

## 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<sub>3</sub>, HF and N<sub>2</sub>O 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<sub>2</sub>O can be used as a tracer of the transport, because they are chemically stable species in the lower stratosphere. O<sub>3</sub> and HF (or N<sub>2</sub>O) 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<sub>3</sub> and HF (or N<sub>2</sub>O) 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<sub>3</sub>-HF correlation. Chemical losses in total ozone were also found from O<sub>3</sub>-HF correlation and O<sub>3</sub>-N<sub>2</sub>O 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 Tsukuba 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

## 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.

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

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

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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.

## Long-term MAX-DOAS network observations of NO<sub>2</sub> 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 NO<sub>2</sub> vertical column density (TropoNO<sub>2</sub>VCD) and aerosol optical depth (AOD). This large data set was used to analyze NO<sub>2</sub> 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 NO<sub>2</sub> retrievals of OMI satellite data (NASA ver. 2.1 and Dutch OMI NO<sub>2</sub> (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 NO<sub>2</sub> 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 NO<sub>2</sub> column densities during summer at Cape Hedo and Fukue in the clean marine atmosphere.

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

## 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<sub>3</sub>) and secondary organic aerosols (SOA) in the troposphere. This process consists of the oxidation of VOCs by hydroxyl radical (OH), O<sub>3</sub>, and nitrate radical (NO<sub>3</sub>). 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<sub>2</sub>, HCHO, CHOCHO, H<sub>2</sub>O, SO<sub>2</sub>, and O<sub>3</sub> 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 CO<sub>2</sub>) and spherical particles. Polystyrene latex sphere is non-light absorbing 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.

## 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

## 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 measuring 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 larger 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

## 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

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### [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°N, long 128.3°E) from 15 to 22 February 2012 and at Fukue Island, Nagasaki (lat 32.8°N, long 128.7°E) 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<sub>2</sub> 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<sup>3</sup>. 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

## 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 ( $\text{NO}_x$ ) in the atmosphere. Since their lifetime is longer than that of  $\text{NO}_x$ , they can be transported over a long-distance and would be important as trans-boundary 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  $\text{NO}_2$  and then  $\text{NO}_2$  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.  $\text{NO}_x$ ,  $\text{NO}_y$ , total inorganic nitrate ( $\text{T.NO}_3$ ),  $\text{O}_3$  and CO concentrations have also been being observed at NOTOGRO.

$\text{NO}_y$  concentrations were in agreement with the sum of observed  $\text{NO}_y$  components ( $= \text{NO}_x + \text{T.NO}_3 + \text{PANs} + \text{ANs}$ ) regardless of seasons.  $\text{NO}_x$  fractions were the highest in  $\text{NO}_y$  constituents.  $\text{T.NO}_3$  fractions were small in winter and increased in spring. Opposite tendencies were observed for PANs fractions. These reflect that wet deposition of  $\text{T.NO}_3$  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

## 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  $\mu$ m and 0.3  $\mu$ m) 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  $23 \pm 25\%$ . 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-embedded 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

## 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 in 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 filter 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<sup>3</sup>, respectively. Hans R. Friedli et al reported that gaseous elemental mercury were found in industrial plumes exiting China, Korea, and Japan ~6.3ng/ m<sup>3</sup>, ~3ng/ m<sup>3</sup> and ~3ng/ m<sup>3</sup>, 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.

## 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,  $\text{PbSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{PbC}_2\text{O}_4$ , 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  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and oxalic acid in droplet through a year. Pb species in the coarse aerosol particles, except for on Asian dust event, were  $2\text{PbCO}_3\text{-Pb}(\text{OH})_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{PbC}_2\text{O}_4$ . These  $2\text{PbCO}_3\text{-Pb}(\text{OH})_2$  and partial  $\text{PbC}_2\text{O}_4$  were derived from road dust, and  $\text{Pb}(\text{NO}_3)_2$  in coarse aerosol particles was formed by chemical reactions with  $\text{HNO}_3$  on the surface of the particle. In Asian dust event, the coarse aerosol particles showed  $\text{PbSiO}_3$  as major Pb species, although other species,  $2\text{PbCO}_3\text{-Pb}(\text{OH})_2$  and  $\text{PbC}_2\text{O}_4$ , 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.

## 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<sub>3</sub>Cl) in the upper troposphere (UT) observed mainly by CARIBIC for the years 2005-2011. The CH<sub>3</sub>Cl 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<sub>3</sub>Cl mixing ratios increase toward tropical latitudes, and the observed UT CH<sub>3</sub>Cl level over these two regions and the Atlantic was higher than that measured at remote surface sites. Strong emissions of CH<sub>3</sub>Cl 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<sub>3</sub>Cl in the UT. We also observed elevated mixing ratios of CH<sub>3</sub>Cl and CO in air influenced by biomass burning in South America and Africa, and the emission ratios derived for CH<sub>3</sub>Cl to CO in those regions agree with previous observations. In contrast, correlations indicate a high CH<sub>3</sub>Cl to CO ratio of  $2.9 \pm 0.5$  ppt ppb<sup>-1</sup> in the Asian summer monsoon anticyclone and domestic biofuel emissions in South Asia are inferred to be responsible. We estimated the CH<sub>3</sub>Cl emission in South Asia to be  $134 \pm 23$  Gg Cl yr<sup>-1</sup>, which is higher than a previous estimate due to the higher CH<sub>3</sub>Cl to CO ratio observed in this study.

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

## 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 atmospheric potential oxygen ( $APO = O_2 + 1.1 \times CO_2$ ) 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

## Separation of gross primary production and ecosystem respiration of a Japanese forest using atmospheric O<sub>2</sub>/N<sub>2</sub> ratio

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The atmospheric O<sub>2</sub>/N<sub>2</sub> ratio ( $\delta(O_2/N_2)$ ) has been observed globally since the early 1990s to elucidate the global CO<sub>2</sub> budget (e.g. Manning and Keeling, 2006). To apply this method, the global average terrestrial biospheric O<sub>2</sub>:CO<sub>2</sub> molar exchange ratio is needed. Keeling (1988) estimated the O<sub>2</sub>:CO<sub>2</sub> 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  $1.10 \pm 0.05$ , 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 O<sub>2</sub> and CO<sub>2</sub> fluxes between the forest ecosystem and the atmosphere above the canopy (hereafter referred to as ER<sub>F</sub>) could be different from 1.1 significantly, based on one-box canopy O<sub>2</sub>/CO<sub>2</sub> budget model analyses. Moreover, the ER<sub>F</sub> 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 CO<sub>2</sub> from the atmosphere to a forest. Therefore, direct observation of the ER<sub>F</sub> at various forests is expected to validate the global average terrestrial biospheric ER. In addition, such the observation of the ER<sub>F</sub> 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<sub>F</sub> 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<sub>F</sub> is  $0.79 \pm 0.08$ , 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 ( $1.10 \pm 0.05$ ). 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<sub>F</sub> in this study as well as the ER<sub>A</sub> (the ER for GPP) and ER<sub>R</sub> (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 CO<sub>2</sub> efflux observed using soil chamber experiments (Mo et al., 2005), to discuss the validity of the observed ER<sub>F</sub> and its implication to the forest and global carbon cycle (Ishidoya et al., in manuscript in prep.).

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Keywords: atmospheric O<sub>2</sub>/N<sub>2</sub> ratio, O<sub>2</sub>:CO<sub>2</sub> exchange ratio between a forest and the atmosphere, gross primary production, ecosystem respiration, forest carbon cycle

## 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<sub>4</sub> and SF<sub>6</sub> mixing ratios, similar values of N<sub>2</sub>O, and larger seasonal changes of CO<sub>2</sub> were found in the upper troposphere. CH<sub>4</sub>, N<sub>2</sub>O and SF<sub>6</sub> 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<sub>6</sub> 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 CH<sub>4</sub> concentration and its carbon isotopic ratio in the lower stratosphere over Japan

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It is expected that  $\delta^{13}\text{C}$  of CH<sub>4</sub> provides us with useful information not only about CH<sub>4</sub> emissions from biogenic and abio-genic sources but also about its oxidation process in the atmosphere. Therefore, measurements of  $\delta^{13}\text{C}$  have been carried out for the major CH<sub>4</sub> sources as well as for the background atmosphere. However, the measurements are still insufficient for elucidating the CH<sub>4</sub> cycle on the earth's surface. In the stratosphere, CH<sub>4</sub> 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 CH<sub>4</sub> loss and their temporal changes have not been yet well understood quantitatively. Measurements of the isotopic ratios of the stratospheric CH<sub>4</sub> are one of the most promising methods to detect possible change of the CH<sub>4</sub> 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 CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub> and SF<sub>6</sub>, and  $\delta^{13}\text{C}$  of CH<sub>4</sub>. In this study, we report the preliminary results of the long-term change of  $\delta^{13}\text{C}$  of CH<sub>4</sub> in the stratosphere. Almost linear and compact relationships between CH<sub>4</sub> and N<sub>2</sub>O concentrations were found for the all observations in the different years. CH<sub>4</sub> concentration and  $\delta^{13}\text{C}$  also showed compact relationships in the lower stratosphere, although those in the mid-stratosphere were less correlated. The tight correlations between CH<sub>4</sub> and N<sub>2</sub>O 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 CH<sub>4</sub> and N<sub>2</sub>O 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 CH<sub>4</sub> and N<sub>2</sub>O would change depending on their increase rates. To elucidate an inter-annual changes of the stratospheric CH<sub>4</sub> and its  $\delta^{13}\text{C}$ , we employed N<sub>2</sub>O-loss, instead of the N<sub>2</sub>O concentration, as an indicator of how the chemical reactions have proceeded during the stratospheric transport. The N<sub>2</sub>O-loss was calculated as a concentration difference between the tropical troposphere and the stratosphere by considering the mean age of air estimated from CO<sub>2</sub> and SF<sub>6</sub> concentrations. This procedure eliminates the effect of the secular N<sub>2</sub>O increase from the relationships between CH<sub>4</sub> and N<sub>2</sub>O, and enables us to detect possible change in the stratospheric CH<sub>4</sub>. As a result, we found that the CH<sub>4</sub> concentration increased at a rate of  $4.5 \pm 0.9$  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 CH<sub>4</sub> concentration and  $\delta^{13}\text{C}$ , and we found no significant changes of  $\delta^{13}\text{C}$  in the lower stratosphere. Considering the fact that  $\delta^{13}\text{C}$  in the troposphere also does not show a clear trend in a recent decade, our result implies that the relative contributions of the CH<sub>4</sub> 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.<sup>1</sup> 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.<sup>2</sup> In addition, oxygenated volatile organic compounds were predominantly emitted during the biomass burning.<sup>3</sup> 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.

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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 NO<sub>x</sub>. 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 thought 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

## Improvement of measurement system for organic nitrates produced in the mixture of VOC, NO<sub>x</sub> and O<sub>3</sub>

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Organic nitrates, ONs, are important as an intermediate of secondary organic aerosols (SOAs). Additionally, the branching ratio between ONs and NO<sub>2</sub> formation after the reactions of NO with peroxy radicals (RO<sub>2</sub>) are critical for tropospheric ozone formation. In this study, laboratory experiments were conducted for the reaction of VOCs/O<sub>3</sub>/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 O<sub>3</sub> 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, NO<sub>x</sub> and O<sub>3</sub> was promising. As a next step, RO<sub>2</sub> productivity of initial reactions (VOC+O<sub>3</sub>) and branching ratio between ONs and NO<sub>2</sub> formation will be explored to clarify characteristics of ONs production in detail.

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

## 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 state 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  $\text{NO}_x$  and (2) the ozonolysis of  $\alpha$ -pinene. The SOAs were generated in a 6 m<sup>3</sup> 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,  $F(\text{RH})$ , 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  $\alpha$ -pinene-SOA with  $F(\text{RH})$  of about 1.05, but the  $F(\text{RH})$  values for the toluene-SOA were increase up to 1.4-1.6 with increasing the  $f_{44}$ . Interestingly, the relationship between  $F(\text{RH})$  and  $f_{44}$  for the toluene-SOAs did not depend on the initial  $\text{NO}_x$  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<sub>2</sub>). 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<sub>2</sub> 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<sup>2+</sup>, Pb<sup>2+</sup>, and Ca<sup>2+</sup>). 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

## 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  $\mu\text{g}/\text{m}^3$  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  $\mu\text{g}/\text{m}^3$ ) 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

## 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 CO<sub>2</sub> 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<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, 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<sup>-1</sup> (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

## 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(I<sub>2</sub>) 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 I<sub>2</sub> is also smaller than the observed I<sub>2</sub>. 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, I<sub>2</sub>(g) and an iodine monoxide radical, IO(g).

The I<sub>2</sub>(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 O<sub>3</sub>(g) were (0.5-4.2)×10<sup>15</sup> molecules cm<sup>-3</sup>. The observed products concentrations were ~10<sup>11</sup> molecules cm<sup>-3</sup> for IO(g) and ~10<sup>14</sup> molecules cm<sup>-3</sup> for I<sub>2</sub>(g). The peak of I<sub>2</sub>(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 I<sub>2</sub>(g) and IO(g) produced depend on [NaI], I<sub>2</sub>(g) production is markedly enhanced at pH <4, and I<sub>2</sub>(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 PM<sub>2.5</sub> concentration (Jan. 31-Feb. 1, 2013), and (c) the periods before and after (a) and (b).

Major ion concentration data showed that Ca<sup>2+</sup>, which is originated from soil, and NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, 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<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, 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<sub>3</sub> 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<sub>4</sub>HSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and hydrated sulfate with high hygroscopicity were main sulfur species in the period (b). Therefore, it is considered that when the concentration of PM<sub>2.5</sub> increases, the indirect cooling effect can be large due to the large fraction of NH<sub>4</sub>HSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 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<sub>3</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> were different at the surface and the bulk. As a result, it was concluded that calcium species changes from gypsum, Ca(NO<sub>3</sub>)<sub>2</sub>, to CaCO<sub>3</sub> 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) Ca(NO<sub>3</sub>)<sub>2</sub>, formed as a result of the reaction of nitric acid and calcite, exists in the middle part, and (iii) unreacted CaCO<sub>3</sub> 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  $\mu\text{m}$  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.  $\text{CaCl}_2$  was found on the surface of the particle and bounded on  $\text{CaCO}_3$ , suggesting that  $\text{CO}_3^{2-}$  was replaced by  $\text{Cl}^-$  ( $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$ ). Fe was included in the particle. There is a possibility that changing insoluble  $\text{CaCO}_3$  to soluble  $\text{CaCl}_2$  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

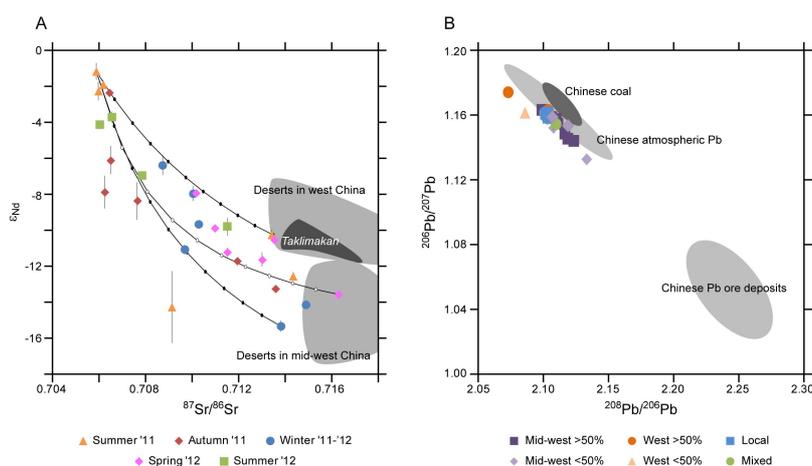
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Lead is one of the major environmental pollutants, which seriously harms human body. Atmospheric lead concentration has been suppressed in Japan after the forbiddance of leaded gasoline in 1970s. However, the cross-border air pollution is getting unable 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-HNO<sub>3</sub> ("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  $\kappa$  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  $\kappa$ -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  $\sim 1$  % 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  $\sim 0.13$ , 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.

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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.<sup>1)</sup> 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  $\alpha$ -pinene, isoprene, toluene, and 1,3,5-trimethylbenzene (TMB) was investigated in the presence of  $\text{NO}_x$ . Ozonolysis of  $\alpha$ -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,  $\phi$ , 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  $\alpha$ -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,  $\phi$ , is an index of oligomer to total SOA ratio, but does not represent an absolute value of that ratio. The  $\phi$  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  $\phi$  value of toluene SOA was the highest, whereas that of  $\alpha$ -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

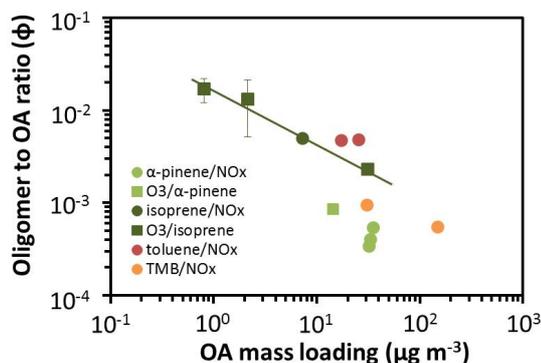


Fig. 1. Effects of OA mass loading on the oligomer to OA signal ratio ( $\phi$ ).

## 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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<sup>1</sup>JAMSTEC

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.

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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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$\text{NO}_x$  emissions have been increasing in East Asia with recent remarkable economic progress.  $\text{NO}_x$  has relatively short lifetime and  $\text{NO}_x$  concentrations are governed by local  $\text{NO}_x$  emissions. On the other hand, descendant photochemical products of  $\text{NO}_x$  such as  $\text{T.NO}_3$  (the sum of gaseous nitric acid and particulate nitrates), PANs (peroxyacyl nitrates) and ANs (alkyl nitrates) have longer lifetime than  $\text{NO}_x$ , 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  $\text{T.NO}_3$ , 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.  $\text{NO}_x$  were determined by an LED photolytic converter /  $\text{NO-O}_3$  chemiluminescence method.  $\text{NO}_y$  and  $\text{T.NO}_3$  were observed by a scrubber difference /  $\text{NO-O}_3$  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  $\text{NO}_x$  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  $\text{NO}_x$ . In order to clarify transboundary pollution of nitrogen oxides, comprehensive measurements of total odd nitrogen species ( $\text{NO}_y$ ), 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  $\text{NO}_2$ , and a CAPS- $\text{NO}_2$  analyzer. This system has three intake lines;  $\text{NO}_2$ , PANs and ANs lines. The  $\text{NO}_2$  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  $\text{NO}_2$ . Concentrations of  $\text{NO}_2$ ,  $\text{NO}_2 + \text{PANs}$  and  $\text{NO}_2 + \text{PANs} + \text{ANs}$  can be obtained from the  $\text{NO}_2$ , PANs and ANs lines, respectively. These concentrations are sequentially measured by switching solenoid valves and then  $\text{NO}_2$ , PANs and ANs concentrations are obtained. Since a part of  $\text{HNO}_3$  is pyrolyzed in the ANs line, annular denuder coated with NaCl to remove  $\text{HNO}_3$  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  $\text{NO}_x$ ,  $\text{NO}_y$ , T. $\text{NO}_3$  (the sum of gaseous nitric acid and particulate nitrate)  $\text{O}_3$ , and CO have also been being conducted.  $\text{NO}_y$  concentrations were in agreement with the sum of observed  $\text{NO}_y$  components (=  $\text{NO}_x + \text{T.NO}_3 + \text{PANs} + \text{ANs}$ ) regardless of seasons.  $\text{NO}_x$  fractions were the highest in  $\text{NO}_y$  constituents. Fractions of T. $\text{NO}_3$  in January and February were lower than those in other months. This reflects that wet deposition of T. $\text{NO}_3$  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 $\text{NO}^+$ as the reagent ion

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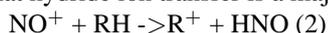
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Proton transfer reaction mass spectrometry (PTR-MS) is a technique that allows for fast and sensitive measurement of volatile organic compounds (VOCs) at trace levels in air. Proton transfer is an example of chemical ionization: it enables soft ionization 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  $\text{C}_{12}$ - $\text{C}_{18}$  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  $\text{NO}^+$  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  $\text{NO}^+$ .



Recently, the PTR-MS instrument has been combined with switchable reagent ion capability, which allows for easy and fast switching between  $\text{H}_3\text{O}^+$  and  $\text{NO}^+$  (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  $\text{R}^+$  by PTR + SRI-MS using  $\text{NO}^+$  as the reagent ion and detection sensitivities were comparable to those of aromatics observed by  $\text{H}_3\text{O}^+$  ionization. We also demonstrated time-resolved measurements of  $\text{C}_4$ - $\text{C}_{16}$  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  $\text{NO}^+$  as the reagent ion.

Keywords: PTR-MS, alkane,  $\text{NO}^+$  chemical ionization, Gasoline vehicle, Diesel vehicle, Exhaust gas

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

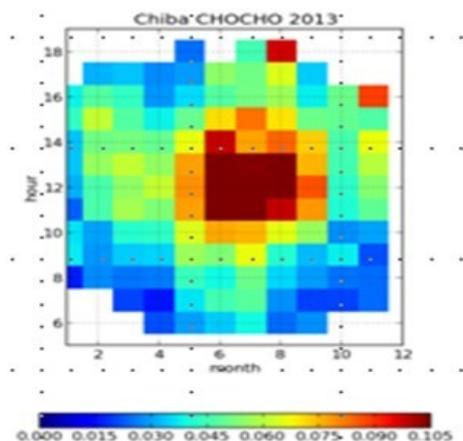
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BVOCs (Biogenic Volatile Organic Compounds) are plant-released organic chemicals that are volatile in air at normal ambient temperature and pressure. Reactions of BVOC in the atmosphere have a great influence on the OH abundance in the atmosphere. 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  $\text{NO}_x$  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  $\text{O}_3$  to  $\text{NO}_2$  in the presence of a high concentration of NO, and then the air is introduced into an  $\text{NO}_2$  measurement system by a laser-induced fluorescence technique. Increment of ozone ( $\Delta\text{O}_3$ ) is defined by the difference of  $\text{NO}_2$  concentrations derived from the reaction chamber and those from reference chamber. The ozone production rate is obtained by dividing  $\Delta\text{O}_3$  by a mean residence time of air in the reaction chamber ( $\tau$ ). In this system,  $\text{O}_3$  concentrations are not directly measured but  $\text{NO}_2$  concentrations converted by the reaction of  $\text{O}_3$  with excess NO are observed. This is because the photostationary states between  $\text{NO}_x$  and  $\text{O}_3$  are different between in the reaction and reference chambers, and ozone concentrations vary apparently. The sum of ozone and  $\text{NO}_2$  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)  $\tau$ , and (3) conversion efficiency of  $\text{O}_3$  to  $\text{NO}_2$  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  $\text{NO}_2$  was added into the reaction chamber and temporal variations of LIF signals were measured.  $\tau$  was calculated to be  $22.1 \pm 0.5$  min using the temporal variation the signals. For (3), quantitative conversions of  $\text{O}_3$  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-i) 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., CH<sub>4</sub>, O<sub>3</sub>) 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 O<sub>4</sub>. In order to quantify the effect of the systematic offset of the elevation angle in O<sub>4</sub> 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 O<sub>4</sub> 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 xCH<sub>4</sub> using TCCON and Airborne Measurements

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As methane (CH<sub>4</sub>) is one of the most important Short-Lived Climate Pollutants (SLCPs), global monitoring of atmospheric CH<sub>4</sub> with enough accuracy is expected to estimate its sources and sinks. For measurements of global distribution of CO<sub>2</sub> and CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> products of the column-averaged dry-air mole fractions (xCH<sub>4</sub>) 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  $-6.0 \pm 16.1$  ppbv.

We also examined the appropriate cloud screening for xCH<sub>4</sub> 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.

### Acknowledgements

This research was supported by the Environment Research and Technology Development Fund of the Ministry of the Environment, Japan (A1202). The RemoTeC-MACC product was provided by Dr. Andre Butz (IMK-ASF, Karlsruhe Institute of Technology; KIT).

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 CH<sub>4</sub> during 1988-2010. The analysis is aided by simulation results using an atmospheric chemistry transport model (i.e. ACTM). Tropospheric CH<sub>4</sub> 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 CH<sub>4</sub> 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, CH<sub>4</sub> mixing ratios show seasonal maximum in August due to efficient transport of air masses influenced by continental CH<sub>4</sub> sources, while LT CH<sub>4</sub> reaches its seasonal minimum during summer due to seasonally maximum chemical loss. Vertical profiles of the CH<sub>4</sub> mixing ratios also vary with season, reflecting the altitude-dependent seasonal cycles. In summer, transport of CH<sub>4</sub>-rich air from Asian regions elevates UT CH<sub>4</sub> levels, forming the uniform vertical profile above the mid troposphere. On the other hand, CH<sub>4</sub> decreases nearly monotonically with altitude in winter-spring. The ACTM simulations with different emission scenarios reproduce general features of the tropospheric CH<sub>4</sub> variations over Japan. Tagged tracer simulations using the ACTM indicate substantial contributions of CH<sub>4</sub> sources in South Asia and East Asia to the summertime high CH<sub>4</sub> values observed in the UT. This suggests that our observation data over Japan are highly valuable for capturing CH<sub>4</sub> emission signals, particularly from the Asian continent.

Keywords: aircraft observation, methane, troposphere, over Japan

## Measurement of CO<sub>2</sub> stable isotope ratio by mid-inferred laser absorption spectrometry; analysis of CO<sub>2</sub> cycle in urban

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CO<sub>2</sub> 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 CO<sub>2</sub> has the most effective on the positive radiative force. The insight of CO<sub>2</sub> emission and absorption flux helps us to estimate the variation of radiative forcing and atmospheric environment. CO<sub>2</sub> concentration changed with the anthropogenic and biogenic emission and absorption. The stable isotope ratio of CO<sub>2</sub> ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) is associated with the CO<sub>2</sub> source such as combustion and biogenic respiration. The contribution of each CO<sub>2</sub> source in the urban area was estimated by using the stable isotope ratio of CO<sub>2</sub>.

We conducted the continuous measurement for CO<sub>2</sub> concentration and stable isotope ratio of CO<sub>2</sub> using the mid-inferred absorption spectrometry which can obtain CO<sub>2</sub> concentration and its isotope ratio with high time resolution. The water vapor and stable isotope ratios of water vapor ( $\delta\text{D}$  and  $\delta^{18}\text{O}\text{-H}_2\text{O}$ ) were measured to show the relationship between H<sub>2</sub>O and CO<sub>2</sub> due to the isotopic exchange reaction. CO and NO<sub>x</sub> concentrations were obtained as a tracer of anthropogenic emission. The measurement was conducted for two weeks in summer and winter. The seasonal variation of CO<sub>2</sub> source was shown according to the comparison of CO<sub>2</sub> concentration and stable isotope ratio. Especially, we focused on the contribution of biogenic process to CO<sub>2</sub> concentration variation in the urban area.

CO<sub>2</sub> concentration and stable isotope ratio of CO<sub>2</sub> in the summer showed the diurnal variation. On the other hand, those in the winter had no diurnal variation. CO<sub>2</sub> concentration variation in the winter was correlated with CO concentration variation. These results suppose that CO<sub>2</sub> 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 CO<sub>2</sub> source.

Keywords: CO<sub>2</sub> stable isotope ratio, Urban area, CO<sub>2</sub> 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