributors to the soil H_2 uptake. Although previous experiments using molecular tritium reported the occurrence of significant H_2 uptake activity in vegetation, there has been no report on the identification and diversity of the responsible microorganisms. This study aimed to verify the existence of plant-associated bacteria possessing the ability to consume atmospheric H_2.

We first investigated the presence of *hhyL* gene in various plant species. The *hhyL* gene, which encodes for the large subunit of the novel group of hydrogenase, has been generally used as a functional biomarker to evaluate the distribution, taxonomic diversity, and abundance of high-affinity H_2-oxidizing bacteria. In total, 42 *hhyL* gene sequences were successfully detected in all tested herbaceous plants, indicating a wide distribution of high-affinity H_2-oxidizing bacteria in plants. It is noteworthy that the abundance levels of *hhyL* gene detected in plants were comparable to those detected in soil. High-affinity H_2-oxidizing bacteria were isolated from inside herbaceous plant tissues. Among 145 isolates, 7 *Streptomyces* strains were shown to possess *hhyL* gene. The H_2 uptake activity was evaluated by gas chromatography. All the isolates reduced H_2 concentration to less than 0.530 ppmv, demonstrating the ability to consume H_2 at ambient level. Sterile plant seedlings were inoculated with selected isolates to verify their ability to penetrate and disseminate in plant tissues and scavenge atmospheric H_2 in plant. After four weeks of seedling inoculation, an internalization of the bacteria in plant tissues was visualized by fluorescence *in situ* hybridization imaging. H_2 oxidation rates measured in plant fractions ranged from 1079 to 3472 pmol $g_{(dw)}^{-1}$ h^{-1}. These rates are comparable to the previously observed activity of atmospheric tritium uptake in other plants. Importantly, atmospheric H_2 is not oxidized in aseptically grown plants, clearly showing that plant-associated bacteria was responsible for H_2 loss. H_2 uptake activity per bacterial cell was comparable between plant and soil, demonstrating that both environments are favorable for the microbial-mediated H_2 uptake.

In conclusion, this study demonstrated the occurrence of plant-associated high-affinity H_2 -oxidizing bacteria and their ability to consume atmospheric H_2 on plant surface or inside plant tissues. From a global perspective, herbaceous and woody plant biomass represent approximately 64 Pg, and 736 Pg, respectively. Considering that high-affinity H_2-oxidizing bacteria may be present and active in these plants, the contribution of plant-associated bacteria deserves more attention to better understand the global cycling of atmospheric H_2.

Keywords: biogeochemistry, microbial ecology, tropospheric H2 cycle, vegetation



Estimating secondary formation of atmospheric HONO using triple oxygen isotopes as tracers

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The photolysis of nitrous acid (HONO) has been recognized as a potentially important source of OH radicals, which is known as a major oxidant in the atmosphere removing reductive trace gases such as methane and NMHCs. Atmospheric HONO originates from both primary sources (direct emissions) and secondary sources (chemical formation in the atmosphere), however, their contributions to atmospheric HONO production have not been well understood. Here, we determined a triple oxygen isotope of HONO because $\Delta^{17}O$ value of HONO produced via “secondary formation” is expected to have highly positive values as those of O_3 ($\Delta^{17}O$ = +30 ±10‰), while no $\Delta^{17}O$ anomaly ($\Delta^{17}O$ = 0‰) should be observed for HONO which is emitted directly from various sources on the ground, making it possible to quantify their contribution to the atmospheric HONO production with $\Delta^{17}O$ measurement. Periodical sampling of atmospheric HONO was carried out once a month starting from December, 2014 at Hokkaido Institute of Environmental Sciences, Sapporo, Japan. The sample collection period was fixed to one week with a flow rate of 10 L/min. $\Delta^{17}O$ value of HONO was determined by combining sensitive determination method on isotope compositions of NO_2^- (Komatsu *et al.*, 2008; Tsunogai *et al.*, 2010) with filter-pack method (Noguchi *et al.*, 2007) in which to collect HONO as NO_2^-. The result of daily mean $\Delta^{17}O$ value of HONO ranged from +6.9‰ to +10.7‰ through the observation periods. $\Delta^{17}O$ value of HONO showed higher value on the day time than night time. The ratios of HONO derived from secondary formation in Sapporo was almost constant throughout the year (day and night : 34±2%, day : 66±8%, night : 21±2%) leading to conclusion that direct emissions are dominant HONO sources in Sapporo.

Keywords: HONO, tripple oxygen isotopes, secondary formation, direct emission, atmosphere

