

Emission of iodine molecule and iodine monoxide from frozen solutions containing iodide ion

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Iodine oxides are receiving increasing attention in atmospheric chemistry, because it may contribute to ozone depletion and atmospheric particle formation in polar region. Iodine monoxide(IO) generates from the reaction of iodine atom with ozone. Iodine atoms may be formed by photolysis of iodine(I₂) or volatile iodocarbons, the main source of which is oceanic biogenic production. Emission processes from inorganic source are also being proposed, but they are so far unexplained. Iodine compounds were found above, below and within the sea ice of the Weddell Sea, and these measurements show the Weddell Sea as an iodine hotspot. But, the calculated fluxes from biological production of iodocarbons are too small to explain the observed atmospheric IO, and the modelled I₂ is also smaller than the observed I₂. This observation suggests there is an unidentified iodine source. One of the candidates is presumably an inorganic source. In this work, we studied the surface reaction between gaseous ozone and a frozen sodium iodide solution by using cavity ring-down spectroscopy to detect gaseous products, iodine, I₂(g) and an iodine monoxide radical, IO(g).

The I₂(g) and IO(g) emissions were observed during ozonolysis of liquid and frozen NaI aqueous solutions. The concentrations of NaI were typically 1 and 5 mM. The concentrations of flowing O₃(g) were (0.5-4.2)×10¹⁵ molecules cm⁻³. The observed products concentrations were ~10¹¹ molecules cm⁻³ for IO(g) and ~10¹⁴ molecules cm⁻³ for I₂(g). The peak of I₂(g) emission was markedly enhanced on a frozen NaI aqueous solution more than that on a liquid at pH 2. The peak of IO(g) emission was also enhanced on a frozen solution under the same condition. The physical structures of the ice substrates supposedly play an important role in this enhancement. Iodide anions are expected to be excluded from ice matrix during freezing. This exclusion process leads to the formation of concentrated iodide anions at the air-ice interface. In fact, sea ice contains brine microchannels that permit transport of reactants over large distances. It was found that the amounts of I₂(g) and IO(g) produced depend on [NaI], I₂(g) production is markedly enhanced at pH <4, and I₂(g) emission is decreased with decreasing temperature of a frozen NaI solution. Acidification of the brine by atmospheric trace acids could potentially lead to low pH. These results imply that a surface reaction between gaseous ozone and frozen iodide could be responsible for the inorganic source of iodine.

Keywords: iodine, iodine monoxide, ice, ozone, heterogeneous reaction, cavity ring-down spectroscopy

Speciation of S and Ca species in aerosols with its relations to global cooling effects and processes of chemical reacti

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Speciation of particles in aerosols is necessary to interpret what effects each species in the aerosols can have on environment. For example, global cooling effect by aerosols influences earth's climatic change (IPCC, 2007). In particular, sulfate aerosols are known to cool the earth by forming cloud condensation nuclei (CCN) because of their high hygroscopicity, which induces indirect cooling effect. Because the hygroscopicity differs depending on the species, sulfate speciation in aerosols is important for the determination of the magnitude of the indirect cooling effect.

In this study, major ion concentrations in aerosol samples were measured by ion-chromatography. In addition, chemical species of calcium and sulfur in the each aerosol sample were determined using X-ray absorption near-edge structure (XANES) measured at BL-9A in Photon Factory, KEK. The speciation analyses can have some implications on the influence on the environment and the processes of chemical reaction of aerosols collected during several periods, such as (a) dust (Kosa) period (March 4-9, 2013), (b) the period with high PM2.5 concentration (Jan. 31-Feb. 1, 2013), and (c) the periods before and after (a) and (b).

Major ion concentration data showed that Ca^{2+} , which is originated from soil, and NO_3^- and SO_4^{2-} , which were from human activities, increased in the period (a) compared with those in the periods before and after the period (a). On the other hand, SO_4^{2-} and NH_4^+ , which were emitted from human activities, increased in the period (b). In the period (a), it is considered that species originated from acids such as sulfate and nitrate which were incorporated into the particles increased in the samples whose aerodynamic diameter is over 1.0 μm , because they have reacted with CaCO_3 which was increased by Kosa event. In addition, from the fitting of XANES spectra, it was found that gypsum with low hygroscopicity were the main sulfur species in the period (a), whereas NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and hydrated sulfate with high hygroscopicity were main sulfur species in the period (b). Therefore, it is considered that when the concentration of PM2.5 increases, the indirect cooling effect can be large due to the large fraction of NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and hydrated sulfat. On the other hand, the indirect cooling effect by sulfate aerosols can be smaller during the dust period due to the formation of non-hygroscopic gypsum by high amount of calcite in the atmosphere.

Using the results of calcium and sulfur speciation both in the bulk and at the surface by fluorescence and conversion-electron yield detection, respectively, in the XANES analyses, we can discuss how chemical reactions occur at the surface of aerosol particles in each period. The abundance ratios of gypsum, CaCO_3 , and $\text{Ca}(\text{NO}_3)_2$ were different at the surface and the bulk. As a result, it was concluded that calcium species changes from gypsum, $\text{Ca}(\text{NO}_3)_2$, to CaCO_3 from the surface to the core of the calcite particle. This results showed that (i) sulfuric acid from the atmosphere forms insoluble gypsum at the surface of calcite, (ii) $\text{Ca}(\text{NO}_3)_2$, formed as a result of the reaction of nitric acid and calcite, exists in the middle part, and (iii) unreacted CaCO_3 remains in the core of the particle.

Keywords: aerosol, XANES, sulfate, grobal cooling effect

Properties of Fe-containing particles and structure of mineral particles in the mountain, urban, and marine atmosphere

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Atmospheric aerosol particles play an important role in global material cycles and global climate by acting as an agent which transports materials over long distances. Iron (Fe) is an essential element for marine phytoplankton growth especially in high nutrient and low chlorophyll (HNLC) area. Long-range transportation of atmospheric aerosols from the continent and subsequent deposition is an important process to supply Fe to the ocean. The dry and wet depositions of aerosol particles depend on the particle size and the mixing states with water-soluble materials. In order to study the properties of Fe-containing particles and modification of individual particles, we collected aerosol particles at the top of Mt. Fuji, at Kagurazaka, Tokyo, and on the ship over the mid-latitude western North Pacific Ocean during the KH-12-1 (EqPOS) Leg 2 cruise of the R/V Hakuho Maru. We collected aerosol particles with a low pressure impactor. Collected particles were analyzed using a transmission electron microscopy (TEM) with a water dialysis method and an energy-dispersive X-ray (EDX) analysis. We chose the samples which were collected in the long-range transportation events from the continent on the basis of 5-day backward air trajectory analysis, number size distribution of aerosols measured by an optical particle counter (OPC), and the results of the TEM-EDX analysis.

Water-insoluble materials such as mineral dusts and industrial anthropogenic metals are main sources of Fe. This study focused on water-insoluble materials and performed the EDX analysis. In each sample, most of water-insoluble materials were internally mixed with water-soluble materials (internal mixed particles). The volume percent of the water-soluble materials in the mixed particles on a marine sample was higher than that of other samples, indicating that water-insoluble materials as well as Fe-containing particles were mixed with water-soluble materials during transportation.

Structures of some mineral particles were verified using the focused-ion-beam (FIB) technique. Particles larger than 5 μm collected on the Ti-plate were sliced into 200 nm in thickness. We performed selected-area electron diffraction (SAED) on the cross section of the sliced particles. On the basis of the diffraction patterns and EDX results, structures of the mineral particles were verified. CaCl_2 was found on the surface of the particle and bounded on CaCO_3 , suggesting that CO_3^{2-} was replaced by Cl^- ($\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$). Fe was included in the particle. There is a possibility that changing insoluble CaCO_3 to soluble CaCl_2 changes the ability of cloud nuclei and/or ice nuclei and the solubility of Fe.

Keywords: aerosol, Fe, water-soluble materials, water-insoluble materials, long-range transportation

Source of atmospheric lead in Omura City, west Japan, tied to the source of mineral particles

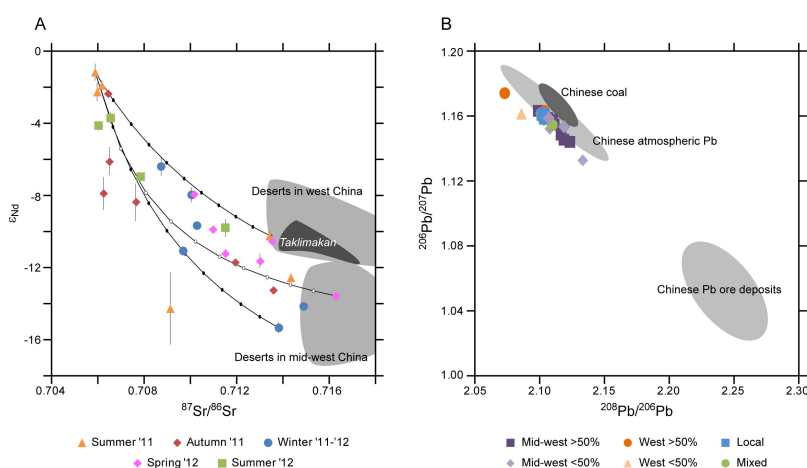
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Lead is one of the major environmental pollutants, which seriously harms human body. Atmospheric lead concentration has been suppressed in Japan after the forbiddance of leaded gasoline in 1970s. However, the cross-border air pollution is getting unable to disregard with industrial development in neighboring countries. Identifying the source of aerosol particles is essential in painting a precise picture of the cross-border air pollution. The northern part of the Kyushu Island is the most affected area of the cross-border pollution in Japan due to closeness to the continent. We conducted isotopic analysis of aerosol particle samples corrected with high temporal resolution, once per a few days, from June 2011 to August 2012 in Omura City in the north Kyushu. Pb isotope ratios of 1M-HCl soluble component ("leachate") of the corrected particles indicate the direct source of anthropogenic lead, while Sr-Nd isotope ratios of the residual mineral component digested by concentrated HF-HNO₃ ("silicate") indicate the source area of the mineral particles. High resolution sampling allowed us to distinguish the sources much more sensitively than commonly adopted monthly order sampling.

Sr-Nd isotope ratios of silicates indicate that the main source area of mineral particles changes seasonally. They have local origin in summer, while they are derived from deserts in mid-west China in fall and winter, and those in west China in spring (Figure A). Pb isotope ratios of leachates are distinct when the source of mineral particles is the mid-west China (Figure B). The values suggest the influence of the Chinese lead ore deposits. On the other hand, Pb isotope ratios of leachates are indistinguishable between samples of local origin and those originated from west China. An additional character of samples of west China origin is high amount of Pb in leachate relative to that of mineral component. Anthropogenic lead may be easier to be entrained to wind when the mineral particles comes from mid-west China because the wind trajectory should be much lower in altitude than when particles come from further distant west China. Cross-border atmospheric Pb pollution is suggested more serious in fall and winter when wind trajectory is low than in spring when the westerly transports vast amount of mineral particles known as "Kosa" from the deserts in west China.

Keywords: dust, anthropogenic lead, PM10, Sr isotope ratio, Nd isotope ratio, Pb isotope ratio



Difference of composition and mixed state of dust particles by height

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Continental Asia has been recognized as one of the most important sources of atmospheric dust particles. Many investigators have pointed out the importance of the atmospheric processing of dust particles in the course of long-range transport. Such processing can potentially change their radiative properties and their ability to act as cloud condensation nuclei. Three major factors that govern the processing of dust particles are dust mineral composition, relative humidity and concentration of acidic gas species. These factors are considered to be closely related with the height at which dust particles are transported. However, there has been no report so far on the direct comparison of the morphology and chemical composition of individual dust particles in the free troposphere and in the planetary boundary layer in the event of a same dust outbreak.

The helicopter was employed as the airborne platform in this study. Aerosol particles were directly collected by aerosol impactor over Hakui city, Isikawa, Japan (36.9 N, 136.7 E) on March 19, 2013. Then, Dust event was observed western Japan by Japan Meteorological Agency. Morphology and elemental composition of the collected particles were later examined on individual basis under SEM-EDX (Scanning Electron Microscope equipped with Energy Dispersive X-ray spectrometry).

Atmospherically processed dust particles (with apparent morphological modification) were hardly found in the free troposphere. On the other hand, large fraction of dust particles was found modified in the planetary boundary layer, showing spherical outline. High proportion of Calcium and Magnesium were detected from the modified particles. Also, dust particles collected in the planetary boundary layer contained Sulfur in higher abundance.

It is suggested that the atmospheric conditions in the free troposphere are less favorable for the dust particles to be modified than in the planetary boundary layer, because the vertical supply of acidic gases and water vapor into free troposphere is generally limited by the temperature inversion layer.

Keywords: mineral dust, free troposphere, planetary boundary layer, SEM-EDX

Demonstration test of atmosphere sampling system using combination of solar and fuel battery at Western part of Yakushim

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We have measured PM 2.5 using solar panel and fuel cell system at Southern area of Yakushima island Japan.

In order to clarify the long-range transport of atmospheric pollutants in the East Asian regions, we have challenged the continuous observation at a mountainous area without the commercial power. Although, we are considered to be better the system with a solar battery, the pump was sometimes stopped for the brownout cause by the lack of insolation. Thereupon, we make an attempt the continuous observation of atmospheric pollutants using the combination of the solar and fuel battery. And thus we achieve the continuous observation of the atmospheric pollutants. Consequently, we will report new monitoring system.

Development of a method to measure the hygroscopicity of black carbon-containing particles

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Black carbon (BC) aerosols are generated by the combustion of fossil fuels and biomass. During transport in the atmosphere, BC particles acquire "coating materials" through the condensation of semi-volatile gaseous components, and coagulation with the other aerosols. Freshly emitted BC particles are generally hydrophobic, so the hygroscopicity of BC-containing particles is largely controlled by the composition and amount of coating materials. Although measurement of the hygroscopicity of ambient BC-containing particles is important to understand their cloud condensation nuclei activity and optical properties, measurement data are still quite limited (McMeeking et al, 2011; Liu et al. 2013). In this study, we present a modified single particle soot photometer (SP2) as a humidified-SP2 (hSP2), which quantifies the BC mass and the amount of coating material within individual aerosol particles, under controlled relative humidity (RH), by detecting both the laser-induced incandescence emitted and laser light scattered from each BC-containing particle. High time-resolved measurements of growth factor (GF: the ratio of wet particle diameter to dry diameter) and hygroscopicity parameter κ for BC-containing particles can be achieved by combining an aerosol particle mass analyzer (APM) or a standard SP2 with the newly developed hSP2.

We have tested the hSP2 in the laboratory using both homogeneous ammonium sulfate, and internally mixed particles of BC (fullerene soot) and ammonium sulfate. These particles were dried and classified by an APM and subsequently measured by the hSP2 between 60% and 90% RH. We assumed a core-shell geometry for the BC-containing particles, and took account of the reduction in refractive index of the coating materials due to their hygroscopic growth. Measured GFs of the laboratory-generated BC-containing particles agreed with GFs predicted by κ -Köhler theory to within measurement uncertainty, demonstrating the applicability of the hSP2 for ambient measurements.

Keywords: black carbon, hygroscopicity

An Empirical Correction Factor for Filter-based Photo-absorption Black Carbon Measurements

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Long-term observations of black carbon (BC) aerosol provide important information regarding seasonal variations, emission source attribution, and regional distribution & transport. Filter-based BC measurement techniques such as the Continuous Soot Monitoring System (COSMOS) are particularly well suited to this application, due to their relative robustness and reliability. However, caution is required when determining the threshold transmittance, Tr_{thresh} (proportional to the time interval between filter changes), in order to ensure that acceptable measurement accuracy is maintained throughout the sampling period. We present a new, empirically derived transmittance-dependent correction factor used to interpret the response characteristics of filter-based aerosol absorption measurements performed by COSMOS. Simultaneous measurements of ambient BC aerosol mass (M_{BC}) were conducted in Tokyo, Japan, using two identical COSMOS instruments operated with different threshold transmittance, Tr_{thresh} , values, of 0.95 and 0.6. The derived values for M_{BC} were consistently underestimated by the COSMOS operating at lower Tr_{thresh} , as a function of decreasing filter transmittance. The 1-hour averaged values of M_{BC} were underestimated by around 10 %, incorporating measurements across the entire range of filter transmittance (1 - 0.6), with a maximum underestimation at around 17 % immediately preceding filter advancement (i.e. $Tr = \sim 0.60$), and a minimum of ~ 1 % immediately following filter advancement (i.e. $Tr = \sim 1$). An empirical second-order correction factor was derived from these ambient measurements, and was applied to M_{BC} as a function of filter transmittance, resolving the instruments to within 2 %.

Furthermore, the operational performance of COSMOS was tested for a new quartz fibre filter (HEPA). A comparison of different filter types demonstrated a systematic overestimation of M_{BC} of around 6 - 8 % when using HEPA filters. A sensitivity study of a radiative transfer model indicated that this enhanced absorption was primarily a result of the increased thickness of the HEPA filter.

Keywords: aerosol, black carbon, filter-based measurements, absorption

Ship-borne measurements of black carbon aerosols over northwestern Pacific and Bering Sea

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Black carbon (BC) aerosol can strongly absorb the solar radiation and act as cloud condensation nuclei depending on the mixing state. Therefore, BC abundance and mixing state are key physicochemical properties to estimate the radiative impacts of BC aerosols [1]. Measurements of BC aerosols over the area where BC concentrations are very low are still limited because of the lack of high-sensitivity analytical methods. Single Particles Soot Photometer (SP2), which has been developed by Droplet Measurement, Inc., allows us to quantify the BC mass of single BC-containing particle and measure the BC number/mass concentration even in ultra-clean air [2]. Here we report the concentrations and mixing state of BC-containing particles observed using a SP2 on the research vessel *Mirai* during the research cruise over the northwestern Pacific and Bering Sea (MR13-05 cruise, 8/12-26, 2013).

BC mass concentrations over the sea near Japan (<145°E) were elevated to $\sim 200 \text{ ng m}^{-3}$, whereas they were less than $\sim 40 \text{ ng m}^{-3}$ over the northwestern Pacific and Bering Sea. Mixing states as a function of BC-containing particles deduced from SP2 raw data were categorized into three types; bare/thinly coated (type1), thickly coated (type2), and non-core-shell (type3) BC. Over the northwestern Pacific and Bering Sea, the number fractions of type1-BC were ~ 0.13 , whereas those of type2-BC were as high as 0.8. We also found the minor but significant presence of type3-BC ($\sim 4\%$) over the remote ocean.

References

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Keywords: Black carbon, Mixing state, Laser Induced Incandescence, Ship-borne measurement, Marine atmosphere

High- m/z ion signal to total mass signal ratios measured for secondary organic aerosol using aerosol mass spectrometer

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A volatility basis-set (VBS) model in which oligomerizations are taken into account has recently been tested for further improvements of conventional VBS models.¹⁾ In order to study the oligomerization rates during secondary organic aerosol (SOA) formation and the ratio of high- m/z ion to total SOA mass spectrum ion signal, SOA particles produced during laboratory chamber experiments were analyzed by using an Aerodyne aerosol mass spectrometer (AMS). Photooxidation of α -pinene, isoprene, toluene, and 1,3,5-trimethylbenzene (TMB) was investigated in the presence of NO_x . Ozonolysis of α -pinene and isoprene was also studied. A stainless steel tube was used as a collection tube for AMS. A mass spectrum measured for organic aerosol (OA) in the region $m/z = 10 - 675$ was divided into seven mass regions; the total signal of each mass region was studied as a function of time. Increase in the signal intensity was observed with increasing of the OA level in a region $m/z < 500$. The oligomer signals increased up to substantial levels within one hour after nucleation. After substantial amounts of oligomers were produced, the ratio of the total signal of each mass region to total OA signal was constant. Next, the ratio of total mass signal in the region $m/z > m_1$ to total OA mass signal, ϕ , was determined:

$$\phi = \text{OA} (m/z > m_1) / \text{OA}(\text{total}),$$
$$m_1 = n m_C (\text{OM}/\text{OC}),$$

where n is the number of carbon atoms in SOA precursor, m_C is the carbon atomic mass, and OM/OC is organic matter to organic carbon mass ratio measured by AMS. The m_1 values of α -pinene, isoprene, toluene, and TMB were determined to be 217, 147, 180, and 204, respectively. We assumed that a contribution from monomer signals is low in a region $m/z > m_1$. Signals measured by electron ionization of AMS contain both the fragment and parent ions of organic compounds. Note that the value, ϕ , is an index of oligomer to total SOA ratio, but does not represent an absolute value of that ratio. The ϕ value of SOA from the same precursor decreased with increasing of SOA mass loading (Fig. 1), showing that oligomer formation is suppressed under high mass loading conditions. In a region $10 - 100 \mu\text{g m}^{-3}$, the ϕ value of toluene SOA was the highest, whereas that of α -pinene SOA was the lowest. No apparent effect of oxidation method (photooxidation or ozonolysis) was observed.

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Keywords: secondary organic aerosol, oligomerizations, aerosol mass spectrometer, aerosol mass loading, chemical structure

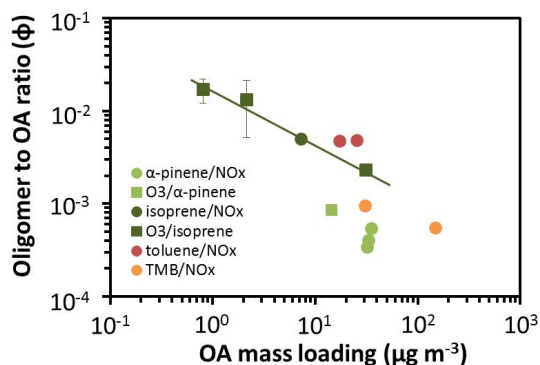


Fig. 1. Effects of OA mass loading on the oligomer to OA signal ratio (ϕ).

Controlling factors of aerosol size distribution over East Asia

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Aerosol is known for its direct and indirect effects on climate, with both effects having a larger uncertainty than other radiative forcing elements, such as carbon dioxide. Investigating ambient aerosol size distributions is an important factor in estimating radiative forcing effects, as aerosol size is a major contributing factor to both the aerosol direct and indirect effects.

Ambient aerosol size and spatial distributions are controlled by various processes; e.g. new particle formation, coagulation, transportation, and wet deposition. For this reason, in situ measurements and analyses based on such processes are essential. However, results from measurements with high time resolution and low detection limits (e.g. of aerosol diameter) are rare. In this research, we introduce measurements of the aerosol size distribution over East Asia using the ultra high sensitivity aerosol spectrometer (UHSAS), and have tried to analyze the results based on wet removal processes.

The UHSAS is an optical particle counter. With its 2 types of photon diode and its efficiency in collecting scattering light, the UHSAS can obtain measurements of aerosol diameter in a wide range (about 70 to 1500 nm). We improved the hardware and software of the UHSAS specifically for use in aircraft measurements, to improve time resolution data and the instrumental precision of measurements of aerosol number concentration and size distribution (assuming spherical particles with refractive index 1.52). In addition, we have installed a robust mass-flow controlling system to deal with the significant changes in pressure associated with aircraft measurements. Scattering light signals obtained from photon diodes are saved to an external storage medium, which aids us in distinguishing signal from noise. We also present results showing the successful estimation of the optics inside UHSAS, in order to obtain highly precise diameter information using known standard particles.

The aerosol radiative forcing in East Asia (A-Force 2013W) aircraft campaign was conducted from late February to early March. We obtained air samples in real time from a forward facing inlet outside of the aircraft, Air was sampled by a variety of instruments including the UHSAS in real-time from a forward facing inlet outside of the aircraft. Data from the UHSAS showed good consistency with other instruments. During the campaign, the mean size distribution shifted to smaller diameters with increasing altitude. The transport efficiency (TE) of BC, which describes the degree of the wet removal of BC (calculated from the carbon monoxide mixing ratio and BC mass concentration), also decreased with increasing altitude (i.e. strong wet removal tendency for higher altitude). As the TE became smaller, the mean size distribution also shifted to smaller diameters, independent of altitude. This shows that the TE is the dominant factor controlling the aerosol size distribution, rather than absolute altitude. When the TE is smaller, the size distribution shifted to smaller diameters; this is the first observation of the size-dependent wet removal of general aerosols based on Köhler theory. This dynamic state of aerosol size distribution observed by the UHSAS surely contributes to quantitative understanding of aerosol direct and indirect effects on climate.

Keywords: aerosol, size distribution, wet removal process, black carbon, transport efficiency, UHSAS

Vertical profiles of aerosol size distribution in small forest within a western suburb of Tokyo

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Forests interact in a complex manner with the atmosphere by acting as sinks for many atmospheric pollutants and trace gases, and by emitting biogenic volatile organic compounds into the air. These constituents influence the atmospheric chemistry and composition, including aerosols related to cloud condensation nuclei (CCN). Aerosol chemical and physical properties vary both temporally and spatially owing to various atmospheric processes (e.g., scavenging, nucleation, evaporation, and condensation) during the dispersion and transportation of air mass within and above forest canopies.

In this paper, we report on the field observations conducted from a 30-m-high tower in a small forest at the Field Museum Tama Hills, an experimental forest of the Tokyo University of Agriculture and Technology, located in a western suburb of Tokyo, between July 27 and August 3, 2013. At this site, atmospheric aerosols were expected to include the particles both from natural and anthropogenic sources. Using five sampling inlets placed at altitudes ranging from 8 m to 30 m, we conducted altitude-resolved measurements of particle number size distributions in the size range of 10-5000 nm. Herein, we present an outline of the observation systems, as well as the preliminary results of variability of sub-micrometer and nano particles within and above the forest canopy.

Keywords: Aerosol, Size distribution, Vertical distribution, Forest canopy

Measurement of fluorescent particles over the western Pacific

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Recently, fluorescence from suspended single particles has been employed to identify and classify the certain types of organic/biological particles. Bioaerosols, including bacteria and other particles derived from living organisms, may explain large unidentified fraction of organic aerosols and play important roles in the cloud formation. In this study, we employed a single-particle fluorescence sensor, WIBS-4, to understand the abundance of bioaerosol particles over the western Pacific.

We conducted ambient air measurements over the western Pacific at July 2011, 2012, and 2013 by R/V MIRAI cruise. In order to avoid analyzing the particles emitted by ship's funnel, we eliminated the data by the wind direction. In the cruises, the bioaerosol particles based on fluorescent pattern were in the range of 0.1-2 particles/cc over the western Pacific. In the presentation, we will compare ocean surface chlorophyll data with detected fluorescence particles.

Keywords: aerosol particles, fluorescence

Impact of the Kuroshio warm SST on low altitude clouds: Numerical model simulation with smoothed SST

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Along the Kuroshio ocean current, high sea surface temperature (SST) is maintained even in winter and a steep SST gradient is formed across the current. In winter and spring, cold northwesterly air often flows from the Asia continent into the East China Sea. Once this cold air reaches the Kuroshio warm current, a large temperature contrast between sea surface and surface air (SAT) causes the marine boundary layer unstable and affect low altitude cloud formation. The northwesterly wind also transports a large amount of anthropogenic aerosols to East China Sea. These aerosols work as cloud condensation nuclei (CCN) and they affect microphysical properties of clouds. Because the marine boundary layer stability affects aerosol activation to form cloud particles, the large contrast between SST and SAT over the Kuroshio can also affect the aerosol-cloud interaction as proposed by Koike et al. [2012].

In order to assess the impact of Kuroshio warm SST on low clouds, we made WRF model calculations for a period between 21 Mar and 30 Apr 2009. In addition to the control calculation, we made sensitivity calculations, in which artificially smoothed SST was given for a lower boundary condition. In this smoothed SST, the SST gradually decreases toward higher latitudes and the maximum along the Kuroshio current no longer exists.

In the control calculation, the monthly mean cloud fraction (frequency of cloud occurrence in April 2009) was high in the south of Kuroshio and had a steep north-south gradient, corresponding to the SST steep gradient. A monthly mean liquid water path (LWP) was large along Kuroshio and small in East China Sea, although it enhanced when cyclones passed. As compared with the control calculation, both the cloud fraction and LWP decreased over the Kuroshio in smoothed-SST calculations, and their north-south gradients became gentler.

LWP differences between control and sensitivity calculations varied depending on the wind direction. In northerly wind conditions, the LWP decreased in warmer flank (downwind) of a SST front. Under calm and horizontally homogeneous wind conditions, water vapor transport convergence was relatively small over the Kuroshio and column-integrated water vapor increased mainly by evaporation from the sea surface. In such case, LWP decreased on the Kuroshio in sensitivity calculation. This suggests that warm SST associated with Kuroshio enhances the evaporation and contributes to increase LWP of low clouds.

Keywords: low clouds, Kuroshio

Measurement of the hygroscopic growth factor distributions of aerosol particles and the mass spectra of single particles

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Hygroscopicity is a property that relates to the lifetime, chemical reactivity and cloud condensation nucleus activity of atmospheric aerosol particles. The amount of water retained by the particles as a function of relative humidity (RH) is governed by the phase state and chemical composition. In this study, hygroscopic growth factor distributions of atmospheric aerosol particles and mass spectra of single particles selected by the growth factors were measured using a combination of hygroscopicity tandem differential mobility analyzer (HTDMA) and a high resolution time-of-flight aerosol mass spectrometer (AMS) in Nagoya.

The observation of urban aerosols was performed on Higashiyama campus of Nagoya University in June and July, 2013. After aerosols were passed through PM1 cyclone and dried in diffusion driers, 300 nm particles were selected in the first DMA of the HTDMA. The growth factor distributions of the particles were measured under humidified conditions (setting RH: 37%, 65%, and 87%). The measurements were performed in both humidification and dehumidification modes. The mass spectra of single particles with specific hygroscopic growth factors g (1.0 at setting RH of 37%; 1.0, 1.1, and 1.25 at setting RH of 65%; 1.0 and 1.5 at setting RH of 87%) were measured using the AMS. The size distributions of aerosol particles were measured separately. The concentrations of organic carbon and elemental carbon in parts of the study period were also obtained.

In the humidification mode, the averages of the growth factor distributions at setting RH of 37% and 65% did not show substantial hygroscopic growth in terms of mean g (1.00 and 1.02, respectively), and those at setting RH of 87% showed large mean g (1.48). In the dehumidification mode, mean g of the averages of the growth factor distributions at setting RH of 37% and 65% (1.07 and 1.18, respectively) were substantially larger than those in the humidification mode, suggesting the presence of metastable-state aqueous solutions in the particles. At setting RH of 87%, the mean g in the dehumidification mode was large (1.44) as in the case of the humidification mode. The mass spectra of single particles with specific g were extracted from the obtained data; the number of these spectra was 349.

Keywords: hygroscopicity, single particle

CCN activity of aerosol and its relation to air mass origins: an analysis based on year-round observation at Noto, Japan

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Atmospheric aerosols play an important role in controlling the earth's radiation balance and/or the hydrological system by acting as cloud condensation nuclei (CCN). For a quantitative evaluation of CCN characteristics in the East Asia, CCN activity of atmospheric aerosols in submicrometer size range were measured at Noto Ground-based Research Observatory (NOTOGRO), located at the tip of Noto peninsula, facing the Sea of Japan. The observation was conducted from October 2012 to September 2013, to investigate the seasonal variability in CCN activity of the atmospheric aerosols.

CCN efficiency spectra, where CCN number fraction is plotted against the diameter of aerosols, were obtained at four different supersaturation (SS) conditions (0.1%, 0.2%, 0.5% and 0.8%) by using a scanning mobility CCN analysis (SMCA) system (Moore et al., 2010). Hygroscopicity parameters kappa (Petters and Kreidenweis, 2007), which depends on the chemical composition of aerosols, were estimated through analyses of the CCN spectra. The bulk chemical composition of non-refractory submicrometer-sized aerosols was also measured by an aerosol chemical speciation monitor (ACSM). Seven-days backward trajectories at the height of 500 m above the sea level were calculated by using NOAA/HYSPLIT4 model.

The CCN activation diameters of the atmospheric aerosols were clearly larger than those of pure ammonium sulfate throughout the year. The mean kappa values ranged between those of pure ammonium sulfate (0.61) and several pure organic compounds (0 to 0.25). These evidences suggest that the atmospheric aerosols were mixture of ammonium sulfate and organics. The bulk chemical composition derived by ACSM also showed that organics, sulfate and ammonium were three major components throughout the observation period. The contribution of organics to the CCN activity of the atmospheric aerosols observed in this study was more apparent than those obtained in the previous studies in the East Asia. As most of the previous CCN studies in East Asia were conducted in the season significantly affected by Asian outflow of pollutants, current numerical models might overestimate CCN concentrations in the East Asia.

The mean kappa values were 0.30, 0.26, and 0.18 during the spring, autumn and summer, respectively. The difference in kappa values among the seasons might be caused by difference in air mass origin. Air masses to the NOTOGRO site came mainly from NW across the Sea of Japan during the autumn and spring, whereas air masses of Pacific origin, those passed over the Japan islands, prevailed in the summer. Relatively high kappa values were observed under the influence of continental polluted air masses with high sulfate concentration. On the other hand, organic aerosols derived by photochemical oxidation were dominant in summer, resulted in low kappa values. The variation in kappa values of organics with air mass origins will also be discussed.

References

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

Long-term observation of initial droplet growth of activated CCN at Noto peninsula, Japan

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Atmospheric aerosols affect the climate indirectly by changing optical property and lifetime of clouds through their ability to act as cloud condensation nuclei (CCN). Size of cloud droplets is an important factor to consider in the climate predictions because it can influence cloud albedo and frequency of precipitation. Important factors controlling the growth of cloud droplets are; 1. water vapor supersaturation (SS), 2. CCN size and 3. CCN chemical composition. Chemical composition of aerosols is a very important factor controlling the initial droplets growth. Recent studies indicate that there is high mass fraction of organics in the CCN relevant particles, and the droplet growth kinetics following the activation of such organic containing CCN is not fully understood.

East Asia is regarded as one of the most aerosol (hence CCN) dense regions in the world, but long-term monitoring of CCN properties in this region is relatively scarce. In this study, we conducted in-site and year-round measurement of CCN activity of submicron aerosols and related cloud droplet growth kinetics at NOTOGRO (acronym for NOTO Ground-based Research Observatory) located Suzu city, Noto Peninsula. A CCN counter (CCNC, CCN-100, DMT) was operated at four different supersaturation conditions (SS=0.1%, 0.2%, 0.5%, 0.8%). The diameters of cloud droplets activated from ambient aerosols ($D_{ambient}$) were compared to those activated from ammonium sulfate (D_{AS}) which is regarded as representative inorganic CCN. In order to identify factors that can potentially influence the initial cloud droplet growth, simultaneously measured chemical composition of aerosols with an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc.).

The measurement result showed that $D_{ambient}$ was not significantly difference from D_{AS} under higher SS conditions (i.e. SS=0.5% and 0.8%) throughout all seasons. However, there are periods that droplet growth was inhibited under lower SS conditions (i.e. SS=0.1% and 0.2%) especially during spring and autumn. Therefore, it was suggested that droplet growth under lower SS condition was more sensitive to other factors (other than SS). Based on the ACSM results, chemical composition of CCN was mainly contributed by various organics, ammonium and sulfate during the entire measurement period. The periods with limited droplet growth coincided with the periods with high organic mass fraction, and the negative correlation was found between the cloud droplets' diameters and organic mass fraction within atmospheric aerosols in CCN relevant sizes. On the other hand, we did not observe significant fluctuation in the cloud droplet diameters in winter. The measurement site is under the strong influence of winter monsoon especially during winter and the chemical species comprising CCN that are carried to the site may be considerably different from other seasons.

Keywords: cloud condensation nuclei, cloud droplet, chemical composition

Seasonal variations of peroxyacyl nitrates and alkyl nitrates concentration at Suzu, the Noto Peninsula

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NO_x emissions have been increasing in East Asia with recent remarkable economic progress. NO_x has relatively short lifetime and NO_x concentrations are governed by local NO_x emissions. On the other hand, descendant photochemical products of NO_x such as T.NO_3 (the sum of gaseous nitric acid and particulate nitrates), PANs (peroxyacyl nitrates) and ANs (alkyl nitrates) have longer lifetime than NO_x , so that they can be transported over a long-distance. In order to understand influences of the cross-border pollution, it is important to clarify the long-range transport of T.NO_3 , PANs, and ANs.

We have been continuously observing several pollutants at NOTOGRO (Noto Ground-based Research Observatory) super-site in Suzu, the Noto Peninsula. NOTOGRO is located at 37.45N and 137.36E. NO_x were determined by an LED photolytic converter / NO-O_3 chemiluminescence method. NO_y and T.NO_3 were observed by a scrubber difference / NO-O_3 chemiluminescence method. CO was monitored by a non-dispersive infrared photometer. PANs and ANs were measured by a thermal dissociation / cavity attenuated phase shift spectroscopy method.

In this presentation, observational results and discussion from December, 2012 to July, 2013 are described, focusing on seasonal variations of PANs and ANs. The air mass origins arriving at Suzu were classified into the following four groups, Russia and North China (RC), Korea and Middle China (KC) and Japan (JP) and Sea (S) using backward trajectory analyses. From winter to spring, both PANs and ANs concentrations from KC were higher than those from the other air mass origins. From spring to summer, their concentrations were independent of air mass origins.

From winter to spring, the lifetimes of PANs and ANs are long because of low temperature and weak solar radiation. In addition, their in-situ photochemical generation rates are low, so that PANs and ANs concentrations in this season are governed by long-range transport. From spring to summer, the lifetimes of PANs and ANs become shorter and their photochemical production rates become higher, that is, local photochemical productions of PANs and ANs are relatively important. Diurnal variations of PANs and ANs also support these concentration variation factors. From winter to spring, no diurnal variations were observed. Meanwhile, PANs and ANs concentrations began to be higher and lower in the daytime and nighttime, respectively, from spring to summer.

Keywords: peroxyacyl nitrates and alkyl nitrates, long-range transport, seasonal variation

Development of a continuous measurement system of PANs and alkyl nitrates in the atmosphere and observations at Suzu, th

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Peroxyacyl nitrates (PANs) and alkyl nitrates (ANs) are generated in the atmosphere by oxidation of NO_x in the presence of solar ultraviolet. They have a comparatively long lifetime, and are important as transboundary air pollutants. On the other hand, PANs and ANs act as the reservoirs of NO_x . In order to clarify transboundary pollution of nitrogen oxides, comprehensive measurements of total odd nitrogen species (NO_y), including PANs and ANs, are required. In this research, a continuous measurement system of total PANs and ANs has been developed by a thermal dissociation / cavity attenuated phase shift spectroscopy (TD/CAPS) method.

This instrument consists of heated quartz tubes to decompose PANs and ANs into NO_2 , and a CAPS- NO_2 analyzer. This system has three intake lines; NO_2 , PANs and ANs lines. The NO_2 line equip of a quartz tube without heating. The PANs and ANs line equip quartz tubes heated at 433 K and 633 K, respectively for thermally decomposing them into NO_2 . Concentrations of NO_2 , $\text{NO}_2 + \text{PANs}$ and $\text{NO}_2 + \text{PANs} + \text{ANs}$ can be obtained from the NO_2 , PANs and ANs lines, respectively. These concentrations are sequentially measured by switching solenoid valves and then NO_2 , PANs and ANs concentrations are obtained. Since a part of HNO_3 is pyrolyzed in the ANs line, annular denuder coated with NaCl to remove HNO_3 is set before the heated quartz tube in the ANs line. The decomposition efficiencies of PANs and ANs were calibrated to be 100 and 95%, respectively, for all kinds of PANs and ANs examined.

Continuous field observations of PANs and ANs have been being performed at NOTOGRO (Noto ground-based Research observatory) supersite in Suzu, the Noto Peninsula, since November 2012. Continuous measurements of NO_x , NO_y , T. NO_3 (the sum of gaseous nitric acid and particulate nitrate) O_3 , and CO have also been being conducted. NO_y concentrations were in agreement with the sum of observed NO_y components (= $\text{NO}_x + \text{T.NO}_3 + \text{PANs} + \text{ANs}$) regardless of seasons. NO_x fractions were the highest in NO_y constituents. Fractions of T. NO_3 in January and February were lower than those in other months. This reflects that wet deposition of T. NO_3 would be accelerated in winter due to snowfall. On the other hand, PANs fractions in spring and summer were smaller than those in winter. This suggests that temperature increasing promotes decomposition of PANs.

Keywords: peroxyacyl nitrates (PANs), alkyl nitrates, total odd nitrogen species, cavity attenuated phase shift spectroscopy

On-line measurements of multiple alkanes by chemical ionization mass spectrometry using NO^+ as the reagent ion

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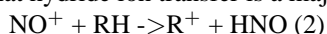
¹NIES, ²NTSEL

Proton transfer reaction mass spectrometry (PTR-MS) is a technique that allows for fast and sensitive measurement of volatile organic compounds (VOCs) at trace levels in air. Proton transfer is an example of chemical ionization: it enables soft ionization of chemical species that have a proton affinity (PA) higher than that of the reagent species (i.e., water):



Unlike gas chromatography, PTR-MS does not require any sample treatment such as drying and/or preconcentration, which makes possible quantitative measurement of alkenes (except ethylene), aromatics, and even oxygenated VOCs. However, the proton transfer in reaction (1) does not occur for alkanes because they have lower PAs than water. Very recently, a method to measure C_{12} - C_{18} alkanes using PTR-MS was demonstrated. They were, however, detected by a series of fragment ions with formula $\text{C}_n\text{H}_{2n+1}$ and were detected not individually, but as an ensemble.

Reactions of alkanes with NO^+ have been investigated by selected ion flow tube mass spectrometry (SIFT-MS). It was reported that hydride ion transfer is a major channel in the reaction of alkanes (RH) with NO^+ .



Recently, the PTR-MS instrument has been combined with switchable reagent ion capability, which allows for easy and fast switching between H_3O^+ and NO^+ (proton-transfer-reaction *plus* switchable reagent ion mass spectrometry (PTR + SRI-MS)).

In the present study, the detection properties of alkanes by PTR + SRI-MS are investigated. We confirmed that alkanes (RH) were usually detected as R^+ by PTR + SRI-MS using NO^+ as the reagent ion and detection sensitivities were comparable to those of aromatics observed by H_3O^+ ionization. We also demonstrated time-resolved measurements of C_4 - C_{16} alkanes in automotive exhaust during the Japanese JC08 transient cycle. It can be concluded that sensitive on-line measurement of multiple alkanes is possible by PTR + SRI-MS using NO^+ as the reagent ion.

Keywords: PTR-MS, alkane, NO^+ chemical ionization, Gasoline vehicle, Diesel vehicle, Exhaust gas

Observation of formaldehyde and glyoxal variations by MAX-DOAS in Chiba and Tsukuba in 2013

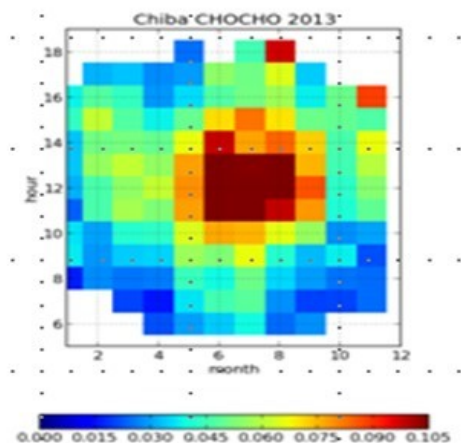
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BVOCs (Biogenic Volatile Organic Compounds) are plant-released organic chemicals that are volatile in air at normal ambient temperature and pressure. Reactions of BVOC in the atmosphere have a great influence on the OH abundance in the atmosphere. In addition, the reactions lead to the formation of ozone, which is not only adversely affecting plants and human health but also acting as a greenhouse gas. Furthermore, part of the products from the oxidation reaction of BVOCs forms aerosols, which play a critical role in cloud formation processes and radiation balance. Thus, BVOCs are deeply related with climate and air quality surrounding us. Recently, formaldehyde and glyoxal are recognized as important indicators of oxidations of BVOCs. However, their observations have been limited. In this study, we use the data got from MAX-DOAS to analysis the diurnal variation, seasonal variation of formaldehyde and glyoxal for the first time. And then we try to find the reason or the factors which makes the variations.

Figure1 shows the data of glyoxal concentration observed in Chiba during 2013. To know the diurnal and seasonal variation, we calculated the average value of every hour in each month. We found the clearly pattern that the concentration of glyoxal is high during the day and summer. At noon of the summer, the concentration of glyoxal was increased to more than 0.105ppbv. We also found the same pattern in Tsukuba. In this study, we observed glyoxal and formaldehyde in the same time, and organize the data of Chiba and Tsukuba in 2013 and try to find the reason of the variation.

Keywords: Formaldehyde, Glyoxal, MAX-DOAS, diurnal variation, seasonal variation



Development of a direct measurement system of photochemical ozone production rate in the troposphere

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Recently, ozone concentrations in the troposphere have been rising in spite of a steady decrease in concentrations of ozone precursors such as NO_x and volatile organic compounds. Photochemical production processes of ozone are non-linear to concentrations of ozone precursors. In addition, ozone concentration variations are influenced by meteorological factors such as transport and deposition processes as well as photochemistry. It is useful that the meteorological and photochemical factors could be divided to discuss ozone concentration variations. In order to discuss only "photochemical" factors for ozone production, a direct measurement system of photochemical ozone production rate has been developed.

Ambient air is introduced into "reaction" and "reference" chambers. The reaction and reference chambers (171-mm inner diameter and 500-mm length) are made of quartz and Pyrex, respectively. Inner walls of both the chambers are coated with Teflon to avoid wall loss of ozone. An outer wall of the reference chamber is coated with a UV-cut film (50%-cutoff wavelength of 405 nm). In the reaction chamber, photochemical reactions proceed to generate ozone. On the other hand, ozone is not produced photochemically in the reference chamber. Air passed from the reaction and reference chambers is introduced into "NO-reaction" tubes to convert O_3 to NO_2 in the presence of a high concentration of NO, and then the air is introduced into an NO_2 measurement system by a laser-induced fluorescence technique. Increment of ozone (ΔO_3) is defined by the difference of NO_2 concentrations derived from the reaction chamber and those from reference chamber. The ozone production rate is obtained by dividing ΔO_3 by a mean residence time of air in the reaction chamber (τ). In this system, O_3 concentrations are not directly measured but NO_2 concentrations converted by the reaction of O_3 with excess NO are observed. This is because the photostationary states between NO_x and O_3 are different between in the reaction and reference chambers, and ozone concentrations vary apparently. The sum of ozone and NO_2 concentrations (abbreviated as PO) are kept in the different photostationary states, so that this instrument measures production rates of PO instead of those of ozone practically.

Important parameters in this system are (1) ultraviolet transmittance of the reaction and reference chambers, (2) τ , and (3) conversion efficiency of O_3 to NO_2 in the NO-reaction tube. For (1), we measured solar spectra at inside and outside of the chambers using a spectroradiometer. Almost a hundred % of solar UV was transmitted into the reaction chamber. A wall of the reference chamber cut off solar UV adequately. For (2), about 10 ppmv of pulsed NO_2 was added into the reaction chamber and temporal variations of LIF signals were measured. τ was calculated to be 22.1 ± 0.5 min using the temporal variation the signals. For (3), quantitative conversions of O_3 up to 160 ppbv by NO in the NO-reaction tube were confirmed under the excess NO condition 0.97 ppmv.

Keywords: photochemical ozone, direct measurement of ozone production rate, laser-induced fluorescence

Transboundary ozone pollution from China to Japan; a case study

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These days, high concentrations of atmospheric ozone are often observed at the ground and/or in the lower troposphere over Japan, and transboundary ozone pollution from China would be one the possibility.

In this study we sampled highly concentrated ozone events observed at the ground and in the lower troposphere, and calculated backward trajectories hourly from the observation sites and compared the trajectories with the ozone map obtained by satellite measurement. The ozone lidar used here is the MRL (Meteorological Research Laboratory) ozone lidar [Nakazato et al., Applied Optics, 2007], which has short wavelengths in UV and thus continuous day-and-night measurements are possible. We also utilized the surface ozone monitoring network organized by Ministry of Environment.

The ozone distribution maps at the lower troposphere were obtained by OMI ozone product provided by Liu et al. [ACP, 2010]. They retrieved ozone profiles from the ground up to about 60 km into 24 layers among which 3 layers are in the troposphere. The lowermost layer (24th layer) is corresponding to 0 ~about 3 km.

From analysis mentioned above, we found some cases indicating clear evidence of transboundary pollution from China to Korea and Japan.

This study was supported by a Grant - in - Aid from the Green Network of Excellence, Environmental Information(GRENE - ei) program. And OMI data were provided by Dr. X.Liu and Dr. K.Chance, and Ozone - lidar data were provided by Dr. M.Nakazato.

Keywords: troposphere, ozone, trajectory, transport, China

Validation observation for the derivation of lower tropospheric ozone by remote sensing

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The lower tropospheric ozone is a major component of photochemical oxidant which causes photochemical smog, adversely affecting human health and vegetation when it comes to high concentration. Therefore knowing their behavior as air pollution is an important. In recent years, contrary to the reduction of lower tropospheric ozone precursor gases, their amount is increasing. It has been suggested that the long-range transport of the lower tropospheric ozone from Asian Continent affects air quality in Japan and other wide areas. Remote sensing from a satellite is effective to observe such extensive/transboundary air pollution. However it has been quite difficult to measure the lower tropospheric ozone from satellite.

We have proposed that it can be evaluated with simultaneous measurement of solar backscattering spectra in the ultraviolet(UV) and visible(Vis) regions. Because the atmospheric Rayleigh scattering cross-section is much larger in UV than that in Vis, lower tropospheric light path length of the solar scattered radiation observed from space is significantly different in these two wavelength regions. This difference of light path enables us to detect the lower tropospheric ozone by the simultaneous measurement of UV and Vis solar backscattered spectra from space.

For the validation of this technique, we carried out aircraft experiments to validate this method over Tsukuba on 10th and 13rd September 2012. UV and Vis backscatter spectra were measured with two spectrometers (Maya2000pro, Ocean Optics, USA) at two altitudes 2500 ft (760 m) and 25000 ft (7600 m). Simultaneously, ozone profile was measured with ozone monitors on-board the aircraft, with ozonesonde launched near Tsukuba, and the tropospheric ozone lidar. Because aerosol scattering may significantly affect the evaluation of the lower tropospheric ozone amount, in situ aerosol observation with the CRDS, PSAP, and PASS instruments and the lidar observation were carried out in the Meteorological Research Institute. From the aircraft, we observed solar scattered radiation from zenith, nadir and 20 degree oblique directions in ultraviolet(300 - 380nm wavelength) and visible(400 - 700nm wavelength) spectral range. Because the surface reflected light greatly contribute to the scattered light from nadir, especially in the visible spectral range, for accurately estimation of the ozone amount, it is particularly important to understand the surface reflection spectrum. In this experiment, ground reflection spectra at different surface conditions such as rice paddy, forest, urban, farm areas and so on were measured at a low altitude of 2500ft (760m). It is necessary to consider the effect of scattering near the aircraft to estimate the surface reflected light. We estimated it with SCIATRAN (Rozanov et al., 2005). Results of these observations will be presented at this session.

Keywords: Remote Sensing, Lower tropospheric ozone

The Relationship between CO Concentration and Biomass Burning over the North China Plain

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Carbon monoxide (CO) controls the greenhouse gasses (e.g., CH₄, O₃) indirectly through a chemical reactions. Therefore, CO is regarded as an indirect-greenhouse gas and thus it is important to understand its spatiotemporal variation.

Wang et al.,[JGR, 2002] suggested that the open crop residue burning in June over the North China Plain affects on CO concentration, and it was confirmed by field campaign at Mt.Tai and investigated by model simulations [Kanaya et al.,2013 and reference therein]. Besides, the recent rapid industrialization in China brought significant increase in emission of CO [Ohara et al., ACP, 2007].

In this study, we analyzed the relationship between fire outbreak and CO concentration over the North China Plain by using satellite data. The CO data are taken from Measurement Of Pollution In The Troposphere (MOPITT). We used the Version 5 product. The fires detected by satellite observations are expressed as the hotspot numbers that are derived from the MODIS thermal anomaly product [Takeuchi and Yasuoka, 2006], using the algorithm by [Giglio et al.RSE,2003]. Here we used the hotspot numbers as proxy of the fire detection index.

CO concentration in June increases accompanied by a large number of the hotspot counts, which is consistent as previous studies. On the other hand, CO concentration gradually increases in fall and winter with only few hotspot numbers. It implies that CO emissions are possibly from industrial activity, automobiles and coal burning for heating rather than biomass burning in fall and winter. In addition, the year-to-year variability of CO concentration in June and in fall and winter was different.

This study was supported by a Grant-in-Aid from the Green Network of Excellence, Environmental Information (GRENE-ei) program.

Development of Atmospheric Environmental Risk Management System in Chile and Argentina

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We started an international collaboration project on research of ozone/UV and aerosol in South America since 2013. This project is supported by Japan Science and Technology Agency (JST) and Japan International Cooperation Agency (JICA) under SATREPS program. The counterpart institutions are CEILAP (Laser Application Research Center) in Argentina and Magellan University in Chile. The major aims of this project are (1) to construct new aerosol lidar network in Chile and Argentina, (2) to consolidate the ozone monitoring capability at the South Patagonian Atmospheric Observatory (OAPA, 52S, 69W) in Rio Gallegos at the southern end of the South American continent. The new aerosol lidar network consists of 9 lidars. Six of them are Raman lidars and the other 3 are high-resolution lidars with an iodine filter. Eight lidars are distributed over Argentine territory to observe volcanic ashes from volcanos in Andes, Patagonian dust, and black carbon from Bolivia and Brazil. From the observatory in Rio Gallegos, we will make comprehensive observations of ozone by using a Differential Absorption Lidar (DIAL), millimeter-wave spectral radiometer, brewer spectrometer, and so on. In addition to the consolidation of observing network, we will develop data analysis and data distribution system to deliver the data to the relevant organizations in the both countries.

In the presentation, we will introduce the overview of this project and present a progress report after the first year.

Keywords: Aerosol, Ozonehole, Lidar, Millimeter-wave spectroscopy, International cooperation, Contribution to society

Observations of horizontal distributions of air pollutants by MAX-DOAS

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In June 2012 we set up a MAX-DOAS device in Chiba University and continuous observations have been conducted since then. The MAX-DOAS method measures the spectra of scattered sunlight in ultraviolet and visible regions at various elevation angles. By analyzing the measured spectra with a radiative transfer model and an inversion method, vertical distributions of aerosol and gas and their column amounts can be retrieved (Irie et al., 2008,2009, Vlemmix, 2010). In this study, firstly, we compared the aerosol optical depth measured by the MAX-DOAS to that measured by the sky radiometer. We found the consistency of differences between MAX-DOAS and sky radiometer AOD values are within 30%. Secondly, we set up two MAX-DOAS devices (machine No.1 and No.2) for simultaneous observations at the same place. For both devices, the wavelength regions of 460-490nm and 338-370nm were analyzed with the DOAS method to derive the differential slant column densities (DSCDs) of O₄. In order to quantify the effect of the systematic offset of the elevation angle in O₄ DSCDs, we have biased the offset of elevation angles by $\pm 0.5, \pm 1.0$ degrees. Comparisons such as correlation analysis etc. show that the effect is insignificant as there is only 20% differences found in the O₄ DSCD comparisons between two devices. Based on such a detailed error evaluation, since December 2013, we have directed the machine No.1 to north and No.2 to west to perform quantitative observations of horizontal-distribution of aerosols. Results will be discussed in this work.

Keywords: MAX-DOAS, Elevation angle offset, vertical profile, tropospheric column amount, differential slant column density

Validation of GOSAT SWIR xCH₄ using TCCON and Airborne Measurements

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As methane (CH₄) is one of the most important Short-Lived Climate Pollutants (SLCPs), global monitoring of atmospheric CH₄ with enough accuracy is expected to estimate its sources and sinks. For measurements of global distribution of CO₂ and CH₄ concentration from space, the Greenhouse gases Observing SATellite (GOSAT) was launched in 2009, and has continued measurements up to the present. However, cloud interferes satellite observation. To understand CH₄ emission from a cloudy region, the selection of an adequate criterion of cloud screening, and validation of data quality are necessary.

In this study, we validate the GOSAT CH₄ products of the column-averaged dry-air mole fractions (xCH₄) derived from Short-Wavelength InfraRed (SWIR) radiation by comparing them with data of Total Carbon Column Observing Network (TCCON). Yoshida et al. (AMT, 2013) had already carried out the validation for the NIES product, but we extended the period and involved more TCCON sites; Yoshida et al. (2013) used data observed at the 13 TCCON sites from June, 2009 to December, 2012 and we used data at the 17 TCCON sites from June, 2009 to August, 2013. We found that the average difference between TCCON and GOSAT for the whole period is -6.0 ± 16.1 ppbv.

We also examined the appropriate cloud screening for xCH₄ product from RemoTeC-MACC. The product was obtained by using the "proxy method" by which we can obtain more data under cloudy conditions. In this study, we also tried to compare GOSAT data with aircraft measurements over Siberia and other areas.

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Keywords: GOSAT, validation, methane, cloud screening, aircraft

Variations of tropospheric methane over Japan during 1988-2010

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Mixing ratios of greenhouse gases and related trace gases have been measured using chartered and commercial aircraft in the lower to upper troposphere (LT and UT) over Japan by Tohoku University. We present variations of CH₄ during 1988-2010. The analysis is aided by simulation results using an atmospheric chemistry transport model (i.e. ACTM). Tropospheric CH₄ over Japan shows altitude-dependent interannual and seasonal variations, reflecting differences in air mass origins at different altitudes. The long-term trend and interannual variation of CH₄ in the LT are consistent with previous reports of measurements at surface baseline stations in the northern hemisphere. However, those in the UT show excursions from those in the LT. In the UT, CH₄ mixing ratios show seasonal maximum in August due to efficient transport of air masses influenced by continental CH₄ sources, while LT CH₄ reaches its seasonal minimum during summer due to seasonally maximum chemical loss. Vertical profiles of the CH₄ mixing ratios also vary with season, reflecting the altitude-dependent seasonal cycles. In summer, transport of CH₄-rich air from Asian regions elevates UT CH₄ levels, forming the uniform vertical profile above the mid troposphere. On the other hand, CH₄ decreases nearly monotonically with altitude in winter-spring. The ACTM simulations with different emission scenarios reproduce general features of the tropospheric CH₄ variations over Japan. Tagged tracer simulations using the ACTM indicate substantial contributions of CH₄ sources in South Asia and East Asia to the summertime high CH₄ values observed in the UT. This suggests that our observation data over Japan are highly valuable for capturing CH₄ emission signals, particularly from the Asian continent.

Keywords: aircraft observation, methane, troposphere, over Japan

Measurement of CO₂ stable isotope ratio by mid-inferred laser absorption spectrometry; analysis of CO₂ cycle in urban

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CO₂ concentration has been increasing from the range of 275 ppmv (parts per million by volume) to 285 ppmv in the previous industrial period to about 400 ppmv in 2013. IPCC reported that CO₂ has the most effective on the positive radiative force. The insight of CO₂ emission and absorption flux helps us to estimate the variation of radiative forcing and atmospheric environment. CO₂ concentration changed with the anthropogenic and biogenic emission and absorption. The stable isotope ratio of CO₂ ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) is associated with the CO₂ source such as combustion and biogenic respiration. The contribution of each CO₂ source in the urban area was estimated by using the stable isotope ratio of CO₂.

We conducted the continuous measurement for CO₂ concentration and stable isotope ratio of CO₂ using the mid-inferred absorption spectrometry which can obtain CO₂ concentration and its isotope ratio with high time resolution. The water vapor and stable isotope ratios of water vapor (δD and $\delta^{18}\text{O}\text{-H}_2\text{O}$) were measured to show the relationship between H₂O and CO₂ due to the isotopic exchange reaction. CO and NO_x concentrations were obtained as a tracer of anthropogenic emission. The measurement was conducted for two weeks in summer and winter. The seasonal variation of CO₂ source was shown according to the comparison of CO₂ concentration and stable isotope ratio. Especially, we focused on the contribution of biogenic process to CO₂ concentration variation in the urban area.

CO₂ concentration and stable isotope ratio of CO₂ in the summer showed the diurnal variation. On the other hand, those in the winter had no diurnal variation. CO₂ concentration variation in the winter was correlated with CO concentration variation. These results suppose that CO₂ concentration variation in the winter was mainly dominated by the anthropogenic emission and that in the summer was related with biogenic process as well as anthropogenic emission. We will discuss the relationship between stable isotope ratio and meteorological condition or water vapor isotope ratio to identify the detail of CO₂ source.

Keywords: CO₂ stable isotope ratio, Urban area, CO₂ cycle, mid-inferred laser absorption spectrometry

Temporal and spatial variations of Radon-222 in the western North Pacific

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A new compact radon measuring system has been developed for high-resolution observation of low-level radon-222 (Rn) for the remote sites, in collaboration with the MRI and AIST. The Rn measuring system was installed at 4 stations of Minamitorishima (MNM), Yonagunijima (YON), Chichijima (CCJ) and Ryori (RYO) operated by Japan Meteorological Agency (JMA) since 2007. The Rn measurements clearly show that distinct seasonal variations as well as frequent episodic events with Rn enhancement peaks on a synoptic scale are successfully captured at all 4 stations. Although the seasonal cycles depended on the stations, significant correlations between the Rn and other trace gases were found for the most of the synoptic-scale events, indicating a large impact of widespread pollutions from the East-Asian countries on the regional air quality over the western North Pacific.

Keywords: Radon