AAS22-01   Room:511   Time:April 30 16:15-16:30

Impacts of the Arctic ozone depletion on Japan observed with FTIR

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The ozone depletion occurs not only in the Antarctic but also in the Arctic. A record Arctic ozone depletion which was comparable to the Antarctic ozone depletion occurred in 2011. The ozone depletion itself occurs inside the polar vortex. But the airmass from the inside of the polar vortex is spread to mid-latitude in spring after its breakup. The purpose of this study is to quantify the impact of Arctic ozone depletion on mid-latitude by comparing the amounts of ozone in mid-latitude airmasses before and after the breakup of the polar vortex.

Vertical profiles of O_3, HF and N_2O have been retrieved from infrared spectra observed with Fourier transform infrared spectrometers (FTIR) at Tsukuba and Rikubetsu using the SFIT2 spectral fitting program. Spectra observed from 2006 to 2013 for Tsukuba and from 1997 to 2008 for Rikubetsu were used in this analysis.

HF and N_2O can be used as a tracer of the transport, because they are chemically stable species in the lower stratosphere. O_3 and HF (or N_2O) usually show a high correlation in the lower stratosphere because both species are stable. But the correlation will be changed when ozone is chemically perturbed. Therefore, we examined the correlations of mixing ratios between O_3 and HF (or N_2O) in the mid-latitude airmasses before and after the breakup and determined the chemical loss amount of ozone at the observational sites.

Some chemical ozone losses were found at the altitudes of 19 km and 21 km from O_3-HF correlation. Chemical losses in total ozone were also found from O_3-HF correlation and O_3-N_2O correlation. Then, these observed chemical loss amounts of ozone were compared with the total chemical loss amounts of ozone in the Arctic derived from Japanese Meteorological Agency [2012], Pommereau et al. [2013] and Rex et al. [2013].

Positive correlations were found between the observed chemical loss amounts of ozone at the altitude of 21 km for Tsukuba and at the altitude of 19 km for Rikubetsu and the total chemical loss amounts of ozone in the Arctic. Observed chemical losses in total ozone for both Tsukuba and Rikubetsu also showed positive correlation with the total chemical loss amounts of ozone in the Arctic.

The half-maximum total ozone loss amounts of 15 DU for Tsukba and 20 DU for Rikubetsu were estimated from the correlations, which result in the increases of 6 % and 7% of UV radiation, respectively.

Keywords: FTIR, Arctic ozone depletion, mid-latitude

AAS22-02   Room:511   Time:April 30 16:30-16:45

The first observation of ozone enhancement in the lowermost atmosphere over China from a spaceborne ultraviolet spectrom

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This is the first report of observation from space using ultraviolet radiance for significant enhancement of ozone in the lowermost altitudes (0 to about 3000 m) over East and Central China. The recent retrieval products of the Ozone Monitoring Instrument (OMI) onboard EOS/Aura satellite revealed the spatiotemporal variation of the ozone distribution in the lowermost troposphere [Liu et al., ACP, 2010]. The ozone enhancement over East and Central China was clear in June and July every year, associated with enhancement of CO observed from Measurements Of Pollution In The Troposphere (MOPITT) and hotspots taken from MODerate resolution Imaging Spectroradiometer (MODIS). It suggests that considerable part of the enhancement can be attributed to the emissions of ozone precursors from residue burning after harvesting winter wheat in this area. Ozone enhancement was also observed in autumn and early winter over East and Central China every year, sometimes not accompanied by signals of burning, It implies that CO emissions from industrial activity, automobiles and coal burning for heating would affect on ozone production rather than biomass burning in winter.

Keywords: tropospheric ozone, satellite observation, ultraviolet radiation, atmospheric pollution

AAS22-03　　　　　Room:511　　　　　Time:April 30 16:45-17:00

The validity of the estimation of ozone origin by sectoral air mass classification verified with tracer-tagging simulati

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The air quality in East Asia has changed rapidly in recent years, especially region-wide transboundary air pollution is the main issue in the atmospheric environment in this region. Therefore, the solution to this issue is of great importance today in East Asia, and the scientific understanding of the structure about this region-wide scale air pollution is necessary. The sectoral air mass classification method has been used to estimate the origin of air pollutants in East Asia, and demonstrated the characteristics of air mass with different origins and extended the understanding of the structure of air pollution. However, this method has a problem to erroneously estimate the origin of air pollutant due to the simpleness of the method. Here, we validate of the estimation of ozone origin by sectoral air mass classification by using the tracer-tagging simulation done by a global chemical transport model (CTM). The analysis suggested that the origin of ozone estimated by these two different methods (sectoral air mass classification and tracer-tagging) generally agreed with each other in the warm season, but the two differ significantly in the cold season. The results suggested that the sectoral air mass classification method should consider the different threshold of residence time to separate the air mass into different origins.

AAS22-04　　　　　　　　　Room:511　　　　　　　　　Time:April 30 17:00-17:15

Long-term MAX-DOAS network observations of NO2 in Russia and Asia: comparisons with OMI satellite observations

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We conducted long-term network observations using standardized Multi-Axis Differential optical absorption spectroscopy (MAX-DOAS) instruments in Russia and ASia (MADRAS) from 2007 onwards. At seven locations (Cape Hedo, Fukue, and Yokosuka in Japan, Hefei in China, Gwangju in Korea, and Tomsk and Zvenigorod in Russia) with different levels of pollution, we obtained 80,927 retrievals of tropospheric NO2 vertical column density (TropoNO2VCD) and aerosol optical depth (AOD). This large data set was used to analyze NO2 climatology systematically, including temporal variations from the seasonal to the diurnal scale. The results were compared with Ozone Monitoring Instrument (OMI) satellite observations and global model simulations. Two NO2 retrievals of OMI satellite data (NASA ver. 2.1 and Dutch OMI NO2 (DOMINO) ver. 2.0) generally showed close correlations with those derived from MAX-DOAS observations, but had low biases of ~50%. The bias was distinct when NO2 was abundantly present near the surface and when the AOD was high, suggesting that the aerosol shielding effect could be important, especially for clean sites where the difference could not be attributed to the spatial inhomogeneity. Except for constant biases, the satellite observations showed nearly perfect seasonal agreement with MAX-DOAS observations, suggesting that the analysis of seasonal features of the satellite data were robust. A global chemical transport model, MIROC-ESM-CHEM, was validated for the first time with respect to background NO2 column densities during summer at Cape Hedo and Fukue in the clean marine atmosphere.

Keywords: Nitrogen dioxide, MAX-DOAS, Satellite data validation, temporal variation

AAS22-05   Room:511   Time:April 30 17:15-17:30

Temporal variations of aerosol, glyoxal, and formaldehyde retrieved by MAX-DOAS based on detailed error analysis

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The degradation of volatile organic compounds (VOCs) results in the formation of ozone (O_3) and secondary organic aerosols (SOA) in the troposphere. This process consists of the oxidation of VOCs by hydroxyl radical (OH), O_3, and nitrate radical (NO_3). Detailed understanding of the VOC degradation mechanism is challenged by the co-existence of vast variety of VOC species in the atmosphere. However, investigations on ubiquitous oxidation intermediates, e.g., formaldehyde (HCHO) and glyoxal (CHOCHO), can help us to test and improve the current knowledge of the VOC sources and degradation pathways.

We installed one ground-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) system in Meteorological Research Institute (MRI) located at Tsukuba, Japan (36.06N, 130.13E) in June 2010. In addition, two more systems were installed in Chiba University at Chiba, Japan (35.63N, 140.10E) in June and December 2012, respectively. Since then, we have retrieved lower-tropospheric vertical profile information for eight components; aerosol extinction coefficients at two wavelengths, 357 and 476 nm, and NO_2, HCHO, CHOCHO, H_2O, SO_2, and O_3 concentrations. For a detailed evaluation for the aerosol retrieval, which is a key step in the MAX-DOAS eight-component retrieval, simultaneous aerosol observations with the Cavity Ring-Down Spectroscopy (CRDS) and the sky radiometer were conducted at Tsukuba on October 5-18, 2010 and September 7-18, 2012. At Chiba, in addition to the comparison with sky radiometer data, a self-consistency test was performed by comparing results obtained from two MAX-DOAS systems operated at the same place. Through these detailed evaluations, our retrieval method was improved significantly, attaining excellent agreement with CRDS and sky radiometer data. On the basis of these efforts, seasonal and diurnal temporal variations in HCHO and CHOCHO concentrations retrieved from our MAX-DOAS system are discussed in this talk.

Keywords: CHOCHO, HCHO, MAX-DOAS, CRDS, sky radiometer

Development of an angle-resolved polar nephelometer and its application to non-spherical particles

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Angular distribution of scattering is one of the important optical properties contributing to the radiation balance in the Earth's atmosphere. Therefore,accurate description of the single-scattering properties of aerosol particles is required. In addition, the angular distribution of scattering of individual aerosol particle provides useful information to determine its size, shape, and refractive index of particles.

We are developing a new polar nephelometer, which can measure angular distribution of the optical light scattered by an individual particle. Laser light at 532 nm from a 300 mW YAG laser was used as light source. The laser beam intersects with a stream of aerosol particles introduced with a sheath flow using a double pipe. There are 21 photodiode detectors arrayed in each plane, totaling 42.Detector apertures were placed to limit sensing angles and minimize background light scattered from walls.

In this system, angular distributions of scattering for an incident light polarized parallel and perpendicular to the scattering plane were measured simultaneously. In the experiments, particles were atomized using a nebulizer and dried using a diffusion dryer. Then, size of particle was selected using a Differential Mobility Analyzer (DMA) and Aerosol Particle Mass Analyzer (APM) and introduced into the polar nephelometer.

The performance of the system was tested by measuring angular distributions of scattering by gaseous molecules (HFC-134 and CO2) and spherical particles. Polystyrene latex sphere is non-light absorpbing spherical particle, while nigrosine are light-absorbing spherical particle. The measured scattering angular distribution was compared with the simulation result calculated from the Mie scattering theory considering detection efficiency and of scattering angle range of each detector.

As a result, the scattering angular distributions could be reproduced by the simulation results for PSL particles with diameters between 150 and 900 nm. The scattering angular distributions for nigrosine particles, were in good agreement with the theoretical curve calculated using a literature refractive index value, $n = 1.63 + 0.24\,i$. This result suggests that light absorbing particles is distinguishable by the scattering angle distribution measurement.

In order to examine the influence of the difference of the shape, we also performed measurements of the scattering angle distributions of non-spherical particles such as sodium chloride and soot particles. In the presentation, capabilities of the system to determine the shape and refractive index of particle will also be discussed.

AAS22-07 Room:511 Time:April 30 17:45-18:00

Lidar With Multiple Field-Of-View Receiver To Determine Aerosol Size-Distribution

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Knowledge of aerosol size distribution is essential for human health studies, because small particles are able to penetrate lung tissues, thus increasing the risk of bronchitis or of lung diseases. Optical remote sensing techniques such as lidar are effective for monitoring aerosols with high temporal and spatial variations. Aerosol instruments that use light with UV, VIS, and near-IR wavelengths have been used to effectively detect particles with diameters comparable to the wavelength. However, to quantitatively estimate the shape of the particle number-size distribution, more information is required with respect to small particles in the size range of sub-micrometer and below.

Conventional lidar employs very small field-of-view (FOV) for profiling aerosol distribution, and thus simply detects single scatter in the direction opposite to that of incident light. Multiple scattered signals are influenced not only by aerosol distribution along the laser path, but also by the size of aerosols. In this study, depolarization UV lidar with a multiple FOV receiver was used for detecting such multiple scattering effects in order to obtain more quantitative information concerning particle-size distribution. Considering the advantage of high scattering cross section for small particles, we employ a UV laser of 266 nm or 355 nm. A program-controlled mechanical FOV selector is used for a receiver system that can change the FOV from 0.1 mrad to 12.4 mrad. In the presentation, we introduce a retrieval method for aerosol size distribution using this feature and show preliminary results from field measurements by the multiple FOV lidar.

Keywords: Lidar, Aerosol

AAS22-08　　　　　　　　Room:511　　　　　　　　Time:May 1 09:00-09:15

Retrieval of decadal record on the deposition of particulate refractory carbon urban and remote sites in Japan

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The atmospheric concentration of refractory carbonaceous aerosol (black carbon, or elemental carbon) concentration are used for the evaluation of their direct radiative forcing. In addition, the deposition of such light absorbing substances on the snow or ice surface will result in the increase of the positive radiative forcing at the surface level. Long-term record of deposition for such relative inert substances is expected to reflect the change in the regional emission strength.

However, the reported measurements of deposition to the ground surface are scarce. We thus have conducted the retrieval of decadal record on the deposition of refractory carbon at two sites in the northern Japan (Rishiri Island: a remote site, and Sapporo City: an urban site). At these sites, the environmental monitoring division of local government have been measurering the total deposition of water-soluble aerosol components in the collected water by use of deposition gauges. To remove insoluble particles from the collected water placed beneath the funnel, a membrane pre-filter is placed at the bottom of the funnel of these deposition gauges. Such pre-filters were stored for more than 18 years for Sapporo site. These can be regarded as the long-term record of the deposited water-insoluble aerosol components in the past, as those in ice-core samples collected in glaciers.

We re-suspend these water-insoluble components into the aqueous phase by dissolving the membrane filter (mixed cellulose acetate) by an organic solvent and re-filter the suspended particles through quartz fiber filters for the analysis of TOT refractory carbon. Before dissolved into organic solvent, carbonate in soil dust particles were removed by the 2N HCl with heat. Collection efficacy of quartz fiber filters were corrected by the amount of retained particulate carbon on the first and second filters placed in series.

The deposition flux of TOT-EC is lager in Sapporo, while that in Rishiri showed a large seasonal variation, in general. In Sapporo, the flux decreased greatly in 2010s compared to those in 1990s, probably due to the introduction of regulations for diesel exhaust emission in 2000s. In addition, the deposition sample has been collected in Oki Island since 2013 spring. The preliminary result for this site will also be shown in the presentation.

Keywords: black carbon, deposition flux, decadal record, forest fire, long-range transport, diesel-powered vehicle exhaust

AAS22-09　　　　　　　　Room:511　　　　　　　　Time:May 1 09:15-09:30

The main controlling factor of black carbon mass concentration in rainwater during 2010-2013 summer in East Asia

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Black carbon (BC) particles are emitted into the atmosphere by incomplete combustion processes, and removed by precipitation. The measurements of BC mass concentration in rainwater improve the quantitative understanding of BC loss because wet deposition is the major sink of BC. We measured BC mass concentration in the air (M_{BC}) and in rainwater (C_{BC}) simultaneously at Cape Hedo on Okinawa Island, Japan, in the East China Sea, from April 2010 to March 2013 in order to understand C_{BC} in each rain event during 2010-2013 summer. The rainwater is collected by an automated wet-only sampler during a 24 period. Photo-absorption photometer with heated inlet (COSMOS) is used to measure M_{BC}. C_{BC} was measured by a system consisting of an ultrasonic nebulizer and a Single Soot Photometer (SP2).

It is often heavy rain by cumulonimbus cloud during summer in East Asia, so that M_{BC} an hour before raining is expected to be related to C_{BC}. However, the correlation between M_{BC} and C_{BC} in all rain events during 2010-2013 summer is not agreed ($r^2 = 0.12$). Then, we extracted the heavy rain events, which had positive convective available potential energy (CAPE). These extraction was performed with the National Centers for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis data every 6 hours. This result was that C_{BC} was correlated with M_{BC} ($r^2 = 0.47$).

In order to investigate if C_{BC} (Estimated C_{BC}) is explained with M_{BC} and the liquid water content, Estimated C_{BC} is verified by comparing the observed C_{BC}. The liquid water content is maximum at the equilibrium level (EL) by the condensation process theoretically if the total water mixing ratio is conserved in the air parcel. If BC in the parcel is active as cloud condensation nuclei (CCN) at lifted condensation level and removed by precipitation at EL, the equation of Estimated C_{BC} at EL is represented as Estimated $C_{BC}=M_{BC}/(m_v*WCR)$. m_v is the water vapor content an hour before raining at the ground level. Water condensation ratio (WCR) is the mass ratio of liquid water content to water vapor content, which is calculated with the NCEP reanalysis data. Compared with the observed C_{BC}, Estimated C_{BC} is correlated with the observed C_{BC} well ($r^2 = 0.68$). It suggests that Estimated C_{BC} is correctly represented as C_{BC} with M_{BC} and the most liquid water content at EL. The observed C_{BC} is three times higher than Estimated C_{BC} because the cloud droplets including BC particles might be collected during falling down.

Keywords: Black Carbon, wet deposition

Number size distribution of ambient aerosols at Cape Hedo, Okinawa and Fukue Island, Nagasaki

MIYOSHI, Takao[1]* ; TAKAMI, Akinori[1] ; IREI, Satoshi[1]

[1]NIES

[**Introduction**]

Recent drastic economical growth in the East Asian region has caused large emission of anthropogenic pollutants to the atmosphere. Some aerosols act as cloud condensation nuclei (CCN) and influence the global climate. There was a report that the higher ratio of inorganic aerosol to the sum of inorganic and organic aerosol and the larger particle size resulted in the higher ratio of CCN to condensation nuclei at the same water vapor supersaturation.

We have conducted field studies for chemical compositions of ambient aerosols at some locations in the East Asian region. In this work, measurement results of number size distribution of aerosols, which potentially influences cloud formation, are presented. Obtained data at two locations were analyzed for better understanding the spatial distribution of aerosol size in the region.

[**Observation**]

The number concentration was measured at Cape Hedo, Okinawa (lat 26.9^oN, long 128.3^oE) from 15 to 22 February 2012 and at Fukue Island, Nagasaki (lat 32.8^oN, long 128.7^oE) from 15 to 28 February 2013 using a Wide-Range Particle Spectrometer (WPS, MSP Corp.), which has a capability to measure a wide particle size range. The WPS consists of two main parts: a combination of a Differential Mobility Analyzer (DMA) and a Condensation Particle Counter (CPC) for particle measurement from 5 to 350 nm (or from 10 to 500 nm) and a Laser Particle Spectrometer (LPS) for measurement from 350 to 10000 nm.

Simultaneously, chemical compositions of ambient aerosols (ammonium, nitrate, sulfate, chloride and organics) were measured by a Quadrupole Aerosol Mass Spectrometers (Q-AMS, Aerodyne Research, Inc.) at Cape Hedo and an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research, Inc.) at Fukue Island. At Fukue Island only, sulfur dioxide concentrations were also measured by an SO_2 analyzer (Model 43i, Nippon Thermo Co., Ltd.). Sulfur dioxide concentrations at Cape Hedo were monitored at Hedo Acid Deposition Monitoring Station (Ministry of the Environment).

[**Results and Discussion**]

The size distributions at Cape Hedo consistently had two peaks at 50 nm and 200 nm. On the other hand, those at Fukue Island varied. There were two peaks at 50 nm and 150 nm after 0:00 a.m. JST on 23 February 2013. Ambient aerosols at 150 nm were largest among the particles which were measured at Fukue Island. There was one peak at 15-25 nm after 12:00 p.m. JST on 24 February 2013 when the number concentration was over 100000 #/cm^3. The concentration was also high on 16 and 25 February 2013. The growth of nucleation mode particles was observed from noon to night of each day. We believed that these cases were new particle formation (NPF) events. Such a case was not observed at Cape Hedo.

The molar ratio of sulfur dioxide to the sum of sulfur dioxide and sulfate was studied at both monitoring sites during the observation period by a WPS. When NPF events occurred at Fukue Island, the ratio increased over 80%. On the other hand, the ratio at Cape Hedo was at most 60% even on 17 February 2012 when the transport time of air masses from China according to back trajectory analyses (NOAA HYSPLIT) was approximately one day. The transport time was as long as that to Fukue Island. It was inferred that enough gases such as sulfur dioxide to cause NPF were around Fukue Island and semi-volatile vapors which were newly generated by photochemical reactions condensed on pre-existing particles because the concentrations of gases were low and those of aerosols such as sulfate were high around Cape Hedo.

Keywords: Number size distribution, East Asia, Wide-range particle spectrometer (WPS), New particle formation

AAS22-11   Room:511   Time:May 1 09:45-10:00

Continuous measurement of organic nitrates at Suzu, the Noto peninsula

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Peroxyacyl nitrates (PANs) and alkyl nitrates (ANs) act as one of the reservoirs of nitrogen oxides (NO_x) in the atmosphere. Since their lifetime is longer than that of NO_x, they can be transported over a long-distance and would be important as transboundary pollutants. In this research, continuous measurement system of total PANs and ANs in the troposphere has been developed by using a thermal dissociation / cavity attenuated phase shift spectroscopy (TD/CAPS) method. Both PANs and ANs are thermally decomposed to produce NO_2 and then NO_2 is measured by CAPS method. This system can observe PANs and ANs with high time resolution while this system cannot separate constituents of PANs and ANs. Total PANs and ANs can be measured separately by setting up decomposition lines at different temperatures.

Continuous field observations of PANs and ANs concentrations have been being carried out at NOTOGRO (NOTO Ground-based Research Observatory) supersite in Suzu, Noto Peninsula, since November 2012. NO_x, NO_y, total inorganic nitrate (T.NO$_3$), O$_3$ and CO concentrations have also been being observed at NOTOGRO.

NOy concentrations were in agreement with the sum of observed NO_y components (= NO_x + T.NO$_3$ + PANs + ANs) regardless of seasons. NO_x fractions were the highest in NO_y constituents. T.NO$_3$ fractions were small in winter and increased in spring. Opposite tendencies were observed for PANs fractions. These reflect that wet deposition of T.NO$_3$ is promoted in winter and temperature increasing accelerates decomposition of PANs.

Seasonal variations of both PANs and ANs concentrations showed spring maximum and summer minimum. From winter to spring, both PANs and ANs concentrations from Korea-China air mass origin were higher than those from the other air mass origins. On the other hand, both PANs and ANs concentrations were independent of air mass origins from spring to summer. These indicate that PANs and ANs concentrations in winter and spring are governed by long-range transport and local photochemical productions of PANs and ANs are relatively important from spring to summer. In addition, PANs and ANs diurnal variations being high and low in the daytime and nighttime, respectively, in spring and summer also imply the local photochemical productions of PANs and ANs.

Keywords: Organic nitrates, Total odd nitrogen species, Long-range transport

AAS22-12 Room:511 Time:May 1 10:00-10:15

Light absorption and morphological properties of soot-containing particle mixed with sulfate observed at Noto Peninsula

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Black carbon (BC) in atmospheric soot particle is known as strongly absorber of visible spectrum solar radiation in the atmosphere. The coating materials on soot particle can enhance the magnitude of light absorption by the soot-containing particles, according to the coating conditions including composition, amount and morphology. Several studies have indicated that the estimation by assuming core-shell shaped particle and simple composition tends to estimate larger than that for the real soot-containing particles (Adachi et al., 2010; Lack and Cappa, 2010; Cappa et al., 2012). To elucidate the enhancement of light absorption of aged soot-containing particles and their relation with the individual particle condition, we made an observation for continental outflow at Noto Peninsula, Kanazawa, Japan, in spring 2013.

Atmospheric observations were conducted at NOTO Ground-base Research Observatory (NOTOGRO) in Suzu City, Kanazawa, Japan from April 17 to May 14 in 2014. Absorption and scattering coefficients at 405, 532, and 781 nm, and soot mass concentrations of PM1 particles were measured using the photoacoustic soot photometer (DMT, PASS-3) and a single-particle soot photometer (DMT, SP2), after passing through diffusion dryers and one of the heaters controlled at 25, 300, and 400 deg C every 10 min. Aerosol samples were collected using two-stage cascade impactors (50% cutoff diameters of the two stages were 1.5 um and 0.3 um) on carbon-coated nitrocellulose (collodion) films for individual analysis using a transmission electron microscope (TEM). Elemental compositions of individual particles were analysed for particles on second stage using an energy-dispersive X-ray spectrometer (EDS) used along with the TEM. Mixing states between non-volatile chain-like soot and volatile materials to high-density electron beam were identified by comparing photograph before and after EDS analysis.

Increase in BC light absorption due to coating was estimated by comparing absorption coefficients at 781 nm with and without heating (300 deg C). The increase in BC light absorption on average was $23\pm25\%$. The maximum values of the increase in BC light absorption ($>40\%$) were observed in air mass condition that derived from around Shanghai across the East China Sea, based on backward air mass trajectory analysis. In the TEM sample obtained at the air mass, most of soot were found as internally-mixed particles, which were well-embeded into round-shaped sulphate. On the other hand, increase in light absorption estimated at 405 nm was usually less than that at 781 nm over the entire observation period. Particularly the increase in light absorption at 405 nm tended to be negative under air mass derived from around Japan or the Korean Peninsula. Because absorption at 405 nm is more affected from OC, the negative values might to be attributed to formation of brown carbon in thermo denuder. In TEM sample obtained when the increase in light absorption were negative at 405 nm and $<25\%$ at 781 nm, most of soot were also internally-mixed particles with sulphate. The differences with sample of air mass from Shanghai were that many soot-containing particles were irregular shape, and that carbonaceous residues other than soot were found in particles after irradiation of high electron beam. Our results suggest that the variation of increase in BC light absorption were attributed to morphology and mixing state with OC of internally mixed soot-containing particles.

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Keywords: Aerosol optical properties, Ambient measurement, Black carbon, electron microscope, Lensing effect

AAS22-13   Room:511   Time:May 1 10:15-10:30

Mixing states of summer time aerosol particles in Noto peninsula

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Mixing state is one of the factors that determine the characteristic of aerosol particles, and it is important for evaluating their climatic impact. Until recently, summer time aerosol particles in the remote region of central Japan didn't attract much attention since human influence was considered minimal during the season. However, our measurement in the last few years showed that particle number concentrations in summer time were the highest in all seasons. In order to understand the characteristics of the summer time aerosols, we analyzed composition and mixing state of individual particles using transmission electron microscopy (TEM) coupled to energy dispersive W-ray spectrometer (EDX). We conducted quasi-daily sampling at research facility NOTOGRO (NOTO Ground-based Research Observatory) situated at tip of the Noto peninsula from 9th, Jun to 23rd, August. Samples collected during episodes of high aerosol loadings were selected and analyzed. Winds tend to transport air-mass from the Pacific Ocean to the sampling site in summer. However, we found that there were some other flow patterns including flow from the continent of Asia, associated with the high aerosol concentrations. Major composition of particles differed depending on the flow patterns. In addition, many particles were internally mixed, and organics were predominant in smaller diameter range, while sulfates were predominant in larger diameter range. Above results showed that, depending e.g. on the difference of the flow patterns, mixing state of aerosols observed in high concentrations in summer exhibit high temporal variability, and such mixing state are often unevenly distributed among different particle sizes.

Keywords: atmospheric aerosols, mixing state, organic aerosol particles, sulfate aerosol particles

Observation of new particle formation event at Noto peninsula

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New Particle Formation (NPF) of atmospheric aerosol particle is an important production process which increases the number concentration of the aerosol particles that would act as Cloud Condensation Nuclei and potentially affect the global climate. The measurement of number size distribution of atmospheric aerosol particles was conducted at the atmospheric observation site, NOTOGRO in Noto peninsula, from October 2012 to September 2013. We identified NPF events throughout the measurement period and this is the first year-round observation reported on the NPF events from coastal region of the Sea of Japan. NPF events tended to occur when Condensation Sink (CS) was relatively low. CS is a measure of the amount of preexisting particle concentration and depends on the particle size distribution. Comparing with meteorological parameters, NPF events were concentrated in daytime, which suggests interaction with solar radiation. However, precipitation preceding the event tended to trigger NPF events by lowering CS (i.e. preexisting particle concentration) especially in winter and summer. On the other hand, NPF events observed in autumn and spring tended to concentrate on days with particularly low relative humidity. Above results suggested that, the conditions favorable for the NPF event is closely related to the seasonal climatic features of the measurement region, that is, the winter monsoon in winter, the rainy season and typhoon in summer and anticyclones in autumn and spring.

Keywords: atmospheric aerosol, new particle formation, condensation sink, precipitation, seasonal variation

Origin of atmospheric gaseous mercury using the Hg/CO ratio in pollution plume observed at Mt. Fuji Weather Station

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Mercury (Hg) is a global pollutant, which is dispersed worldwide mainly is gaseous elemental form via long-range atmospheric transport. Due to the increasing fossil fuel consumptions and industrial emissions, Asia now contributes more than 50% of the global anthropogenic Hg emission with China being the largest atmospheric Hg emitter. Previous studies have demonstrated that the trans-Pacific Asian Hg export could impact North America. Therefore, we would like to study its transport mechanism in the free troposphere by monitoring atmospheric Hg concentrations at high elevation site in Japan. The sampling site is at the summit of Mt. Fuji Weather Station, which is 3,777 m above sea level.

Gaseous mercury and particulate mercury in the atmosphere were separately collected by using a mercury sampler developed by Kagaya et. al., (2007). A quartz filter (Palflex2000, Tokyo Dylec) was attached at the tip of a mercury absorbing tube in which amalgamated gold was impregnated, and the air was aspirated by an air pump through the filter and the mercury absorbing tube at a rate of 0.5L/min. Particulate mercury was filtered by the quartz filter and gaseous mercury was absorbed by the amalgamated gold in the tube. Both particulate and gaseous mercury were analyzed by an atomic absorbance spectrophotometer (Nippon Instruments, MA-2000) after vaporization by heating.

The mercury sampler was set in a place 5m or more away from the building at summit of Mt. Fuji (N35.21'.38", E138.43'39"). The sampling was performed from 11 to 18 August, 2008. The filer and the absorbing tube were changed with 12-24 hour-intervals.

Atmospheric mercury concentrations observed at summit of Mt. Fuji and Japan. High concentrations of both gaseous and particulate mercuries were observed at the summit of Mt. Fuji. Swartzendruber et al. reported the gaseous and particulate mercury concentrations in the free troposphere at the Mt. Bachelor as 1.54 and 0.0043 ng/m^3, respectively. Hans R. Friedli et al reported that gaseous elemental mercury were found in industrial plumes exiting China, Korea, and Japan ~6.3ng/ m^3, ~3ng/ m^3 and ~3ng/ m^3, respectively. The higher atmospheric mercury concentrations at the summit of Mt. Fuji may imply that there is a specific pollution source in the East Asia. Because from the result of the back trajectory calculation, the air mass came from the China during this observation periods.

AAS22-16　　　　　　　　Room:511　　　　　　　　Time:May 1 11:15-11:30

Clarification of lead (Pb) species and its formation mechanisms in coarse and fine aerosol particles using X-ray absorpt

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There are very few studies on chemical speciation and atmospheric chemistry of trace elements. Among the trace elements in the aerosol particles, lead(Pb) has long been measured due to the toxicity of this element. The measurement of Pb isotope ratios in aerosol particles has also been employed as a powerful tracer for air-mass transportation because Pb isotope ratios differ significantly depending on the emission area/source. However the speciation of Pb has not been clarified, although their solubility is important to estimate the health effects for human/animal body. Furthermore, Pb in the aerosol particle is the dominant source of Pb, which is used as oceanic circulation tracer, in the surface seawater. Thus, the speciation of Pb in the aerosol particle is one of the important issue. In this study, we attempted to determine the Pb species in aerosol samples using X-ray absorption fine structure (XAFS) analysis.

Size-fractionated aerosol particles were collected by a high-volume aerosol sampler with cascade impactor at Higashi-Hiroshima. Lead LIII-edge (absorption edge: 13.04 keV) X-ray absorption near-edge structure (XANES) spectra were recorded on SPring-8 on BL01B1 and at KEK PF-AR on NW10A to identify the Pb species. The analyzed sample-sets of size-fractionated aerosol particles are follows: Spring (Asian dust event), summer (two sample sets), fall, and winter (transboundary pollution event).

Lead species in size-fractionated aerosol particles are different between fine and coarse aerosol particles. In the fine aerosol particles, the dominant Pb species were two or three components, $PbSO_4$, $Pb(NO_3)_2$ and PbC_2O_4, in all seasons. That is, the seasonal variation of Pb species in the fine aerosol was not found. It is because the Pb species in the fine aerosol particles are formed by uniform chemical reaction with H_2SO_4, HNO_3 and oxalic acid in droplet through a year. Pb species in the coarse aerosol particles, except for on Asian dust event, were $2PbCO_3$-$Pb(OH)_2$, $Pb(NO_3)_2$ and PbC_2O_4. These $2PbCO_3$-$Pb(OH)_2$ and partial PbC_2O_4 were derived from road dust, and $Pb(NO_3)_2$ in coarse aerosol particles was formed by chemical reactions with HNO_3 on the surface of the particle. In Asian dust event, the coarse aerosol particles showed PbSiO3 as major Pb species, although other species, $2PbCO_3$-$Pb(OH)_2$ and PbC_2O_4, were also obtained. Thus we could found the clear seasonal variation in the coarse aerosol particles. These results will be able to estimate the accurate estimation of Pb solubility to the surface seawater.

AAS22-17 Room:511 Time:May 1 11:30-11:45

Methyl chloride in the upper troposphere observed by CARIBIC: large-scale distributions and Asian summer monsoon outflow

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CARIBIC is a flying observatory onboard a Lufthansa A340-600 aircraft that observes various atmospheric compounds at almost monthly intervals. In this study, we present spatial and temporal variations of methyl chloride (CH_3Cl) in the upper troposphere (UT) observed mainly by CARIBIC for the years 2005-2011. The CH_3Cl mixing ratio in the UT over Europe was higher than that observed at a European surface baseline station throughout the year, indicative of a persistent positive vertical gradient at NH mid latitudes. A series of flights over Africa and South Asia show that CH_3Cl mixing ratios increase toward tropical latitudes, and the observed UT CH_3Cl level over these two regions and the Atlantic was higher than that measured at remote surface sites. Strong emissions of CH_3Cl in the tropics combined with meridional air transport through the UT may explain such vertical and latitudinal gradients. Comparisons with carbon monoxide (CO) data indicate that non-combustion sources in the tropics dominantly contribute to forming the latitudinal gradient of CH_3Cl in the UT. We also observed elevated mixing ratios of CH_3Cl and CO in air influenced by biomass burning in South America and Africa, and the emission ratios derived for CH_3Cl to CO in those regions agree with previous observations. In contrast, correlations indicate a high CH_3Cl to CO ratio of 2.9 ± 0.5 ppt ppb^{-1} in the Asian summer monsoon anticyclone and domestic biofuel emissions in South Asia are inferred to be responsible. We estimated the CH_3Cl emission in South Asia to be 134 ± 23 Gg Cl yr^{-1}, which is higher than a previous estimate due to the higher CH_3Cl to CO ratio observed in this study.

Keywords: CARIBIC, aircraft observation, methyl chloride, upper troposphere

AAS22-18   Room:511   Time:May 1 11:45-12:00

Flattening of the equatorial bulge of annual mean APO observed in the Western Pacific during the 09/10 El Nino event

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A tracer known as **a**tmospheric **p**otential **o**xygen (APO=O_2+1.1xCO_2) has been proved to be useful to study air-sea gas exchange. Although both atmospheric CO_2 and O_2 concentrations are affected from the air-sea and air-land gas exchanges, APO mainly reflect the air-sea gas exchange because APO is invariant with respect to the land biotic gas exchanges (-1.1 in the definition represents the molar land biotic -O_2:C exchange ratio). To investigate the spatio-temporal variations in the APO over the Pacific region, we have been observing the atmospheric CO_2 and O_2 concentrations onboard commercial cargo ships sailing between Japan and US/Canada and Australia/New Zealand since December 2001. Our previous studies based on the shipboard flask measurements for 7-year period (2002-2008) revealed that the average latitudinal distribution of the annual-mean APO in the Western Pacific (from 40 deg. S to 50 deg. N) show a maximum near the equator and decreasing trends toward the mid-latitude in both hemisphere (Tohjima et al, 2012). This latitudinal distribution of the annual-mean APO is mainly attributed to the latitudinal differences in the air-sea gas exchange: outgassing fluxes around the equator and ingassing fluxes in the mid and high latitude. In the previous study, the equatorial bulge was robust and always observed during the 7-year period. However, the equatorial bulge disappeared and the latitudinal distribution was flattened especially in the Southern Hemisphere during the period from July 2009 to June 2010, when the most recent El Nino event occurred. Simulated APO based on an atmospheric transport model (NIES99) driven by a set of climatological oceanic O_2 and CO_2 fluxes also shows suppression of the equatorial bulge during El Nino periods, indicating that the atmospheric transport substantially contributes to the inter-annual change in the latitudinal distribution of the annual-mean APO. The simulated APO, however, cannot fully reconstruct the flattening of APO in the Southern Hemisphere. Thus, the suppression of the Eastern Pacific upwelling during the El Nino period might reduce O_2 and/or CO_2 outgassing around the equatorial ocean.

Keywords: atmospheric potential oxygen, APO, air-sea gas exchange, El Nino, Tropical western Pacific ocean

AAS22-19   Room:511   Time:May 1 12:00-12:15

Separation of gross primary production and ecosystem respiration of a Japanese forest using atmospheric O2/N2 ratio

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The atmospheric O2/N2 ratio (δ(O2/N2)) has been observed globally since the early 1990s to elucidate the global CO2 budget (e.g. Manning and Keeling, 2006). To apply this method, the global average terrestrial biospheric O2:CO2 molar exchange ratio is needed. Keeling (1988) estimated the - O2:CO2 exchange ratio (hereafter referred to as ER) of 1.05 by surveying the results from various elemental abundance studies. Severinghaus (1995) revised the ER to be 1.10±0.05, which has been used for the global average terrestrial biospheric ER in recent studies. However, Seibt et al. (2004) and Ishidoya et al. (2013) observed the ER values associated with respiration and photosynthesis in forests and reported that the ER for net turbulent O2 and CO2 fluxes between the forest ecosystem and the atmosphere above the canopy (hereafter referred to as ER_F) could be different from 1.1 significantly, based on one-box canopy O2/CO2 budget model analyses. Moreover, the ER_F reported by Seibt et al. (2004) is quite different from that by Ishidoya et al. (2013); the former is larger than 1.1 and the latter is smaller than 1.0 under the condition of uptake of CO2 from the atmosphere to a forest. Therefore, direct observation of the ER_F at various forests is expected to validate the global average terrestrial biospheric ER. In addition, such the observation of the ER_F will lead to estimate the gross primary production (GPP) and the ecosystem respiration (RE) of the forest separately.

In this study, we present the average daily mean ER_F at Takayama deciduous broadleaf forest site in central Japan (36∘09′ N, 137∘25′ E, 1420 m a.s.l.; designated as TKY in the Asia Flux site code database) for the period May 24 – August 28, 2013, observed firstly based on an aerodynamic method (Yamamoto et al., 1999). The observed average daily mean ER_F is 0.79±0.08, which is not only smaller than 1.0 as predicted by Ishidoya et al. (2013) but also significantly smaller than the assumed global average terrestrial biospheric ER (1.10±0.05). We also separate the average daily mean NEP for the corresponding period observed by the eddy covariance method (Saigusa et al., 2005) into average daily mean GPP and RE, by using the observed average daily mean ER_F in this study as well as the ER_A (the ER for GPP) and ER_R (the ER for RE) at TKY reported by Ishidoya et al. (2013). Then, the separated average daily mean RE is compared with that estimated from an empirical function of air temperature (Saigusa et al., 2005) and the soil CO2 efflux observed using soil chamber experiments (Mo et al., 2005), to discuss the validity of the observed ER_F and its implication to the forest and global carbon cycle (Ishidoya et al., in manuscript in prep.).

Reference
Ishidoya, S., Murayama, S., Takamura, C., Kondo, H., Saigusa, N., Goto, D., Morimoto, S., Aoki, N., Aoki, S., Nakazawa, T. (2013) O2:CO2 exchange ratios in a cool temperate deciduous forest ecosystem of central Japan. Tellus 65B, 21120, http://dx.doi.org/10.3402/tellusb.v65i0.21120.

Keywords: atmospheric O2/N2 ratio, O2:CO2 exchange ratio between a forest and the atmosphere, gross primary production, ecosystem respiration, forest carbon cycle

AAS22-20   Room:511   Time:May 1 12:15-12:30

Seasonal changes of greenhouse gases in the upper troposphere/lower stratosphere observed by commercial airliner

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Atmospheric mixing ratios of greenhouse gases at about 11 km altitude were analyzed from monthly air sampling aboard commercial airliner during the flights between Europe and Japan from April 2012 to August 2013. Compared to the subtropic, higher CH_4 and SF_6 mixing ratios, similar values of N_2O, and larger seasonal changes of CO_2 were found in the upper troposphere. CH_4, N_2O and SF_6 in the lower stratosphere, above the tropopause up to 30 K in potential temperature, showed simultaneous increases from June to October, and faster decreases at higher altitudes from January to March. Mean age of the air in the lower stratosphere was estimated based on SF_6 mixing ratios to be about 2 years in late spring and 1 year in autumn, suggesting stronger influences on the mixing ratios in the stratosphere from troposphere in summer.

Keywords: Atmospheric Chemistry, Greenhouse Gas, Upper Troposphere/Lower Stratosphere

Long-term changes of CH4 concentration and its carbon isotopic ratio in the lower stratosphere over Japan

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It is expected that d13C of CH4 provides us with useful information not only about CH4 emissions from biogenic and abiogenic sources but also about its oxidation process in the atmosphere. Therefore, measurements of d13C have been carried out for the major CH4 sources as well as for the background atmosphere. However, the measurements are still insufficient for elucidating the CH4 cycle on the earth's surface. In the stratosphere, CH4 is destroyed by reactions with OH, O(1D) and Cl atom. These destruction processes play an important role in the stratospheric chemistry, but the respective contributions to the CH4 loss and their temporal changes have not been yet well understood quantitatively. Measurements of the isotopic ratios of the stratospheric CH4 are one of the most promising methods to detect possible change of the CH4 destruction processes in the stratosphere on the basis of the different isotopic fractionations occurring in the different reactions. However, only a few measurements have been made so far, due mainly to difficulty of collecting air samples in the stratosphere. Systematic collections of stratospheric air samples have been carried out over Japan since 1985 using a balloon-borne cryogenic sampler. We analyzed the air samples collected in the period of 1994-2010 for concentrations of CH4, N2O, CO2 and SF6, and d13C of CH4. In this study, we report the preliminary results of the long-term change of d13C of CH4 in the stratosphere. Almost linear and compact relationships between CH4 and N2O concentrations were found for the all observations in the different years. CH4 concentration and d13C also showed compact relationships in the lower stratosphere, although those in the mid-stratosphere were less correlated. The tight correlations between CH4 and N2O in spite of the different destruction processes suggest that the ratio of both destruction rates has been kept as almost constant during the transport process in the stratosphere. It is well known that tropospheric CH4 and N2O have been secularly increasing in the recent decades. Such increasing trends should have been propagated into the stratosphere, and the compact relationships between the stratospheric CH4 and N2O would change depending on their increase rates. To elucidate an inter-annual changes of the stratospheric CH4 and its d13C, we employed N2O-loss, instead of the N2O concentration, as an indicator of how the chemical reactions have proceeded during the stratospheric transport. The N2O-loss was calculated as a concentration difference between the tropical troposphere and the stratosphere by considering the mean age of air estimated from CO2 and SF6 concentrations. This procedure eliminates the effect of the secular N2O increase from the relationships between CH4 and N2O, and enables us to detect possible change in the stratospheric CH4. As a result, we found that the CH4 concentration increased at a rate of 4.5+-0.9 ppbv/year in the lower stratosphere during 16 years. This increase rate is consistent with those observed in the troposphere. The same technique was applied to the correlations between CH4 concentration and d13C, and we found no significant changes of d13C in the lower stratosphere. Considering the fact that d13C in the troposphere also does not show a clear trend in a recent decade, our result implies that the relative contributions of the CH4 destruction processes have been unchanged in the lower stratosphere over the observed period.

Keywords: stratospheric methane, carbon isotopic ratio

Laboratory biomass burning experiments to investigate the dependence of emissions of volatile organic compounds on burni

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Biomass burning is one of major sources of primary fine carbonaceous aerosols and organic compounds.[1] A field observation campaign in a rural area of the Yangtze River Delta, China, was carried out during the harvest season in June of 2010 and air masses of open crop residue burning were frequently observed. It was found that the emission ratios of elemental carbon (EC) and organic carbon (OC) to CO were enhanced during the biomass burning episodes compared with those in urban pollution.[2] In addition, oxygenated volatile organic compounds were predominantly emitted during the biomass burning.[3] To investigate the emission properties of aerosols and organic compounds under controlled conditions, we carried out biomass burning experiments in the laboratory. Two types of crop residues, wheat straws and oilseed rapes, which were actually burned during the campaign, were used as the sample. We will mainly show the dependence of the emission ratios of volatile organic compounds to CO on burning conditions and compare with the field observation.

References
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2) Pan et al., J. Geophys. Res. 117, D22304, 2012.
3) Kudo et al., submitted to J. Geophys. Res., 2013.

Keywords: Biomass burning, Volatile organic compounds, Crop residue, Combustion efficiency, PTR-MS, SP2

Impact of VOC emission from gasoline cars on ozone formation

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Ozone has been known that it was produced by the atmospheric reactions of volatile organic compounds (VOC) and NOx. The impact of VOC on ozone formation varies species by species. Thus, to evaluate the ozone formation in atmosphere, discussion based of ozone formation potential (OFP) is important.

This study discussed VOC emission from gasoline vehicle with OFP. Usually it is though that main source of VOC from vehicles were tailpipe emissions, however our former study suggested that main source from gasoline cars is not tailpipe emissions but evaporative emissions. So in this study, addition to tailpipe emissions, OFP of evaporative emissions were measured.

Keywords: ozone, ozone formation potential, evaporative emissions, gasoline cars, tailpipe emissions

AAS22-24 Room:511 Time:May 1 14:45-15:00

Improvement of measurement system for organic nitrates produced in the mixture of VOC, NOx and O3

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Organic nitrates, ONs, are important as an intermediate of secondary organic aerosols (SOAs). Additionally, the branching ratio between ONs and NO2 formation after the reactions of NO with peroxy radicals (RO2) are critical for tropospheric ozone formation. In this study, laboratory experiments were conducted for the reaction of VOCs/O3/NO mixture. After the reactor, total ONs were monitored by the thermal-desorption laser-induced fluorescence (TD-LIF) technique. At this time, an improved glass double-tube flow reactor was constructed. The inner tube (Pyrex, O.D. 10 mm, I.D. 8 mm) was for the O3 flow, and the outer (Pyrex, O.D. 150 mm, I.D. 143 mm, length 500 mm) was for the additional flow (VOC sample and NO) to reduce the wall loss of ozone at the edges of reactor. As a result, after the improvement of the reactor and its conditions, the sensitivity of formed ONs was three times as large as the previous system. The sensitivity was defined as the slope of the regression line between VOC concentration and ONs increment. Observed sensitivities for isoprene and limonene were 0.00085 and 0.013 ppbv/ppbv, respectively. Sensitivity for limonene was 15 times as large as that for isoprene. Meanwhile, the reaction rate constant of limonene with ozone is 16 times larger than that of isoprene with ozone. It was experimentally indicated that the initial reaction of VOCs with ozone be critical for production of organic nitrates. It was also confirmed that measurements of ONs produced in the mixture of VOC, NOx and O3 was promising. As a next step, RO2 productivity of initial reactions (VOC+O3) and branching ratio between ONs and NO2 formation will be explored to clarify characteristics of ONs production in detail.

Keywords: Nitrogen oxides, Volatile organic compounds, Tropospheric ozone, Organic nitrates, Laboratory experiments, Gas phase reactions

AAS22-25 Room:511 Time:May 1 15:00-15:15

Humidity dependence of extinction coefficients of secondary organic aerosols and its relation with chemical properties

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Atmospheric aerosols scatter and absorb solar radiation, thereby influencing the Earth's radiation balance. Light extinction is the sum of scattering and absorption. The aerosol extinction coefficient depends on chemical composition, particle size, shape and mixing sate in addition to wavelength of light. The uptake of water by aerosol particles can change extinction coefficients by changing size and refractive index of particles. Therefore, the detailed understanding of the relative humidity (RH) dependence of the extinction coefficients is important to estimate the impact of aerosols on radiation balance. However, the RH dependence of optical properties for secondary organic aerosol (SOA) has not been studied in detail.

In this work, we have determined the RH dependence of extinction coefficients of the SOAs generated during (1) the photooxidation of toluene in the presence of NO_x and (2) the ozonolysis of α-pinene. The SOAs were generated in a 6 m_3 teflon coated stainless-steel chamber in the absence of seed particles. The RH dependence of aerosol extinction coefficients at 532 nm was measured using a custom-made cavity ring-down spectrometer (CRDS). The CRDS has two measurement cells, in which the RH were controlled at <10% and 80%, respectively. The size distributions and chemical compositions of the SOAs were also measured using a scanning mobility particle sizer (SMPS, TSI) and a time of flight aerosol mass spectrometer (ToF-AMS, Aerodyne), respectively.

The ratio of extinction coefficients measured under high RH condition (RH=80%) to those measured under dry condition, F(RH), were compared with the relative abundance of the ion signal m/z=44 measured by the ToF-AMS to total organic signal, f_{44}. The f_{44} factor is known as a maker of oxygenated species such as organic di-acids, poly-acids, oxo-acids, hydroxy-acids, and acyl peroxides. Small RH dependence of extinction coefficients was found for the α-pinene-SOA with F(RH) of about 1.05, but the F(RH) values for the toluene-SOA were increase up to 1.4-1.6 with increasing the f_{44}. Interestingly, the relationship between F(RH) and f_{44} for the toluene-SOAs did not depend on the initial NO_x concentrations. Our results suggest that the increase in hygroscopicity due to oxidation of the SOAs mainly contributes to the observed RH dependence of extinction coefficients for the toluene-SOA.

Keywords: Secondary organic aerosol (SOA), Optical property, Humidity dependence, Chemical property, Climate change

Insoluble metal-oxalate complexes in the atmosphere: its stability and global cooling effect

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Aerosols have cooling effect on the earth, which is divided into direct and indirect effects. The direct effect is reflection of sunlight directly by aerosols, whereas the indirect effect is the reflection by clouds formed by the aid of aerosols working as cloud condensation nuclei (CCN). Oxalic acid is a main component of secondary organic aerosols and abundant in the atmosphere, which is formed by degradation of organic matters with longer carbon chain such as cyclic olefin. Oxalic acid is hygroscopic, which can work as CCN with indirect cooling effect. It has been estimated that the degree of cooling effect by the aerosols are equal to that of the warming effect of carbon dioxide (CO_2). However, there is large uncertainty in the estimation. In addition, it is suggested that oxalic acid may form insoluble metal-oxalate complexes and does not have the indirect cooling effect. Therefore, it is important to re-evaluate the cooling effect of aerosols for precise prediction of global warming. Although dicarboxylic acid including oxalic acid is decomposed into CO_2 by photolysis, oxalic acid is more abundant than the other dicarboxylic acids. It is possible that oxalic acid can be stabilized by forming metal-oxalate complexes. This study was aimed (i) to measure the concentration of metal-oxalate complexes in the atmosphere to contribute to precise prediction of global warming and (ii) to measure the half-life time to evaluate the stability of metal-oxalate complexes during photoreaction.

Size-fractionated aerosol samples were collected at Higashi-Hiroshima in winter (Dec., 2012-Jan., 2013), spring (April, 2013), and summer (July-Aug., 2013). The ratio of oxalic acid and total metal-oxalate complexes was estimated based on the X-ray absorption fine structure (XAFS) spectroscopy for zinc (Zn), lead (Pb), and calcium (Ca). Photolysis experiments were conducted by ultraviolet ray for oxalic acid, Zn complex, and magnesium (Mg) complex, while absorption spectra were measured to evaluate photoreactivity.

As a result, metal-oxalate complexes were found in finer particles. There was a positive correlation between the ratio of oxalate/nitrate and ratio of metal-oxalate complexes/total oxalate species. Therefore, it is considered that metal-oxalate complexes are formed by relative increase of oxalate for nitrate. Although concentration of total oxalate species was largest, the ratio of metal-oxalate complexes/total oxalate species was smallest in summer. Concentration of total oxalate species was higher than that of metal ions (Zn^{2+}, Pb^{2+}, and Ca^{2+}). Therefore, it is considered that the ratio of metal-oxalate complexes is smallest in summer.

This ratio was about 30% to 50% for each sample through the year. This result showed that the cooling effect of oxalic acid may be smaller than previous estimation.

As a result of photolysis experiments, half-life time of oxalic acid, Mg complex, and Zn complex is 19 min, 71 min, and 172 min, respectively. This result showed that photoreactivity of oxalic acid was decreased by forming metal-oxalate complexes. Compared to absorption spectra between oxalic acid and metal-oxalate complexes, absorbance was decreased by forming metal-oxalate complexes. Therefore, it is considered that the increase of half-life time may be caused by the decrease of absorbance by forming metal-oxalate complexes.

Keywords: Aerosol, Metal-Oxalate Complex, Global Cooling Effect, Photoreactivity, X-ray Absorption Fine Structure Spectroscopy

AAS22-27   Room:511   Time:May 1 15:30-15:45

Volatility basis-set approach simulation of organic aerosol formation in East Asia

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Organic aerosol (OA) accounts for a significant mass fraction of the submicron aerosols in the atmosphere, and it influences the Earth's climate either directly (by scattering/absorbing of solar radiation) or indirectly (by modifying cloud microphysical properties). Recent studies show that secondary OA accounts for a large fraction of OA globally. However, as secondary OA formation processes are very complicated, estimates of the secondary OA burden in the atmosphere and its impact on climate and human health remain highly uncertain compared with those of other aerosols such as inorganic species.

In this study, OA simulations using the volatility basis-set approach were made for East Asia and its outflow region. Model simulations were evaluated through comparisons with OA measured by aerosol mass spectrometers in and around Tokyo (at Komaba and Kisai in summer 2003 and 2004) and over the outflow region in East Asia (at Fukue and Hedo in spring 2009). The simulations with aging processes of organic vapors reasonably well reproduced mass concentrations, temporal variations, and formation efficiency of observed OA at all sites. As OA mass was severely underestimated in the simulations without the aging processes, the oxidations of organic vapors are essential for reasonable OA simulations over East Asia. By considering the aging processes, simulated OA concentrations considerably increased from 0.24 to 1.28 μg/m^3 in the boundary layer over the whole of East Asia. OA formed from the interaction of anthropogenic and biogenic sources was also enhanced by the aging processes. The fraction of controllable OA was estimated to be 87 % of total OA over the whole of East Asia, showing that most of the OA in our simulations formed anthropogenically (controllable). A large portion of biogenic secondary OA (78 % of biogenic secondary OA) formed through the influence of anthropogenic sources. The high fraction of controllable OA in our simulations is likely because anthropogenic emissions are dominant over East Asia and OA formation is enhanced by anthropogenic sources and their aging processes. Both the amounts (from 0.18 to 1.12 μg/m^3) and the fraction (from 75 % to 87 %) of controllable OA were increased by aging processes of organic vapors over East Asia.

Keywords: aerosol, organic aerosol, regional three-dimensional model, anthropogenic-biogenic interaction, East Asia, volatility basis-set

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Impacts of BVOCs changes on global atmospheric chemistry: off-line coupling of CHASER and VISIT

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Biogenic volatile organic compound (BVOC) is one of important factors to control global atmospheric environment and climate change, affecting tropospheric chemistry which involves ozone production/loss, OH radical abundance (atmospheric oxidizing power), and global production of secondary organic aerosols (SOA). Emissions of BVOCs are basically determined by land ecosystem processes, but also tightly linked to climate factors (such as temperature and precipitation), atmospheric CO2 concentration, and deposition of nitrogen species. Therefore, a modelling framework to couple atmospheric chemistry with land ecosystem is needed for considering BVOCs changes and associated impacts. In this study, coupled simulation of global atmospheric chemistry and terrestrial ecosystem has been developed by combining atmospheric chemistry model CHASER (Sudo et al., 2002, 2007) and land ecosystem/trace gas emission model VISIT (Ito et al., 2008). The CHASER model, also developed in the framework of the MIROC earth system model (MIROC-ESM-CHEM), simulates detailed chemistry in the troposphere and stratosphere with an on-line aerosol simulation including SOA production. The VISIT model calculates terrestrial emissions of CO_2, CH_4, N_2O, and BVOCs. This paper focuses on isoprene as a proxy of BVOCs, and discusses the impacts of the past isoprene emission changes on global atmospheric chemistry using the CHASER model constrained with off-line input from the VISIT simulation. VISIT calculates an increase in global isoprene emissions from 420 to 520 TgC a^{-1} (24%) from the first half of the 20th century to 2011. As a response to this emission change, CHASER simulated a ~2% increase in global ozone production causing ~4% increases in ozone concentration in the tropical middle-upper troposphere. The model also showed that OH decreases by 5-10% in the most of NH due to the isoprene emission change, resulting in 2-4% decreases of CO in NH. Also, SOA is largely increased by more than 30% in the major part of the troposphere (especially in the tropics).

Keywords: biogenic VOCs, chemistry climate model, land ecosystem model, secondary organic aerosol, atmosphere-land interaction