

Time and space variations of the O₂/N₂ ratio observed over the western North Pacific using a cargo aircraft C-130H

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The atmospheric O₂/N₂ ratio ($d(O_2/N_2)$) has been observed at many ground-based stations since the early 1990s to elucidate the global CO₂ budget (e.g. Manning and Keeling, 2006), however, airborne observations of $d(O_2/N_2)$ in the free troposphere are very limited (e.g. Ishidoya et al., 2012). In this study, the air samples collected using a cargo aircraft C-130H in service between Atsugi Base (35.45 N, 139.45 E) and Minamitorishima (MNM; 24.28 N, 153.98 E) have been analyzed for $d(O_2/N_2)$, Ar/N₂ ratio ($d(Ar/N_2)$), $d^{15}N$ of N₂, $d^{18}O$ of O₂ and $d^{40}Ar$ to clarify time and space variations of the $d(O_2/N_2)$ in the mid-troposphere.

The observations onboard the C-130H are conducted once per month, and 24 air samples are collected into 1.7 L Titanium flasks during the level flight at an altitude about 6 km and descent toward MNM (Tsuboi et al., 2012). 6 air samples are also collected into the similar flasks at the ground surface in MNM around the same time period with the C-130 H observation. The total of 30 air samples are analyzed for CO₂, CH₄, N₂O and CO concentration at Japan Meteorological Agency, then analyzed for $d(O_2/N_2)$, $d(Ar/N_2)$, $d^{15}N$ of N₂, $d^{18}O$ of O₂ and $d^{40}Ar$ at AIST since May 2012.

The $d^{15}N$ of N₂, $d^{18}O$ of O₂ and $d^{40}Ar$ are known to be almost constant in the troposphere, and the $d(Ar/N_2)$ shows slight seasonal cycle at the ground surface with the peak-to-peak amplitude of 10-30 per meg (e.g. Casser et al., 2008). However, the $d(Ar/N_2)$, $d^{15}N$ of N₂, $d^{18}O$ of O₂ and $d^{40}Ar$ from the C-130H observations were found to be significantly different from the surface values at MNM. Especially, the $d(Ar/N_2)$ of the air samples collected during the level flight were higher by about 800 per meg than the surface values. Such the large variations in the $d(Ar/N_2)$ were considered to be due to some sort of the artificial fractionations of Ar and N₂. Therefore, we examined the relationships between $d(Ar/N_2)$, $d^{18}O$ of O₂ and $d^{40}Ar$ and $d^{15}N$ of N₂ to clarify the cause of the fractionation. The obtained relationships were highly consistent with those expected from the fractionation due to the thermal diffusion (Ishidoya et al., 2013), which would be attributed to the branching of flow paths (e.g. Bender et al., 2005) of the ambient air supplied from the jet engine to pressurize the cabin of the C-130H. Taking these facts into consideration, we corrected the $d(O_2/N_2)$ obtained from the C-130H observation for the fractionation by using an experimentally-determined relationship of the $d(Ar/N_2)/d(O_2/N_2)$ due to the thermal diffusion and the measured values of the $d(Ar/N_2)$. Because the $d(Ar/N_2)/d(O_2/N_2)$ ratio due to the thermal diffusion and the measurement precision of the $d(Ar/N_2)$ were about 4.5 and +5 per meg, respectively, the uncertainty of $d(O_2/N_2)$ associated with the correction was estimated to be about +1 per meg. This uncertainty is smaller enough than +4.8 per meg (+1 ppm) of the precision required for the precise observation of the atmospheric $d(O_2/N_2)$. Therefore, it is suggested that variations of the $d(O_2/N_2)$ in the free troposphere are observable using the C-130H by applying the correction method.

The corrected $d(O_2/N_2)$ and CO₂ concentration varied seasonally almost in opposite phase at all heights. The average Atmospheric Potential Oxygen (APO = O₂ +1.1 x CO₂) (Stephens et al., 1998) during the observation period (May - December 2012) decreased with increasing altitude, which implied the net O₂ outgassing from the ocean around MNM for the period. In the presentation, we will also discuss the characteristic variations of the $d(O_2/N_2)$ observed in the free troposphere based on the analyzed results of comparisons of the $d(O_2/N_2)$ with the CO₂, CH₄, N₂O and CO concentration as well as the backward trajectories for the observation dates. The correction method employed in this study will make it possible to observe the $d(O_2/N_2)$ precisely using air samples collected without special sampling techniques to reduce the fractionations of the molecules.

Keywords: aircraft observation, atmospheric O₂/N₂ ratio, Atmospheric Potential Oxygen (APO), correction method for fractionation of O₂ and N₂

Analyses for CO₂ source in the urban area: measurement of stable isotope ratio of CO₂ and CO₂, CO, NO_x

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CO₂ has the most effect on the global climate change because CO₂ has the largest positive radiative forcing (IPCC 2007). The accurate estimation of the CO₂ emission and loss flux are necessary to improve the prediction of the global climate change in the future, because the variations of CO₂ concentration substantially contributes to the variations of the global radiative forcing. CO₂ concentration varies due to the emission from the gasoline and natural gas combustion, biomass burning, and ecosystem respiration, the absorption due to the photosynthesis, the absorption into ocean and emission from the ocean surface. In the urban area, the variation of CO₂ concentration depends on the anthropogenic emission such as the fossil fuel combustion (gasoline and natural gas) and background CO₂ concentration mainly.

We conducted the continuous measurement of carbon and oxygen isotope ratios of CO₂ ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) using the infrared absorption laser spectrometer. The infrared absorption laser spectrometer can continuously measure $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ in high time resolution (10 seconds). The measurement period was from July 20 to August 10, 2012 at Nagoya University. Simultaneously, we measured the concentrations of nitrogen oxides, CO, water vapor and stable isotope ratios of water vapor (δD and $\delta^{18}\text{O}$). The variations of CO₂ concentrations, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ shows the contribution of the fossil fuel combustion and ecosystem respiration to the carbon cycle in the urban area.

Measured CO₂ concentrations and stable isotope ratios ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) show the diurnal variation in the measurement period. CO₂ concentrations decreased in the daytime and had a peak in the nighttime. On the other hand, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ had a peak in the daytime and decreased in the nighttime. This indicates that the variations of CO₂ concentration were substantially affected by the ecosystem respiration and photosynthesis in the urban area. We conducted the keeling plot analyses for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the nighttime to estimate the contributions of the fossil fuel combustion, biomass burning, and ecosystem respiration. In addition of the keeling plot analyses, we estimated CO₂ source from the relationship between the variations of CO and CO₂ concentrations. CO is emitted by the fossil fuel combustion and biomass burning mainly, while, CO₂ generated by the fossil fuel combustion, biomass burning and ecosystem respiration. Therefore, the relationship between CO and CO₂ concentration shows CO₂ source; the larger ratios of CO to increment of CO₂ from the background level (δCO_2) shows the contribution of the fossil fuel combustion or biomass burning, on the other hand, the smaller ratios of CO to δCO_2 shows the contribution of the ecosystem respiration. We will discuss the source of CO₂ from the analyses of the ratios of CO to δCO_2 and keeling plot.

Keywords: Carbon dioxide, Stable isotope ratio, Laser spectrometry, CO₂ Source estimation, Carbon monoxide

NO₂ observed by MAX-DOAS at Fukue Island: Comparison to ground-based observations and long-term variations

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Since spring 2009, we conduct observations of NO₂ and aerosols at Fukue Island (32.75N, 128.68E) using MAX-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy), in addition to surface monitoring of O₃, PM_{2.5} and black carbon, to elucidate regional air pollution over East Asia. Differential slant column densities (DSCDs) of NO₂ and O₄ are first determined for the UV/vis spectra observed at low elevation angles (3, 5, 10, 20, and 30 degrees) with respect to the zenith observations used as reference. Aerosol profile is first retrieved such that the O₄ DSCDs are consistent with radiative transfer and then the tropospheric column density of NO₂ and its vertical profile are optimally estimated. At Fukue Island, in-situ NO₂ observations were made using a chemiluminescence instrument equipped with a photolytic converter in May-June 2009 and a laser-induced fluorescence instrument in March-June 2010, respectively. These data were successfully used to evaluate the NO₂ quantities derived from MAX-DOAS observations. We analyzed diurnal to seasonal variations of NO₂ in 2009-2012, derived from MAX-DOAS. Wintertime maxima were regularly observed during this period. High NO₂ concentrations were recorded when air mass was rapidly transported from Korean Peninsula. Such transport was sometimes evident in spring period, affecting the ozone production regime there.

Keywords: Nitrogen Oxides, MAX-DOAS, instrument comparison, long-term variation, aerosol

An evaluation of the CMAQ reproducibility of satellite tropospheric NO₂ data at different local times over East Asia

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Despite the importance of the role of nitrogen dioxide (NO₂) in the troposphere, causes leading to a discrepancy between satellite-derived and modeled tropospheric NO₂ vertical column densities (VCDs) over East Asia remain unclear. Here the reproducibility of satellite tropospheric NO₂ VCD data by a regional atmospheric chemistry model (CMAQ) with the Regional Emission inventory in ASia (REAS) Version 2 is evaluated from the viewpoint of the diurnal variation of tropospheric NO₂ VCDs, where satellite observations at different local times (SCIAMACHY/ENVISAT, OMI/Aura, and GOME-2/Metop-A) are utilized considering literature validation results. As a case study, we concentrate on June and December 2007 for a detailed evaluation based on various sensitivity runs, for example with different spatial resolutions (80, 40, 20, and 10 km) for CMAQ. For June, CMAQ generally reproduces absolute values of satellite NO₂ VCDs and their diurnal variations over all selected 12 diagnostic regions in East Asia. In contrast, a difficulty arises in interpreting a significant disagreement between satellite and CMAQ values over most of the diagnostic regions in December. The disagreement cannot be explained by any sensitivity runs performed in this study. To address this, more investigations, including further efforts for satellite validations in wintertime, are needed.

Keywords: NO₂, CMAQ, satellite data, diurnal variation

Multiple species constraints on surface NO_x emission inversion

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Satellite NO₂, CO, O₃, and HNO₃ data are assimilated into a chemical transport model to estimate global surface NO_x emissions and their seasonal variation in 2007. The data assimilation of data for multiple species provides comprehensive constraints on the NO_x emissions by limiting model errors in NO_x chemistry. The non-NO₂ data changed the regional and hemispheric monthly total NO_x emissions by 50% and 13-29%, respectively. These large changes introduced by the inclusion of non-NO₂ data imply a large uncertainty in the NO_x emissions inverted from NO₂ data only. Compared to the emission inventories, the estimated NO_x emissions show enhanced seasonal variations with the maximum emissions at most of the northern mid-latitudes occurring 1-2 months earlier. An analysis of the background error covariance demonstrates that additional constraints from other chemically related species (e.g., isopren and formaldehyde) have the potential to further improve surface NO_x emission analyses.

Keywords: NO_x emission, Data assimilation, Satellite observation

Trend and interannual variation of the stratospheric CO₂ in the past 25 years

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Systematic collections of stratospheric air samples have been carried out over Japan since 1985, using a balloon-borne cryogenic sampler. The stratospheric air samples have been collected almost once a year or two years at 11 assigned heights, ranging from the tropopause to 30 - 35 km. The air samples were analyzed for various gas concentrations, such as CO₂, CH₄, N₂O, and SF₆, and their isotopes. Measurements of the stratospheric CO₂ concentration are one of the most promising methods to detect possible changes in the stratospheric circulation, because chemical loss and production are negligible in the stratosphere and its long-term trend in the troposphere is propagated into the stratosphere, with some time lag. Increasing trend of the CO₂ concentration was clearly found at heights above 20-25 km, where the CO₂ concentration becomes almost constant vertically. To clarify the difference of the secular CO₂ increases between the mid-stratosphere and the troposphere, the average values of the CO₂ concentration, calculated from the balloon data obtained at heights above 20-25 km, were compared with annual mean CO₂ concentrations at Mauna Loa (MLO) observed by NOAA/ESRL. The average increase rate of the CO₂ concentration in the mid-stratosphere, calculated by using a least-squares method, was 1.55(+0.03) ppmv/year. This value is significantly smaller than 1.73(+0.03) ppmv/year calculated for the same period for MLO data. Considering that the mid-stratospheric CO₂ concentration corresponds to the tropospheric values earlier by 4-5 years, the CO₂ increase rate in the stratosphere should be compared with the tropospheric values shifted by the same years. The average increase rate, thus calculated for the period 1981-2005, was 1.62(+0.03) for MLO data. This value is slightly smaller than those described above, due to interannual variations of CO₂ increase rate in the troposphere, but still larger than the stratospheric value. These facts imply that the concentration difference between the troposphere and mid-stratosphere gradually increased during the last 25 years. The interannual CO₂ variation in the mid-stratosphere was first discovered by our balloon measurements. The secular CO₂ increase in the mid-stratosphere is not monotonous, probably due to the propagation of interannual variations in tropospheric CO₂, being accompanied by time delay. The CO₂ anomalies in the mid-stratosphere, calculated as deviations from the second order polynomial trend and then shifted by -4.5 years, are fairly correlated with those in the troposphere. Such a correlation is found especially in CO₂ anomalies observed in the troposphere for a few years after 1991, which is known as the Pinatubo anomaly. This result suggests that the stratospheric air age can be newly estimated from the phase shift of the interannual CO₂ variations.

Keywords: CO₂, Stratosphere, Long-term trend

Relationship between polar stratospheric cloud types and ozone destruction

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Polar stratospheric clouds (PSCs) can appear at a temperature lower than nitric acid trihydrate (NAT) saturation temperature in the polar lower stratosphere. PSCs cause large ozone destruction by heterogeneous reactions on particle surface and denitrification by gravitational sedimentation in the polar spring. PSCs can be classified into three major types (Type Ia, Ib, and II). Type Ia is a solid particle which is comprised of NAT. Type Ib is a liquid particle called supercooled ternary solution (STS) which is composed of HNO₃, H₂SO₄, and H₂O. Type II is water ice particle.

In general, the probability of PSC formation is closely related to the magnitude of chemical ozone loss. However, Terao et al. (2012) showed that the average ozone destruction rate in 1996 and 2000 Arctic winter were different when the average PSC sighting probabilities were similar. As one of the possible reason, we assumed a hypothesis that PSC types may influence the magnitude of ozone destruction. Therefore, we investigated the relationship between PSC types and the ozone destruction rate statistically.

We used the observational data from CALIOP lidar on board the satellite CALIPSO. PSCs observed by CALIOP were categorized into 6 types; i.e. Mix 1, Mix 2, Mix 2-enhanced, Ice, Wave-ice, and STS (Pitts et al. 2007, 2009, 2011). Mix is a PSC type category which contains NAT and STS. We quantified the ozone destruction rate of PSC types observed in 2007 Antarctic winter and in 2009/10 Arctic winter by using a Satellite-Match technique with the observational data of MLS on board the satellite Aura. As a result, it was confirmed that the average ozone destruction rate were different in every PSC type. Especially, the average ozone destruction rate of STS and Mix were larger.

Furthermore, we investigated the relationship between backscatter ratio as an index of particle number density and ozone destruction rate for every PSC type. As a result, it was confirmed that there are positive correlation between backscatter ratio and ozone destruction rate in all PSC types. As a result of the simple linear regression fitting using backscatter ratio as an independent variable, the regression coefficient for Mix PSC is the largest. It is thought that PSCs including NAT and STS have the highest potential for large-scale ozone destruction.

Keywords: Polar stratospheric cloud, Ozone destruction, Satellite-Match technique, CALIPSO

Unusual aerosol enhancement in Antarctic troposphere during spring

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Antarctic region is isolated from the other continents with human activities. Nevertheless, high aerosol concentrations (Antarctic haze) were observed occasionally near surface at Syowa Station, Antarctica, during winter ? spring (Hara et al., JGR, 2010). Vertical distributions of the Antarctic haze were obtained in a few tethered-balloon-borne aerosol measurements and a lunched-balloon borne aerosol measurement at Syowa Station (Hara et al., ACP, 2011). Spatial features of the aerosol enhancement, however, have not been discussed well. This study aims to elucidate spatial features of aerosol enhancement (Antarctic haze) over Syowa Station by simultaneous measurements in near surface ~ upper atmosphere. Condensation particle counter (CPC), optical particle counter (OPC), and aethalometer were used to measure physical properties of aerosols near surface. Micro-pulse LIDAR (MPL) and aerosol sonde (balloon-borne OPC) were used to measure vertical distributions of aerosol particles over Syowa Station in this study. Balloon-borne aerosol measurements carried out under aerosol enhanced conditions near surface on 14 August and 6 September, 2012. High aerosol enhanced conditions near surface on 13-16 August, 2012 were observed immediately after storm condition. MPL measurements exhibited that aerosols were enhanced in ~ ca. 2.5 km on 13 - 16 August. In contrast, aerosol enhancement near surface on 5 - 7 September, 2012 appeared suddenly under the calm wind conditions. Although aerosol number concentrations near surface dropped markedly before the aerosol enhancement (00-15UT on 5 September), strong aerosol enhancement was found around 1-1.5 km since 05UT on 5 September in the MPL measurements. Although strong aerosol enhanced layer was distributed mostly in ~3km, high relative backscatter was observed occasionally in 3 ~ 4 km on 6 September. Here, we discuss aerosol features and distributions in the twice simultaneous measurements.

Identification of Sources of Lead in the Atmosphere by its Speciation and Isotopic Composition

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1. Introduction

Recently, chemical reactions of major elements occurred in the atmosphere have been clarified, whereas those of trace metals have not. In particular, formation processes of Pb species, which is concerned to cause a health hazard, are still unclear. The identification of species and formation process of Pb is important to evaluate the human hazards. In addition, Pb species is expected to be used as a transboundary pollution tracer, because Pb species are different depending on each emission area. In this study, Pb species in size-fractionated aerosol sample were determined by XAFS spectroscopy together with the Pb isotope ratios to identify the formation mechanisms of Pb species in aerosol.

2. Sampling and Analysis Methods

Size-fractionated aerosol samples were collected by a high-volume cascade impactor in Higashi-Hiroshima. Sampling period was from 9th Oct. 2012 to 23th Oct. 2012 (2 weeks). Candidates of Pb source in atmosphere, fly ash of municipal solid incinerator (MSWI), heavy oil combustion, road dust and resuspension particles on the roof, were also collected. Weathered Hiroshima-granite, which is crustal material of the sampling area, was also collected as a possible natural Pb source. Lead species were determined by X-ray absorption fine structure (XAFS) spectroscopy. Heavy metals concentrations were measured by ICP-MS. Lead isotope ratios were determined by MC-ICP-MS with Tl doping technique after appropriate treatments.

3. Results and Discussion

Lead species were different between coarse and fine aerosol particles. Lead species in coarse aerosol particles were PbC_2O_4 , $2\text{PbCO}_3\text{-Pb(OH)}_2$, and $\text{Pb(NO}_3)_2$. Lead sources of coarse aerosol particles can be road dust because main Pb components in road dust were PbC_2O_4 and $2\text{PbCO}_3\text{-Pb(OH)}_2$. This result was also suggested by EFs of Cu and Sb which are good indicators of road dust. Lead nitrate in coarse aerosol, which was not contained in road dust, might be formed by chemical reaction of natural Pb with gas-phase HNO_3 in the atmosphere. In contrast, Pb species of fine aerosol particles were PbC_2O_4 , PbSO_4 , and $\text{Pb(NO}_3)_2$. Major Pb sources in fine aerosol particles are fly ash of MSWI and heavy oil combustion based on the determination of Pb species in these materials examined in this study. This result was also supported by size-distributions of Cd, Ni and V.

In our presentation, the results of Pb isotopic composition will be discussed together with Pb species in aerosol samples.

Keywords: Aerosol, Lead species, Lead isotope, XAFS spectroscopy, MC-ICP-MS

Behavior of Heavy Metal-containing PM_{2.5} Transported from the Asian Continent :Single-particle MS and Chemical Analysis

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The Asian continent is an important source region of atmospheric aerosols with different origins and metals including combustion, dust storms and industrial and residential emissions. Some studies were reported polluted aerosols are transported from the Asian continent over from winter to spring by the outflow of the Asian air masses. In order to better understand characteristics of these aerosols, we investigated the chemical characteristics of individual aerosol particles by using a laser ionization single-particle mass spectrometer (LISPA-MS) along with other aerosol and gas measurements in the spring and winter of 2010 in Fukue Island, Nagasaki. Trace gas concentrations, total mass concentration of atmospheric aerosols (TEOM), mass concentrations of sulfate, nitrate, organics, and ammonium (AMS), and organics, trace metals (HVI2.5) were utilized to get quantitative information during the field campaign. We focused on the fine particle with lead (Pb) -containing aerosols as lead is considered a criteria air pollutant with wide range of health effects.

Over the measurement period, the LISPA-MS obtained ca. 90,000 (spring) and ca. 30,000 (winter) positive single-particle mass spectra. Pb-containing particles accounted for 2-4% of all the measured particles. Pb-containing aerosols were classified four major particle types from the obtained mass spectral patterns. The K-Fe-Zn type is characterized by the presence of an intense K ion peak with Fe, sodium Na, and zinc Zn and it makes up 40-60% of the total Pb-containing particles. The aerosol type with intense K, Fe, Zn without Al, Sn, and V is attributed coal combustion from the previous laboratory experiment. The Al-Ca type is characterized by the specific presence of aluminum (Al) ion peak and calcium (Ca). Since Al and Ca is a marker of mineral dust, the Al-Ca type is assigned dust aerosols. The V type is characterized the specific presence of vanadium ion peaks (V and VO) which is a marker of fuel oil combustion and refining. The Sn type is characterized by the specific presence of a tin (Sn) which is a marker of industrial waste incineration. While air mass reached to Fukue Island from China continent for back trajectory, the number of Pb-containing particles showed a significant increase. The temporal variation of Pb-containing particles except from V-type shows well-correlated with that of the fraction of dust particles which is SiO₃ containing particles analyzed from the negative mass spectra. In conclusion, the LISPA-MS measurements indicated that Pb-containing particles originated from the anthropogenic source such as coal combustion and industrial waste incineration accounted for 40-70% and were mainly transported from China continent.

Keywords: PM_{2.5}, long-range transport, single-particle laser ionization mass spectrometer, Heavy metal-containing aerosols

Solubility of iron in aerosols of volcanic origin with iron speciation analysis

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In high nutrient low chlorophyll (HNLC) region, which covers 20% of the world oceans, growth of phytoplankton is limited by iron (Fe) concentration (Martin and Fitzwater, 1988). It has been suggested that aerosols can be an important supply source of Fe to the HNLC region. The solubility in ocean of Fe in aerosols, in turn, depends on its chemical species, but the Fe species in the aerosols have not been fully clarified. Therefore, the aim of this study is to determine the Fe chemical species and its solubility in aerosols of various sources. In particular, there have been few studies on the Fe speciation and solubility in aerosols of volcanic origin. Thus, marine aerosol samples of volcanic origin were examined in this study. The aerosol samples were collected from the Northwestern Pacific during research cruise of Hakuho-Maru (KH-08-2) in summer in 2008. As a result of backward trajectory analysis for the sample (Leg.1-5) when high sulfate concentration was detected, it was suggested that the aerosol samples was supplied from the Okmok volcano in the Aleutian Islands of Alaska as volcanic ashes. Hence, the volcanic ashes (< 20, 20-32, and 32-250 micron) of Okmok volcano received from Alaska Volcano Observatory were also studied as well as yellow dusts (CJ-1, CJ-2, and Gobi Kosa Dust) for comparison.

The Fe/Al ratio in the Leg.1-5 sample was identical to that of the volcanic ash sample, showing that the aerosols collected during the Leg.1-5 is supplied from the eruption of the Okmok volcano, which reinforces the suggestion by the backward trajectory analysis. Sulfur K-edge XANES showed that sulfide originally contained in the volcanic ash changed into sulfate possibly due to the alteration during the transport to the Northwestern Pacific. Iron K-edge XANES analysis showed Leg.1-5 contained ferrihydrite (60%), magnetite (28%), and iron(II) sulfate (12%), whereas volcanic ashes (< 20 micron) contained augite (57%), fayalite (25%), and pyrite (18%). CJ-1 and CJ-2 contained illite, ferrihydrite, and chlorite, while Gobi Kosa Dust contained illite, ferrihydrite, and hematite. In addition, the average valence of Fe determined by pre-edge fitting of Fe K-edge XANES showed that the ratio of ferric iron of Leg.1-5 (average valence of Fe = 2.4) is higher than that of volcanic ashes (average valence of Fe = 2.1). These results showed aerosols of volcanic origin released into the atmosphere were altered and oxidized while being transported.

The total Fe concentration (T-Fe) in samples after acid decomposition and the dissolved Fe concentration (D-Fe) in samples extracted by MQ water or simulated seawater (pH 8) were determined by ICP-AES. The Fe solubility (Fe_s) here was defined as the percentage of Fe released in the solution after 24 h: $Fe_s (\%) = (D-Fe/T-Fe) \times 100$. The results showed that the solubility to seawater (Fe_s -SW) of Fe contained in the aerosol samples of volcanic origin is larger than that of yellow dusts by a factor of more than 1000. Generally speaking, Fe solubility depends on the valence of Fe, that is, the solubility decrease with the increase in the ratio of ferric iron for ferrous iron. In this study, however, the Fe solubility of the aerosol samples is higher than that of volcanic ashes mainly due to the formation of iron(II) sulfate, highly soluble species, as shown in the XAFS spectra. This is why volcanic ashes which originally contained insoluble Fe changed into the aerosols with high soluble Fe content.

Although the average emission of fine volcanic ash (176-256 Tg/yr; Durant et al., 2010) into the atmosphere is less than that of annual terrigenous dust load (1000-3000 Tg/yr; Tegen and Schepanski, 2009) by a factor of 1/10, the soluble Fe content in the aerosols supplied as volcanic ashes cannot be underestimated due to the very high soluble Fe content in the aerosols of volcanic origin.

Keywords: Fe, speciation, solubility, aerosol, volcanic ash, dust

Molecular distributions of organic aerosols collected over the western North Atlantic

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Marine aerosols were collected over the western North Atlantic from Boston to Bermuda during the cruise of R/V Ronald H. Brown in August 2012 using a high volume air sampler and quartz fiber filter. Aerosol filter samples were analyzed for OC/EC, ions, dicarboxylic acids and various SOA tracers using carbon analyzer, ion chromatograph, GC/FID and GC/MS, respectively. Homologous series of low molecular weight dicarboxylic acids (C2-C12) were detected with a predominance of oxalic acid. Their concentrations decreased from the coastal region to the open ocean. Isoprene SOA tracers and monoterpene SOA tracers were also detected with the higher concentrations near the east coast of North America. Sugar compounds that are derived from pollen (sucrose and fructose) and fungal spores (arabitol, mannitol and trehalose) showed higher concentrations in the coastal region than the open ocean.

Keywords: marine aerosols, organic compounds, LMW dicarboxylic acids, SOA tracers, Biomass burning tracers, pollen and fungal spore tracers

Investigation on the SOA formation mechanism in isoprene ozonolysis by chemical ionization mass spectrometry

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Isoprene is the most abundant volatile organic compound (VOC) emitted from the earth and is producing a large amount of SOA by oxidation processes in the atmosphere. There are three oxidation processes for isoprene. The OH reaction is a major oxidation process in daytime. SOA yield and mechanism have been extensively investigated in many research groups so far. The NO₃ reaction occurs in night time. SOA yield of the O₃ reaction is known to be small compared with those of other reactions. The O₃ reaction occurs in both daytime and nighttime. Since the ozone reaction could couple with other oxidation processes, we think that it is important to understand the mechanism of SOA formation in the O₃ reaction. For the purpose, we detected semi-volatile organic compounds produced in the oxidation processes in both gaseous and aerosol phases by chemical ionization mass spectrometry that allows for sensitive measurement of VOC without any pretreatment.

The reaction was investigated using 6 m³ smog chamber. The initial concentrations of isoprene and ozone were fixed as 2 ppmv and 4 ppmv, respectively. In this reaction, OH radical is regenerated, so we did the experiments with OH radical scavenger. Cyclohexane and CO were used as an OH radical scavenger. The experiment was carried out under dry conditions and without sees particles. Gaseous reactants and products were monitored by FT-IR and proton transfer reaction-mass spectrometer (PTR-MS). SOA size distribution and concentration were monitored by Fast Mobility Particle Sizer (FMPS) within 10 minutes from the start of the reaction and Scanning Mobility Particle Sizer (SMPS) for the whole reaction time. After 2 hours, formed SOA was collected on three filters and was analyzed by PTR-MS, GC/MS and LC/MS. In addition to the smog chamber experiments, similar experiments were carried out using 1 m³ Teflon bag in order to compare PTR-MS data with negative ion-chemical ionization mass spectrometer (NI-CIMS) data.

Same ion signals were observed in both gaseous and aerosol phases by NI-CIMS and were assigned to oligomeric hydroperoxides involving Criegee intermediate (molecular weight 46) as a chain unit. PTR-MS detected the oligomeric hydroperoxides as [M-OH]⁺ ion. Since these compounds were observed in both gaseous and aerosol phases, it is concluded that they are key species for the SOA formation of isoprene ozonolysis. In SOA, hemiacetals involving formaldehyde (MW30) and/or MACR (MW70) were observed by PTR-MS. So, we found that the SOA formed in the isoprene ozonolysis consists of oligomeric hydroperoxides involving Criegee intermediate as a chain unit and hemiacetals involving formaldehyde and/or MACR.

Gas-aerosol partitioning of each VOC was estimated from ion signals in both gaseous and aerosol phases by PTR-MS. Gas-phase concentrations at each mass number were determined from mass spectrum observed after the reaction. Aerosol-phase concentrations were estimated from total ion signals summed during the heating of the filter. We assume that VOC is evaporated during the analysis time of 2 hours. From the ratio of aerosol-phase concentration to gas-phase concentration, we estimated saturation vapor pressures of compounds in the mass range between 100 and 200 to be approximately 10⁻⁴ Torr. On the other hand, from the fitting of SOA yield curve by four-product volatility basis model, model suggested that species 10⁻⁴ Torr of saturation vapor pressure are dominant in SOA. These are consistent with the compounds observed in the mass range between 100 and 200 and we assigned those as oligomeric hydroperoxides and hemiacetals.

Keywords: isoprene, ozonolysis, chemical ionization mass spectrometry, proton transfer reaction mass spectrometer, secondary organic aerosol, Criegee intermediate

Analysis of gas and particle phase products in the ethylene ozonolysis using negative ion chemical ionization mass spect

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The reaction of ozone with alkenes is a significant loss process of both ozone and alkenes in the atmosphere and plays an important role in air pollution processes in urban areas. The alkene ozonolysis produces Criegee intermediates, which have relatively high reactivity and partly decompose to produce radicals such as OH, HO₂ and RO₂. Especially, the formation of OH in alkene ozonolysis can be important as a nighttime source of OH. Additionally, ozone-alkene reaction can contribute to the formation of secondary organic aerosols (SOAs). Despite of its importance, the reaction process of the ozone-alkene reaction is not fully understood. This is the case even in the ozonolysis of ethylene, which is the simplest alkene, widely used in industry, and one of the most significant volatile organic compounds (VOCs) released into the environment.

In this study, we investigated the ethylene ozonolysis in laboratory experiments with a Teflon bag by using negative ion chemical ionization mass spectrometry (NI-CIMS). NI-CIMS is a powerful tool with less fragment, high selectivity, and high sensitivity for analysis of compounds such as carboxylic acids and hydroperoxides, which are expected to be produced in the ethylene ozonolysis.

As gas-phase products, we detected oligomeric hydroperoxides composed of Criegee intermediates as a chain unit, as well as formic acid and hydroperoxides which are previously reported. Additionally, the formation of SOAs in the ethylene ozonolysis was observed and their components were analyzed using NI-CIMS. The oligomers composed of the Criegee intermediates were also found as particle components. The formation of gas-phase oligomers and SOAs was strongly suppressed by adding methanol as a Criegee scavenger, clearly indicating that the Criegee intermediate plays a main role in the formation of oligomers and SOAs in the ethylene ozonolysis. The sequential addition of Criegee intermediates to hydroperoxides was proposed as the oligomer formation mechanism.

Keywords: ozonolysis, ethylene, SOA, hydroperoxide, oligomerization

Mixing states of soot particles from transmission electron microscopy: their mixing state, size, shape, and composition

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Mixing state, size, shape, and composition of atmospheric aerosol particles influence their climate and health effects. Transmission electron microscopy (TEM) can magnify the particles and reveal the internal structures at a single particle scale. We study aerosol particles collected from urban mountain sites in Japan. In this study, we focused on soot particles and their mixing states, shape, size, and compositions of the coating materials, if any, since they absorb light and have great influence on the climate.

Together with scanning transmission electron microscopy (STEM), which is one of the technique of TEM, and energy dispersive X-ray spectroscopy (EDS), which measures the composition of interest within TEM, we analyze the compositions and mixing states of soot particles as well as elemental distribution within individual particles. We use the STEM-EDS system that automatically measures sizes, shape factors, and compositions of all aerosol particles within a field of view (~300 particles). The results suggest that ~75% of soot particles were coated (internal mixture) at the mountain site (remote area) and the larger aerosol particles include the more soot particles. At the mountain site, soot particles were mostly coated by ammonium sulfate. On the other hand, soot particles from urban site were coated by both organic aerosol and sulfate, and the ratio varied depending on the time of the day. These data are useful to understand the optical properties, atmospheric lifetime, and climate effects of soot particles and to improve climate modeling.

Keywords: aerosol, electron microscope

Light absorption properties of carbonaceous particles in Nagoya

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Aerosol particles have an important role in radiation balance in the atmosphere by scattering and absorbing incident light. Black carbon (BC) particles are an important global warming agent with radiation forcing similar in magnitude to CO₂. The light absorption of BC is generally considered to be increased by internal mixing with other compounds but the amount of absorption enhancement depends on factors such as refractive index of BC and coating materials, size and location of the BC core (e.g. Bond et al. 2006). In addition, recently light-absorbing organic carbon "brown carbon", involving humic-like substance (HULIS) and nitro-aromatics etc., has been proposed as a source of significant absorption, particularly in the near-UV (e.g. Nakayama et al. 2012). However, observational studies of the enhancement of BC light absorption and brown carbon are still limited mainly because of the difficulty in the accurate measurement of light absorption of internally mixed BC particles without collecting on filter. In this work, by applying photoacoustic spectroscopy (PAS), light absorption enhancement of BC and contributions of light absorption by brown carbon is examined.

Observations were conducted during summer (August, 2011) and winter (January, 2012) at the Higashiyama-campus of Nagoya University. Absorption and scattering coefficients at 405, 532, and 781 nm of PM1 particles were measured using the photoacoustic soot photometer (DMT, PASS-3), after passing through diffusion dryers and one of the heaters controlled at 25, 100, and 300 degC (summer) or 25, 300, and 400 deg C (winter) every 30 (summer) or 10 (winter) min. Mass concentrations of elemental carbon (EC) and organic carbon (OC) were also measured by thermo-optical technique using a semi-continuous EC/OC analyzer (Sunset Lab., model 4) every 90 min.

By comparing absorption coefficients at 781 nm with and without heating (300 or 400 deg C), increase in BC light absorption due to coating was found to be small (<10 percent) both during winter and summer. The result is consistent with a recent observation by Cappa et al. (2012) conducted in California, USA. Contributions of light absorption by OC are estimated by assuming that the enhancement of BC light absorption due to coating does not depend on wavelength. As a results, contributions of 405 nm light absorption by OC, which is vaporized at 300 (or 400) deg C, are found to be small during summer in Nagoya (<5 percent) but significant (~20 percent) during winter. Larger absorption cross section of OC (MAC_{OC}) was observed especially when CO/ Δ -CO₂ ratio was higher. The result suggests that OC emitted from incomplete combustion processes such as biomass and coal burning for heating may contribute to the observed light absorption by OC during winter.

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Keywords: Aerosol optical properties, Ambient measurement, Black carbon, Lensing effect, Brown carbon, Climate change

Aging and long-range transport processes of black carbon: global simulation with a chemistry-aerosol climate model

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Present global aerosol models generally have a severe tendency to underestimate atmospheric concentrations of black carbon (BC) especially in remote areas like the polar regions as shown by the recent model intercomparison project under the IPCC (ACCMIP/AeroCOM). Such underestimates of BC are basically coming from large uncertainties in aging process which makes hydrophobic BC to hydrophilic, and subsequent removal by precipitation. This problem in global BC modeling causes still a large uncertainty in the estimate of atmospheric heating and climate impacts of BC (Kerr, Science, 2013). This study attempted to improve global simulation of BC and re-evaluate radiative forcing of BC in the framework of a chemistry-aerosol coupled climate model MIROC-ESM-CHEM. Our previous study (Sudo and Endo, 2011) had successfully reproduced the concentration and seasonal cycle of BC observed at the Syowa station in the Antarctic, by applying a simplified aging scheme that considers coating of BC with SO_4^{2-} (Liu et al., 2011) to the MIROC-ESM-CHEM model. Our model, however, could not reproduce well the observed BC levels and seasonality in the northern high latitudes including in the Arctic. This study developed a new scheme to simulate more explicitly aging of BC associated with condensation of SO_4^{2-} and organic compounds from oxidation of VOCs. Additionally, several improvements were also added to the model for better simulating dry/wet deposition and emissions seasonality. Our improved model with the new aging scheme appears to relatively well reproduce the observed BC concentrations and seasonality in the Arctic region. Our simulation also showed that Arctic BC comes mainly from fossil fuel burning in winter to spring, but from the Siberian biomass burning in summer. The new model estimated radiative forcing of BC to be 0.83 W m^{-2} which is about two times larger than the estimate by our original model with no aging scheme (0.41 W m^{-2}), or the model ensemble mean in the IPCC report.

Keywords: black carbon, soot, aging, long-range transport, radiative forcing, global model

Seasonal variations of Asian black carbon outflow to the Pacific using a tagged three-dimensional model

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The Community Multiscale Air Quality model with a source and process tagged method (CMAQ/PASCAL) was used to understand source regions and types (anthropogenic (AN) and biomass burning (BB)) of Asian black carbon (BC) outflow to the Pacific during 2008 - 2010. The model calculations generally reproduced absolute concentrations and temporal (seasonal, monthly, and day-to-day) variations of BC mass concentrations observed by both surface and aircraft measurements in outflow regions in East Asia. These model calculations show that both the total eastward flux and transport efficiency (fractions transported from sources) of BC are the highest during spring (26 kg s⁻¹ and 33% at 150E) and the lowest during summer (8 kg s⁻¹ and 20% at 150E). These seasonal variations of Asian BC outflow are generally controlled by transport patterns (monsoons, frontal passages, and convection) and emissions from the following three sources: (1) AN emissions from China (China AN), (2) BB emissions from Southeast Asia and South China (SEA BB) during February - April, and (3) BB emissions from Siberia and Kazakhstan (Siberia BB) during April - July. In our calculations, China AN dominates the total eastward BC flux on period average (61%, 17%, and 6% from China AN, Siberia BB, and SEA BB, respectively, at 150E). On the other hand, SEA and Siberia BB account for 30 - 50% of the total eastward BC flux (150E and 175E) during spring and summer, and they intensify seasonal contrast of Asian BC outflow flux. BC from Siberia BB is also found to be transported to the Pacific more efficiently than that from other sources. Although the amounts of BB emissions are currently highly uncertain, our results suggest that the control of Siberia BB will be important in terms of the trans-boundary transport of BC to the Pacific, North America, and the Arctic.

Keywords: black carbon, regional three-dimensional model, tag model, East Asia, source contribution, biomass burning

Vertical transport mechanisms of black carbon over East Asia in spring during the A-FORCE aircraft campaign

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Black carbon (BC) aerosols efficiently absorb solar radiation in the atmosphere. The absorption leads to heating of the atmosphere and melting of some additional snow or sea ice, therefore exerting a substantial impact on radiation budget in the climate system. The vertical transport processes of BC from the planetary boundary layer (PBL) to the free troposphere (FT) are critically important, because they directly control the global- and regional-scale spatial distributions of BC; however an understanding of this process is still limited. In order to understand these points, the Aerosol Radiative Forcing in East Asia (A-FORCE) aircraft campaign was conducted over East China Sea and Yellow Sea in March-April 2009 and 120 vertical profiles of BC were obtained at 0-9 km in altitude. The major objective of this study is to understand the vertical transport mechanisms of BC particles and their transport pathways over East Asia in spring using results from the 3-D chemical transport model (WRF-CMAQ) calculations and the A-FORCE observation data.

The original CMAQ model does not take into account differences in rainout and washout processes. In this study, we modified the CMAQ model to treat rainout and washout processes separately. We conducted the WRF-CMAQ model calculations with horizontal resolution of 81 km * 81 km and with 21 layers in vertical, and used the model results in March-April 2009. We also estimate transport efficiency of BC on the basis of the calculation with wet deposition and that without wet deposition using the modified CMAQ model.

Comparisons of the model results with the A-FORCE observations show that the model reproduces relatively well the vertical distributions of mass concentration and transport efficiency of BC, including dependences on precipitation that air parcels had been experienced during transport, although the model overestimated the mass concentrations of BC in the FT.

Using the validated model results during the A-FORCE period (20 March to 30 April 2009), we find that the pronounced convergences of mean horizontal mass fluxes of BC integrated within the PBL (700-1000-hPa column) over northern-eastern and inland-southern (around the high-altitude mountains) China. Corresponding to the convergence areas, we find two types of the pronounced upward mass fluxes of BC from the PBL to the FT (at the 700-hPa level) over northern-eastern and inland-southern China. The major uplifting mechanism of BC over northern-eastern China is cyclones with modest amounts of precipitation. In addition to cumulus convections, orographic lifting along the high-altitude mountains plays important role for the upward transport of BC to the FT over inland-southern China, in spite of the largest wet deposition amounts of BC in East Asia due to large amounts of precipitation. The latitudinal difference of precipitation induced by the moisture supply by the low-level southerlies is responsible for the spatial distributions of BC and its transport efficiency in the atmosphere.

The mean eastward mass fluxes of BC were pronounced in the lower troposphere over the midlatitude region (35°-50°N) and in the middle troposphere over the subtropical region (20°-35°N) at the 140°E vertical cross section during the A-FORCE period. We find that the upward transports over northern-eastern and inland-southern China, followed by the westerly transports in the lower and the middle FT, respectively, make major contributions to the exports of BC from East Asia to the Pacific in spring.

Keywords: Aerosol, Black carbon, Transport, Wet deposition, East Asia, Regional-scale aerosol model

Corona-imaging colorimetric method for accurate measurement of the size of water droplets in an expansion chamber

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Accurate and time-resolved measurement of the size of water droplets is a pre-requisite for the study of microphysical processes of cloud formation using an expansion chamber. We developed a new method using color images of corona observed under illumination of a white-light beam, also known as the corona-imaging colorimetry (CIC) method. In the CIC method, RGB data from images obtained by a commercial digital camera are converted into standard colorimetric parameters. The droplet size is estimated by optimizing the agreement of the measured colorimetric parameters with those estimated using Mie theory. For polystyrene latex spheres suspended in water, the particles size estimated by the CIC method agrees to within 2% of the pre-determined value. We apply this method to the time-resolved measurement of the size of water droplets formed in an expansion chamber. The CIC method is technically simple and enables accurate and instantaneous measurements of the size of droplets with diameters larger than about 10 μm . In addition, the CIC method is advantageous over the Constant Angle Mie Scattering (CAMS) method, which requires a specially designed optical system with a laser light source and complete information of the growth history of the droplets.

In our presentation, the details of the theoretical aspects and colorimetric treatments of the CIC method will be discussed.

Keywords: Corona, Cloud Droplets, Sizing, Chamber, Condensation

Influences of near-surface stratification for aerosol impact on clouds over the East China sea

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Cloud microphysical properties and aerosol concentrations were measured aboard an aircraft over the East China Sea and Yellow Sea in April 2009 during the Aerosol Radiative Forcing in East Asia (A-FORCE) experiment. We sampled stratocumulus and shallow cumulus clouds over the ocean in 9 cases during 7 flights 500-900 km off the east coast of Mainland China. Cloud droplet number concentration (highest 5%, N_{c_max}) correlates well with the accumulation-mode aerosol number concentration (N_a) below the clouds. N_{c_max} correlates partly with near-surface stratification evaluated as the difference between the sea surface temperature (SST) and 950-hPa temperature ($SST - T_{950}$). Cold air advection from China to the East China Sea was found to bring not only a large number of aerosols but also a dry and cold air mass that destabilized the atmospheric boundary layer, especially over the warm Kuroshio ocean current. Over this high-SST region, greater updraft velocities and hence greater N_{c_max} likely resulted. We hypothesize that the low-level static stability determined by SST and regional-scale airflow modulates both the cloud microphysics (aerosol impact on clouds) and macro-structure of clouds (cloud base and top altitudes, hence cloud liquid water path).

Keywords: aerosol, cloud, SST, Kuroshio Ocean current, East Asia

Characteristics of cloud condensation nuclei observed at Noto peninsula, Japan, in autumn 2012

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Atmospheric aerosols can act as cloud condensation nuclei (CCN) and therefore play an important role in regulating radiative properties and lifetime of clouds. Along with the development of the industrial activities, the loading of atmospheric aerosols tends to increase, especially in East Asia. To access the radiative balance and/or hydrological cycle of the Earth in the future, quantitative evaluations of CCN characteristics are needed based on in-situ atmospheric observations.

In this study, CCN activity of submicrometer-sized aerosols were measured at Noto Ground-based Research Observatory (NOTOGRO), located at the tip of Noto peninsula, facing the Sea of Japan, in autumn 2012. Ambient aerosols were sampled through the PM10 inlet (14.7 m A.G.L.). The dried aerosols were introduced into a differential mobility analyzer (DMA) for size selection, and the resulting monodisperse aerosol was then transferred to a water-based condensation nuclei (CN) counter and a continuous flow thermal gradient CCN counter to measure the number concentrations of CN and CCN, respectively. The CCN efficiency spectra, where CCN number fraction is plotted against the diameter of aerosols, were obtained at four different supersaturations (0.1%, 0.2%, 0.5% and 0.8%). The bulk chemical composition of non-refractory submicrometer-sized aerosols was also measured by an aerosol chemical speciation monitor (ACSM).

Parameters related to the mixing state and hygroscopicity of the aerosols were obtained at high time resolution based on the analysis of the CCN efficiency spectra. The slope of the CCN efficiency spectra (diameter at which 50% of CN act as CCN) for ambient aerosols was not as steep as that for pure ammonium sulfate particles, indicating heterogeneity in the mixing states of the ambient aerosol. The hygroscopicity parameter kappa (Peters and Kreidenweis, 2007), estimated from the CCN activation diameter, suggested that organics contributed on the aerosol mass especially in the size range of less than 100 nm. The bulk chemical composition obtained by ACSM also indicated the large contribution of organics on the total aerosol mass, however, the size resolved CCN measurements provided a clue to the elucidation of the size-dependant chemical composition of submicrometer-sized aerosols.

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Keywords: atmospheric aerosols, cloud condensation nuclei, organic aerosols, hygroscopicity parameter, East Asia

Cloud droplet size measured for different supersaturations at Noto Peninsula, Japan, in autumn 2012.

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The size of cloud droplets is one of the important factors that control the radiative properties and lifetimes of clouds. In general, it has long been accepted that growth rates of cloud droplets depend solely on water vapor supersaturation (SS). To challenge this established theory, we conducted in-situ measurement of atmospheric aerosols and related cloud growth kinetics in East Asia, in order to investigate the relative importance of other factors that can potentially influence the initial cloud droplet growth. In this study, diameters of cloud droplets were measured by using cloud condensation nuclei counter (CCNC) at Suzu, Noto Peninsula (NOTOGRO) in October, 2012. CCNC was operated at four different SS conditions (SS=0.1%, 0.2%, 0.5%, 0.8%). The diameters of cloud droplets activated from ambient aerosols were compared to those activated from ammonium sulfate (regarded here as representative inorganic CCN). The negative correlations between the cloud droplets' diameters and organic aerosol mass fractions were observed. The initial growth rate of cloud droplets activated from ambient aerosol were considered to be inhibited by the existence of organics especially under the lower SS conditions (SS=0.1% and 0.2%).

Keywords: cloud condensation nuclei, cloud droplet size, atmospheric aerosol, chemical composition