

Evolution of HCl and HF above Rikubetsu observed with FTIR between 1995 and 2009

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FTIR(Fourier transform infrared spectrometer) was installed at Rikubetsu (43.5 N, 143.8 E, 370 m a.s.l) located in the northern mid-latitude and infrared solar spectra have been obtained with FTIR since 1995. FTIR enables us to observe several trace gases such as O₃, HF, HCl, and HNO₃ at the same time.

HCl is a reservoir of ozone-depleting substance, chlorine(Cl), and HF is a reservoir of fluorine(F). They are included in the CFCs. Some reports said ozone depletion has slowed down or stopped due to the regulation of emission of CFCs thanks to the Montreal Protocol. To project the variation of ozone in the future, it is important to observe variations of HF and HCl. In addition, it becomes possible to monitor the situation of CFCs emissions. We here report the analytic results for the evolution of total column amounts of HCl and HF.

We used Bruker's IFS-120M FTIR for measurements, and SFIT2 program developed by NIWA, NCAR and Univ. of Wollongong for spectral analysis to deduce column amounts.

We analyzed the data for the period between May 1995 and December 2009.

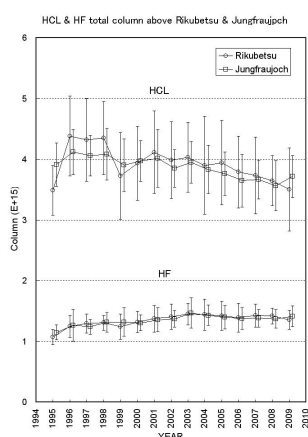
We also compared our results with the ones at Jungfraujoch (46.5 N, 8.0 E, 3580 m a.s.l.) for the evaluation of total column amounts. Jungfraujoch is also located in the northern mid-latitude and has long-term data derived from FTIR.

We show the evolution of annual average column amounts of HCl and HF in the figure.

It is shown that HCl started to decrease after the peak at around 1995. We don't understand the reason for a tentative large decrease in 1999.

It looks like HF peaked at around 2003, and started to decrease afterwards.

Keywords: stratosphere, trace gases, FTIR, midlatitude



Ozone loss rates and PSC occurrence in the Arctic winter stratosphere during 1994-2000 observed by POAM II/III and ILAS

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Quantitative chemical ozone loss rates at the 475 K isentropic surface inside the Arctic polar vortex are evaluated for six winters (January through March) using a satellite-based Match technique. Satellite observational data are taken from the Polar Ozone and Aerosol Measurement (POAM) II for 1994-1996, the Improved Limb Atmospheric Spectrometer (ILAS) for 1997, and the POAM III for 1999-2000. The largest ozone loss rates occurred in January 1995 (50 ppbv/day), February 1996 (40-50 ppbv/day), February 1997 (40 ppbv/day), January 2000 (60 ppbv/day), and early March 2000 (40 ppbv/day). Large derived ozone loss rates were typically associated with air masses that experienced low temperatures (187-195 K) within the previous 10 days. The ozone loss rates clearly increase with decreasing the minimum temperature. The particularly large ozone losses of 9+/-3 ppbv/sunlit-hour in February 1996 and January 2000 were associated with very low minimum temperatures of 187-189 K, simultaneously with high PSC probabilities.

We have quantified the probability of polar stratospheric cloud (PSC) existence at the 475 K level using aerosol extinction coefficient (AEC) data from POAM II/III and ILAS. The results show that patterns of high PSC probabilities are very similar to those of high ozone loss rates. The highest positive correlations between monthly PSC probabilities and ozone loss rates per sunlit hour occurred in February ($r^2=0.88$) and January ($r^2=0.64$). No correlation is found for March; however, this lack of correlation is solely due to small ozone loss rates in 1996. A correlation is found for March when considering only 1995, 1997, and 2000 ($r^2=0.91$). This relationship demonstrates that interannual variability (IAV) in the magnitude of ozone losses is tied to IAV in PSC probabilities. The regression coefficient between the PSC probabilities and ozone loss rates per sunlit hour was almost constant throughout JFM, however, for ozone loss rates per day, the seasonal increase from January to February/March in the regression coefficient was found due to more sunlight in late winter to spring. Regression analysis for the full JFM season indicates that, on average, an absolute increase of 10% in the PSC probability contributes an additional ozone loss of approximately 25+/-6 ppbv/day or 3.2+/-0.7 ppbv/sunlit-hour. Relationships between average Arctic winter ozone loss rates and various PSC- and temperature-related indices are investigated, including the area of polar vortex that is colder than the threshold temperature for PSC existence (APSC; e.g., Rex et al., 2004), the PSC formation potential (PFP), and the potential for activation of chlorine (PACl) (Tilmes et al., 2008). Of these three, PACl provides the best proxy representation of interannual variability in Arctic ozone loss at the 475 K level.

We used HALOE H₂O and POAM/ILAS AEC to calculate the IAV in the threshold temperature for activation of chlorine (TACl; Drdla and Mueller, 2010). TACl decreased from 194.6+/-0.6 K during the winter of 1994 to 193.3+/-0.8 K during the winter of 2000. This decrease is associated with reductions in background sulfate aerosols. The decrease is interrupted in 1997 and 1998, when weak diabatic descent inside the vortex led to higher SAD, which in turn led to higher TACl. The low value of TACl in 1996 (193.6+/-0.9 K) caused the decrease in PACl, which significantly contributed to the higher correlation between ozone loss and PACl rather than PFP. Our observational evidence shows the high correlation between Arctic ozone loss and TACl/PACl, as well as Tilmes et al. (2008). The injection of sulfate aerosols into the stratosphere either by huge volcanic eruptions or by "geoengineering" schemes to counteract global warming would lead to increases in TACl, probably resulting in enhanced ozone loss in the Arctic winter stratosphere.

Keywords: stratospheric photochemistry, polar stratospheric cloud, satellite measurement, polar vortex, stratospheric temperature

The effect of the surface BRDF on the measurement of tropospheric NO₂ from a geostationary orbit and ISS

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BRDF (Bidirectional Reflectance Distribution Function) is the dependency of the surface reflectance on incident and output directions. Zhou et al. [2010] showed that the surface BRDF affects the retrieval of the tropospheric NO₂ column density with sun-synchronous low Earth orbit (LEO) satellites, as line-of-sight angles largely change in the sun-synchronous LEO measurements. In the present study, we have estimated the influence of BRDF on the tropospheric NO₂ DOAS retrieval supposing the observations of air pollution over Tokyo from a geostationary orbit (GEO) and ISS. In the analysis, we used the results of actual surface measurements: the MODIS BRDF product released by NASA. The result showed that the use of the assumption of Lambertian surface instead of BRDF would cause up to a 30% difference in the reflectance value. We also show the influence of such a difference on the tropospheric NO₂ column density measurements.

Keywords: Geostationary orbit, ISS, tropospheric chemistry, NO₂, BRDF

First quantitative bias estimates for tropospheric NO₂ columns retrieved from SCIAMACHY, OMI, and GOME-2 using a common

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For the intercomparison of three different satellite sensors (SCIAMACHY, OMI, and GOME-2) currently observing global distributions of nitrogen dioxide (NO₂) vertical column densities (VCDs) in the troposphere, we use a common standard to quantify the biases for the respective data sets. As the standard, a regression analysis using a single set of collocated Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) observations at several sites in Japan and China in 2006-2010 is adopted. Examination of various coincidence criteria suggests that the slope of the regression line is biased when the distance between the MAX-DOAS and satellite observation points exceeds the satellite measurement pixel size. Using strict coincidence criteria we estimate biases in SCIAMACHY, OMI, and GOME-2 data (TM4NO2A and DOMINO version 1 products, with cloud fractions smaller than 10%) to be -19%, +6%, and +20%, respectively, compared to the MAX-DOAS data. The recently released new satellite products, version 2, show better agreement, with biases of -5%, -4%, and +9%, respectively. The estimates will enable analyses combining these satellite data for air quality studies that are more systematic and quantitative than possible previously.

Keywords: NO₂, satellite data validation, MAX-DOAS

An attempt to profile the vertical distributions of trace gases and aerosol particles in the surface layer

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Dispersion and transport processes of gaseous molecules and aerosol particles that are emitted near the surface are strongly influenced by meteorological conditions within the surface layer. For instance, during daytime positive buoyancy flux at the surface creates a thermal instability and thus generates additional or even major turbulence, which may result in an effective vertical mixing of trace gases and aerosol, whereas during nighttime negative buoyancy inhibits turbulent mixing, thus vertical transport is slower at night than during the day. Most of the available observational studies of atmospheric trace constituents are ground-based campaigns which will not be adequate to reveal their spatiotemporal variations near the surface layer. Airborne-based campaigns are powerful approach to examine the spatiotemporal variations of atmospheric trace constituents in the free troposphere, but will be inadequate to expand the assessing heights into the surface boundary layer because of minimum safe altitude. We want to overcome the shortcomings posed by the poor understanding of the influence of vertical mixing near the surface, and the lack of altitude resolved measurements of the chemical composition in the surface boundary layer. We are developing a new methodology to reveal the vertical distributions of trace gases and aerosol particles and to investigate their variations with the meteorological parameters. In this presentation, we introduce the preliminary results from the simultaneous measurements using lidar, sodar and tethered balloon profiling, which were conducted at Kyoto University Middle and Upper Radar site (34.9 N, 136.1 E) in Shiga Prefecture, Japan, during the summer of 2011.

Keywords: aerosol, trace gases, surface layer, tethered balloon, vertical distributions

Measurements of particle effective density distributions during summer in Nagoya: Relationship with chemical composition

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Tropospheric aerosols are known to be a complex mixture including mineral dust, inorganic salts, organic compounds, and soot particles. Mixing state and shape of aerosols are strongly affects optical properties. However, real-time (bulk) measurements of mixing state and shape of ambient aerosols are limited. Measurements of 'effective' density distribution have a potential to provide useful information about the mixing state and shape. In this work, based on aerosol density distribution measurements, the mixing state and shape of aerosols in an urban area are estimated.

Simultaneous observations of aerosol density distributions and chemical properties were conducted on August, 16-26, 2011 at the Higashiyama-campus of Nagoya University. The effective density of ambient particle with a mobility diameter of 100 and 200 nm was measured by combinations of a differential mobility analyzer (DMA, TSI, model 3081), an aerosol particle mass analyzer (APM, Kanomax, model 3601), and a condensation particle counter (CPC, TSI, model 3776). Chemical compositions of the aerosol were measured by a time-of-flight aerosol mass spectrometer (Aerodyne, HR-ToF-AMS). The density distributions and chemical compositions were measured after passing through diffusion dryers and one of the heaters controlled at 25, 100, and 300 degree-C by switching ball valves every 30 min.

As a result, ambient aerosols with a diameter of 100 nm have two distinct density peaks at 0.7-0.9 (peak 1) and 1.2-1.6 (peak 2) g/cm³. The changes in peak areas after heating imply that peak 1 and 2 mainly consist of soot and volatile compounds (such as inorganic salts and organics), respectively. In the presentation, the temporal variations of the effective densities and their relationship with chemical properties will be discussed.

Keywords: Aerosol density distributions, Ambient measurements, Aerosol chemical compositions, Mixing states

Measurements of optical properties of aerosols in Nagoya: Contributions of lensing effect and brown carbon

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

Simultaneous observations of optical and chemical properties as well as size and density distributions of ambient aerosols were conducted on August, 16-26, 2011 at the Higashiyama-campus of Nagoya University. Optical properties of PM₁ particles were measured using the PASS-3 (DMT, PASS-3, absorption and scattering at 405 and 781 nm). Chemical compositions of the aerosol were measured by a time-of-flight aerosol mass spectrometer (Aerodyne, HR-ToF-AMS). The optical properties and chemical composition were measured after passing through diffusion dryers and one of the heaters controlled at 25, 100, and 300degree-C by switching ball valves every 30 min. Mass concentrations of elemental carbon (EC) and Organic carbon (OC) were also measured by thermo-optical technique using a semi-continuous EC/OC analyzer (Sunset Lab., model 4) every 90 min.

By comparing absorption coefficients at 781 nm with and without heating (300degree-C), increase in BC light absorption due to coating is estimated to be 20-30%. Relatively higher amplification factors are observed during the period when large SO₄/Org ratio is observed. Contributions of light absorption by OC are estimated by assuming that the enhancement of BC light absorption due to coating does not depend on wavelength. As a results, contributions of 405 nm light absorption by OC, which is vaporized at 300degree-C, are found to be small, at least, during summer in Nagoya (<5%).

Keywords: Aerosol optical properties, Ambient measurement, Lensing effect, Brown carbon, Photoacoustic spectroscopy

Hygroscopicity of aerosol particles and CCN activity of less hygroscopic aerosol particles observed in Nagoya in summer

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Hygroscopic property of atmospheric aerosol particles closely relates to the cloud condensation nuclei (CCN) activity. Thus, a detailed understanding of this property is important for the assessment of the effect of aerosols on climate. In the urban atmosphere, aerosol particles could be externally mixed in view of hygroscopicity by the emissions of hydrophobic particles (primary organics and black carbon) and the inflow and in-situ formation of hydrophilic particles. The hygroscopicity of aerosol particles and the mixing state may change by the condensation of secondary components on both hydrophobic and hydrophilic particles, especially in summer. Mochida et al., (2008) measured the hygroscopic growth factor (HGF) of aerosol particles and examined the correlation between the mass concentrations of chemical species and the particle number concentrations in specific HGF ranges in Tokyo. They reported that the particle hygroscopicity changed rapidly by the secondary formation of organics. In this study, we also analyzed the correlations between the number concentrations of aerosol particles in specific HGF ranges and the mass concentrations of chemical species. In addition, we analyzed the fraction of CCN for less hygroscopic particles and assessed the diurnal variations.

Atmospheric aerosol measurements were performed in August 2011 in Higashiyama campus, Nagoya University, and the data in the period from 16 to 25 August were used for the analysis. The sampled aerosol was classified according to the differences in particle HGF at 85% relative humidity, using the hygroscopicity tandem differential mobility analyzer (HTDMA). The CCN fraction of the aerosol particles selected using the HTDMA were measured in combination with a cloud condensation nuclei counter (CCNC). The HGF distributions of aerosol particles with the dry mobility diameter of 150 nm were observed every 6 hours. The CCN fraction of particles with HGF of unity was measured under 1% supersaturation (SS) condition every 1.5 to 4.5 hours and under 0.5% SS condition every 6 hours. The CCN fraction of particles with HGF of 1.1 was measured at 1% SS every 6 hours.

The HGF distributions in the observation period were bimodal. In 23 August, more hygroscopic particles accounted for a large fraction of 150 nm particles. One possible reason is that air masses with sulfate aerosol formed in the plume from Sakurajima were transported to Nagoya without large influences from other urban areas from which less hygroscopic particles were supplied. Correlations between the number concentrations of particles in specific HGF ranges and the mass concentrations of chemical species were found, being similar to the study by Mochida et al., (2008). In our study, however, the correlation between moderately hygroscopic particles and ozone was weak. It is possible that oxygenated organics were not formed locally, but were transported mainly from outside the Nagoya metropolitan area in the first three days. The number fraction of CCN in less hygroscopic aerosol (HGF = 1) varied greatly with time, suggesting the changes in the amount of hydrophilic components in the particles with apparent HGF of unity during the observation period.

Reference

Mochida, M., T. Miyakawa, N. Takegawa, Y. Morino, K. Kawamura, and Y. Kondo (2008), Significant alteration in the hygroscopic properties of urban aerosol particles by the secondary formation of organics, *Geophys. Res. Lett.*, 35, L02804, doi:10.1029/2007GL031310.

Keywords: urban aerosol, cloud condensation nuclei, HTDMA, hygroscopic growth

REE pattern of aerosol collected in Tokorozawa city, Japan.

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In this study, REE (Rare Earth Elements) patterns of aerosol samples which were collected in Tokorozawa city, Japan are examined. La/Sm is traditionally used as an index of aerosols originated from oil burning (Hikoi et al., 2009). Recently, many products including parts made by REE spread. There is possibility that the other REEs can be new indices of human activities.

Keywords: aerosol, rare earth elements, lanthanoid

New particle formation and growth observed at a forest site in Wakayama, Japan

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The oxidation products of biogenic volatile organic compounds (VOCs) from terrestrial vegetation contribute to both the mass and number concentrations of atmospheric aerosol particles. These aerosol particles may affect the Earth's climate through acting as cloud condensation nuclei (CCN) and modifying cloud droplet properties. Characterization of biogenic aerosols remains as an important research subject, especially in the regions where they are rarely investigated. We report the aerosol properties, including those during the new particle formation (NPF) events, observed at a forest site in Wakayama, Japan. The potential significance and the influence of NPF over the studied area are discussed.

The number size distributions of aerosol particles (from 14 to 710 nm) were measured using a scanning mobility particle sizer (SMPS) at the forest site in Wakayama, Japan (34.07 degrees N, 135.52 degrees E), in summer 2010. Aerosol particles with diameters no larger than 0.95 micron were collected on quartz fiber filters, and were subjected to the chemical analysis of ionic species, organic carbon (OC), and elemental carbon (EC). The maritime air mass condition days in the years from 2006 to 2010 were identified from the daily backward air mass trajectories, which were computed using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4) Model. The precipitation rates around the forest area were calculated for the maritime air mass condition days in August of 2006 to 2010.

NPF was observed in four days during the studied period. The NPF events were characterized by large increases in the number concentrations of sub-30 nm particles and their growth for several hours. These events occurred preferentially under the conditions of low vapor condensation sink and less pre-existing particles. The calculated growth rates of 14 to 30 nm particles on the four NPF event days were from 5.0 to 15.7 nm/h. The mass fraction of OC on the NPF event days (on average 43.4% of the sum of ionic species, OC, and EC) was relatively high, which is in contrast to that on non-event days (on average 24.6%). The biogenic aerosol originated from forest vegetation presumably contributed to the relatively high OC fraction. The trajectory analysis shows that the clean maritime air masses arrived at the studied area on the NPF event days. According to the classification of trajectories, the maritime air mass conditions occurred on 10% to 16% of days for the individual year of 2006 to 2010. If new aerosol particles formed under the maritime air mass conditions as observed during this intensive campaign, the NPF may not be a rare phenomenon around the studied forest area. The large increases in the number concentrations of >90 nm particles and the enhanced precipitation rates in the afternoons of NPF event days further suggest that newly-formed particles grow up to involve in the convective cloud formation and precipitation over the region.

Keywords: biogenic aerosol, growth rates, maritime air

Closure study on concentration of cloud condensation nuclei at the summit of Mt. Fuji

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1. Introduction

According to the report on radiative forcing of IPCC (2007), the impact of aerosol on cloud and the corresponding feedbacks of cloud are currently considered as the largest uncertainty in climate system. Therefore, it is necessary to measure cloud condensation nuclei (CCN) in various areas. In recent studies, the parameterization of contributing to CCN activity, such size and chemical composition or hygroscopicity of aerosol particles, is often carried out for applying Global Climate Model. In this study, we measured CCN number concentration at the summit of Mt. Fuji and carried out CCN closure study. CCN closure study is referred to compare calculation of CCN number concentration (N_{ccn_cal}) from these parameters with direct measurement (N_{ccn}) by k-Kohler theory (Petters and Kreidenweis, 2007) to investigate most contributing to CCN activity. Ultimately, our purpose is to find parameters or models which can estimate CCN concentration without actually measuring that.

The summit of Mt. Fuji (3776m a.s.l.) is almost located in free troposphere and affected little local pollution. Therefore it is expected to be measured background atmosphere and long-range transport of pollutant from the Continent. The example of CCN observation in free troposphere is a few, so CCN observation at the summit of Mt. Fuji is invaluable.

2. Method

This observation is done at the Mt. Fuji Weather Station from 14 July 2011 to 25 Aug. 2011. We used SMPS (Scanning Mobility Particle Sizer ; TSI Inc., Model 3936N75), OPC (Optical Particle Counter ; RION Inc., KR12A) and CCNC (Cloud Condensation Nuclei Counter ; DMT Inc., CCN-100) as measuring instrument. We continuously measured dry particle number concentration and size distribution through diffusion dryer by SMPS and OPC, and CCN concentration with six different supersaturation (SS) conditions (SS=0.10, 0.19, 0.27, 0.36, 0.44, 0.52%) by CCNC.

3. Results and Discussion

N_{ccn_cal} was calculated in two ways and compared with N_{ccn} measured by CCNC. One method is to utilize averaged particle size distribution and real-time measurement of hygroscopicity (k) or chemical composition (Method 1), the other is to utilize real-time particle size distribution and averaged k (0.13 at 0.1% and 0.28 at 0.52% ; Method 2). As a result, the relative deviation ($=|N_{ccn_cal}-N_{ccn}|/N_{ccn}$) between N_{ccn} and N_{ccn_cal} in Method1 was larger than that in Method2. Therefore, it can be seen that the particle size distribution affect CCN activity more than particle hygroscopicity at the summit of Mt. Fuji.

During this measurement period 2011, CCN concentration when the summit of Mt. Fuji was located in free troposphere (FT) is about twice larger than that in the time of others. This result is opposite to that of observations at Jungfrauoch (Juranyi et al., 2010). Also, geometric mean diameter in FT was larger, and continental air exceeded in this time. Consequently, particles were grown by long-range transport from the Continent, and CCN concentration increased because CCN activity is more affected by the particle size distribution than the particle chemical composition.

We will consider whether CCN concentration at the summit of Mt. Fuji is estimated as well as other regions by k-Kohler theory and how much contribution to CCN concentration particle chemical composition has even though the particle size distribution mainly affects CCN activity.

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Keywords: cloud condensation nuclei, CCN, Mt. Fuji, free troposphere, closure study, k-Kohler theory

Decrease of hygroscopicity of oxalic acid by the formation of metal-oxalate complex

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Atmospheric aerosols have both a direct and an indirect cooling effect that influences the radiative balance at the Earth's surface. It has been estimated that the degree of cooling is large enough to cancel the warming effect of carbon dioxide. Among the cooling factors, secondary organic aerosols (SOA) play a key role in the solar radiation balance in the troposphere as SOA can act as cloud condensation nuclei (CCN) and extend the lifespan of clouds because of their high hygroscopic and water soluble nature. Oxalic acid is one of the major components of SOA, and is produced via several formation pathways in the atmosphere. However, it is not certain whether oxalic acid exists as free oxalic acid or as metal oxalate complexes in aerosols, although there is a marked difference in their solubility in water and their hygroscopicity. We employed X-ray absorption fine structure spectroscopy to characterize the calcium (Ca) and zinc (Zn) in aerosols collected at Tsukuba in Japan with fractionation based on particle size using an impactor aerosol sampler. It was shown that 10%~60% and 20%~100% of the total Ca and Zn in the finer particles (< 2.1 micrometer) were present as Ca- and Zn-oxalate complexes, respectively. Oxalic acid can act as CCN because of its hygroscopic properties, while Ca oxalate (metal oxalate) complexes are not hygroscopic, and so cannot be CCN. Based on the concentration of noncomplexed and metal-complexed oxalate species, we found that most of the oxalic acid is present as metal oxalate complexes in the aerosols, suggesting that oxalic acid does not act as CCN in the atmosphere. Similar results are expected for other dicarboxylic acids, such as malonic and succinic acids. Thus, it is possible that the cooling effect of organic aerosols assumed in various climate modeling studies is overestimated because of the lack of information on metal oxalate complexes in aerosols.

Keywords: oxalic acid, metal complex formation, XAFS, hygroscopicity

AMS and LC/MS analyses of SOA from the photooxidation of aromatic hydrocarbons: chemical structure and aging rate

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Oxygenated organic aerosol (OOA) observed in remote areas is believed to be aged secondary organic aerosol (SOA); however, the reaction processes relevant to SOA aging remain unclear. Recently, we measured mass spectra of SOA formed from the photooxidation of aromatic hydrocarbons using an Aerodyne aerosol mass spectrometer (AMS), and suggested that SOA aging delayed with increasing the number of alkyl groups involved in a precursor aromatic molecule. In this study, we selected benzene and 1,3,5-trimethylbenzene (TMB) as the SOA precursor to analyze SOA formed from the photooxidation chamber experiments in the presence of NO_x using a high-resolution time-of-flight AMS (H-ToF-AMS) and a liquid chromatograph/time-of-flight mass spectrometer (LC/TOF-MS). A van Krevelen diagram was studied using the O:C and H:C ratios obtained by H-ToF-AMS for SOA. The results showed that organics present in SOA are rich in carboxylic acids or hydroxy carbonyls, and the O:C ratio of SOA formed by the reaction of 1,3,5-TMB is lower than benzene. Analytical results of LC/TOF-MS showed that particulate products formed by the reaction of 1,3,5-TMB are rich in ketocarboxylic acids. These results indicated that SOA aging proceed mainly by formation of carboxylic acids, and the rate of SOA aging in laboratory chambers is limited by the oxidation of ketone groups. Aging of SOA formed by laboratory chamber experiments is delayed compared with ambient OOA; this is because, the experimental duration is insufficient, or conventional laboratory chamber experiments cannot simulate the ketocarboxylic acid oxidation known to proceed in the aqueous phase. Further, it was newly suggested that the ratio of particulate nitrophenols formed by the reaction of 1,3,5-TMB to total SOA mass is lower than benzene.

Keywords: aromatic hydrocarbons, secondary organic aerosol, aerosol aging, photochemical smog chamber, liquid chromatography-mass spectrometry, aerosol mass spectrometry

Atmospheric aerosols in wet seasons at Phimai, Thailand—Long range transport of soil dusts from west Asia

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According to the analysis of the field study on atmospheric aerosols measured at Phimai, Thailand, dust particles were transported from East China and Indochina, in the early- and the late-dry season, respectively. In contrast, the dust concentration in wet season was usually low compared with that in the dry season, while high concentration of dust was measured even in the wet season, comparable to that in the dry season due to transport of the edge of dust storms in East Asia. The purpose of this study is to clarify if the high dust particles were caused by the local sources or by long range transport. The case study on the episode of high dust concentration during 17-20 June 2008 was made, by comparing the surface data with CALIOP data (<http://www-calipso.larc.nasa.gov/data/BROWSE/production/V3-01/>), NIES RIDAR data(<http://www-lidar.nies.go.jp/Phimai/archives/>), and the result of the SPRINTARS model(<http://sprintars.riam.kyushu-u.ac.jp/archivej.html>). The CALIOP data showed that high dusts were measured during 14-20 June 2008, from Saudi Arabia to Somalia, from Pakistan to Arabian Sea, from Bangladesh to the Bay of Bengal, and the maximum vertical height of the dust layer reached up to 7 km. According to the RIDAR data, high dust aerosols were observed up to the height of 2-3km during 15-17 June 2008 (missing data from 18 June). Furthermore, the backward trajectory analysis by NOAA HYSPLIT MODEL (<http://www.arl.noaa.gov/ready/hysplit4.html>) showed that the air masses arrived at Phimai on 17-20 June 2008, was transported a few days after in the lower troposphere from over the Bay of Bengal, and in the layer of 2-4km height one week after from the east coast of north Africa. On the other hand, the SPRINTARS model, a high dust layer existed up to the height of 2-3km at least for a week from 14 June 2008, spreading horizontally from the eastern part of North Africa to the Bay of Bengal through west Asia, India, and the edge of the large-scale dust storm reached Indochina. All these data strongly suggest that the high dust particles at Phimai in the wet season could be caused by the long range transport of dust generated in the desert areas of west Asia, in addition to the local dust.

Keywords: atmospheric aerosols, soil dusts, long range transport, CALIOP, west Asia

Measurements of atmospheric mercury concentration at remote islands, western Japan

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Asia continent contributed about 50% of the global anthropogenic mercury (Hg) emissions, while China alone contributed about 30%. Therefore, much amounts of Hg are estimated to transport and deposit to Japan in the lee of East Asia. UN Environmental Program (UNEP) required to reduce Hg emissions into environments and its health risk. Therefore, the global partnership was established by six countries including Japan in 2006 in order to encourage atmospheric Hg study at remote areas including high mountainous and polar ones and on long-range transport in the atmosphere. However, atmospheric Hg monitoring and deposition is not studied at all on remote areas of high mountains and islands in Japan. In the present study, we report to monitor atmospheric Hg and related pollutants at the remote islands (Tsushima, Yakushima and Okinawa Islands), western Japan in order to reveal atmospheric Hg variations and acquire observational data to depositional and transport model.

We began to continuously determine atmospheric Hg with using mercury monitors (Mercury Instruments Inc., UT3000) at the Korea view point in northern Tsushima Island and Isso Junior High School in northern Yakushima Island since 2011. We also determined atmospheric Hg with using gold beads into quartz tubes on an active sampler without commercial electric power at near the summit of Mt. Fuenchidi, northern Okinawa Island. We have determined atmospheric ozone and sulfur dioxide with using ozone monitors and sulfur dioxide monitors at Tsushima and Yakushima Islands, too. Atmospheric Hg concentrations ranged from 0.1 to 1.5 ng m⁻³, which were the same level or less than back ground level, at these sites. There was showed no diurnal variations, and sometimes spike-likely high concentrations more than 1 ng m⁻³.

We will also present atmospheric ozone and sulfur dioxide concentrations and variations at the islands with atmospheric mercury concentrations.

Keywords: atmospheric mercury, remote islands, Tsushima Island, Yakushima Island, Okinawa Island

Temporal variations of the vertical profiles of CH₄ at Tsukuba observed with a Fourier transform spectrometer

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Fourier transform spectrometer (FTS) has advantages in its high resolution and the wide wavenumber range. Vertical profiles of some species can be derived from the high-resolution spectra. The vertical profiles and column densities of CH₄ were retrieved from the solar spectra observed at Tsukuba, Japan with SFIT2 spectral fitting program developed by Rinsland et al. (1998). It needs to select an appropriate wavenumber region and the optimization of fitting parameters is also needed. Now we are investigating these parameters in the NDACC/IRWG group and we will reanalyze the vertical profiles and column densities of CH₄. We found that the seasonal variation of the mixing ratios in the troposphere shows minimum in summer and maximum in winter, indicating that the chemical reaction with OH is main sink. And those in the lower stratosphere shows minimum in spring and maximum in autumn, indicating downward and upward shift due to stratospheric global circulation. The temporal variation of total column shows steplike increase in 2007 from preliminary analysis.

Keywords: FTIR, Trace Species, Methane

Development of the precise measurement of carbon dioxide in the atmosphere with optical spectrum analyzer

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Carbon dioxide is the greenhouse gas which is most significant effect on global warming. So it's necessary to observe transition of carbon dioxide precisely to understand global warming. Around 20 Fourier transform spectrometer (FTS), which is one of the precise measurement, have been operated in the world to observe column density of carbon dioxide in the atmosphere (XCO_2). However, FTS have a high cost and are unsuitable for portable use and emissions and absorption of carbon dioxide have locality. So it's necessary to observe carbon dioxide in atmosphere all over the world to understand emissions and absorption of carbon dioxide. Therefore we need the instrument which is compact, portable and can measure precisely. So the purpose is development of compact and precise measurement with optical spectrum analyzer (OSA). The instrument measures XCO_2 to incorporate sunlight in OSA through an optical fiber and to measure sunlight's absorption spectrum in the wavelength region of around 1600nm of carbon dioxide. Resolution of OSA is 0.02nm. We estimated the instrumental line shape (ILS) for OSA with laser and gas cell in the laboratory and include ILS in the result of Line-By-Line Radiative Transfer Model (LBLRTM). We show the measuring and analysis result and discuss ways to improve the accuracy.

Keywords: optical spectrum analyzer, carbon dioxide, precise measurement

Pressure broadening effects of inert gases on CO₂ and CH₄ measurements using a wave scan cavity ring down spectrometer

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A wavelength-scanned cavity ring-down spectrometer (CRDS, available from PICARRO, Inc., Santa Clara, CA) is a rapidly spreading observation instrument which can detect atmospheric CO₂, CH₄, and H₂O simultaneously based on the principle of laser absorption technique (Crosson, 2008). Chen et al. (2010) made airborne observations of CO₂ and CH₄ over the Amazonian rain forest using a CRDS and evaluated its performance for CO₂ measurement in comparison to NDIR. These investigators reported the CRDS measurements were affected by the variations in inert gaseous species (N₂, O₂, and Ar) due to pressure broadening effects (PBE) on absorption spectrum of CO₂ and CH₄. However, the magnitudes of the pressure broadening effects were not tested. In this work PBE of N₂, O₂, and Ar on the CO₂ and CH₄ measurements by means of a wave scan cavity ring-down spectrometer was examined through the experimental approach. Our experiments revealed similar PBE behaviour on CO₂ and CH₄. The relative increase of N₂ in the sample gas shows negative PBE while those of O₂ and Ar show positive PBE. Maximum PBE was observed for N₂, followed by O₂ and minimum for Ar. For example, PBE of N₂ on the CO₂ measurement at the 2.5% increase is estimated to be -0.93 ppmv while those of O₂ and Ar is +0.23 ppmv and +0.01 ppmv, respectively. For CH₄, PBE at 2.5% increase is estimated to be -1.08 ppbv while those of O₂ and Ar is +0.22 and +0.02 ppbv, respectively. Based on the experimental results, possible PBE during the synthetic standard gas measurements was considered. We inferred substantial PBE for both CO₂ and CH₄ within +/-0.6 ppmv for CO₂ and +/-0.6 ppmv for CH₄ during the measurement of the standard gas balanced with the synthetic air consists of N₂, O₂, and Ar. On the contrary, negligible PBE was estimated empirically up to -0.05 ppmv for CO₂ and -0.07 ppbv for CH₄ during the measurements of purified air-balanced standard gases. Our results clearly indicated that natural air-based standard gas should be used to remove the possible bias during the ambient air measurements and otherwise purified air-balanced standard gas should be used after the isotope correction

Keywords: cavity ring-down spectrometer, carbon dioxide, methane, pressure broadening, continuous measurements

Continuous measurements of the atmospheric O₂/N₂ ratio at suburban and coastal sites in the northeastern part of Japan

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To contribute to a better understanding of the global carbon cycle in terms of atmospheric O₂, a high precision continuous measurement system of the atmospheric O₂ concentration (defined as d(O₂/N₂)) was developed. Using this measurement system, systematic and continuous observations of the atmospheric d(O₂/N₂) were initiated at Aobayama (AOB), Japan in February 2007 and on Enoshima Island (ENS), Japan in October 2008.

At AOB, d(O₂/N₂) showed a clear seasonal cycle with the minimum value in late March to early April and the maximum value in late July to early August, superimposed on a secular decrease. The CO₂ concentration increased secularly and varied seasonally in opposite phase with d(O₂/N₂). Short-term variations on time scales of several hours to several days were also clearly observed. In winter, it was often seen that d(O₂/N₂) sharply declined in a short time, accompanied by an increase in the CO₂ concentration, and the low values last for several hours to a few days. The -O₂:CO₂ exchange ratio was found to be 1.39-1.38 ppm/ppm for such wintertime short-term variations. Since these ratios are in good agreement with a mean value of the -O₂:CO₂ exchange ratio calculated for fossil fuel consumption in Japan, the observed decline in d(O₂/N₂) is ascribed to the transport of urban air influenced by human activities. In summer, a clear diurnal cycle was observable for both the atmospheric d(O₂/N₂) and CO₂ concentration, due mainly to terrestrial biological activities near the site. The average -O₂:CO₂ exchange ratio over the summer periods of 2007-2010 was found to be -1.08 (0.10[#]) ppm/ppm for the daytime and -1.08 (0.10[#]) ppm/ppm for the nighttime, which are in excellent agreement with -1.10 (0.05[#]) ppm/ppm reported by previous studies. ([#]: standard deviation)

At ENS, d(O₂/N₂) and CO₂ concentration varied seasonally, the respective temporal patterns being similar to those at AOB. However, the seasonal peak-to-peak amplitude of APO (=O₂-1.1*CO₂), which varies mainly by the air-sea O₂ exchange, is twice larger at ENS than at AOB. This implies that the seasonal cycle of d(O₂/N₂) at ENS is much more strongly affected by the air-sea O₂ exchange, compared to that at AOB. In addition to the clear seasonal cycle, irregular short-term fluctuations of APO were observed especially in spring and summer. By comparing the backward trajectories with the distributions of marine biotic net primary production (NPP) around Japan, it was suggested that the short-term APO fluctuations are closely related to O₂ emissions due to marine biological production.

Relationship between seasonal cycle of APO at Cape Ochi-ishi and net primary production in the western North Pacific

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We examine the seasonal variation of the atmospheric potential oxygen ($APO=O_2+1.1 \times CO_2$) observed at Cape Ochi-ishi (COI; 43.2°N, 145.5°E) during the period from 1999 to 2011. Because APO is invariable with respect to the terrestrial biotic exchanges, its seasonal variations mainly reflect air-sea exchanges of O_2 . Generally, the ocean takes up O_2 in fall and winter, and releases O_2 in spring and summer. This seasonal variation in the O_2 fluxes, partially explained by the temperature-induced solubility changes in surface waters, is strongly driven by ocean biological and dynamical processes in the mid and high latitude region. In fall and winter, surface cooling causes the oceanic ventilation, which brings deeper waters with depleted O_2 in contact with the atmosphere. In spring and summer, O_2 production occurs during the phytoplankton blooms. Actually, APO observed at COI shows minimum in February-March and maximum in June-July, and the seasonal peak-to-peak amplitude is about 70 per meg. However, the seasonal amplitude increased during 2004-2006; especially in 2005 the amplitude reached about 90 per meg. As was previously reported, in-situ observation of APO at COI showed large short-term variations with significantly elevated values from late May to early July in 2005. The backward trajectory analysis suggested that the elevated APO were associated with occurrences of strong net primary production (NPP), which is satellite-derived estimation from the Vertically Generalized Production Model (VGPM), in the Okhotsk Sea and the western North Pacific. Comparing the seasonal amplitude of APO with the NPP from the VGPM for the rectangular region (35-55°N, 140-160°E) in the western North Pacific, we find there is positive correlation between the APO seasonal amplitude and the NPP in June. This result suggests that the seasonal amplitude of APO at COI may reflect the strength of the NPP in the Okhotsk Sea and the western North Pacific.

Keywords: atmospheric O_2 , APO, ocean primary production, VGPM

The vertical profiles and its variations of methane at Poker flat observed by ground-based FTIR spectrometer

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Abundance of methane has increased in long term, but no growth in 2000-2006. In this paper, we report variations of the vertical profiles of methane observed from 2004 to 2010 at Poker Flat, Alaska.

In the terrestrial atmosphere, methane is thought as the second important greenhouse gas, because its global warming potential is 21 times of CO₂. Methane is primarily produced by the anthropogenic activity, i.e., ruminants of cattle, paddy fields, natural gases, and biomass burning. They cause 70 percent of total methane emissions. Natural emissions occur from wetlands, termites and so on.

According to IPCC AR4, methane abundance is reported to increase from the Industrial Revolution, from 800ppb to 1900ppb. However, it show little change in 2000- 2006. Its origin is still not established.

We are analyzing the vertical profiles of methane and its seasonal and annual variations based on the FTIR (Fourier Transform Infrared Spectrometer) observation from 2004 to 2010 at Poker Flat, Alaska. The observed spectra are fitted by the program SFIT2 using Rodgers Optimal Estimation Method (OEM). Five microwindows between 2600 and 3000 cm⁻¹ are used for this retrieval. In this paper, we will present the seasonal and annual variations at several altitudes. It will be validated by the methane data obtained by ACE-FTS (2003-) or MIPAS (ENVISAT, 2002-) spacecraft measurements in same term.

Keywords: methane, FTIR

Development of a near-infrared laser based spectrometer for measurements of CO₂ stable oxygen isotopes

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1. Introduction

In recent years, due to human activities such as burning of fossil fuels and deforestation, the anthropogenic CO₂ in the atmosphere which causes global warming and environmental impacts is increasing. CO₂ originated in the various sources such as anthropogenic emissions, plant photosynthesis, and the ocean. Since CO₂ stable isotope ratio depends on the CO₂ sources, the continuous measurement of CO₂ stable isotope ratio in the atmosphere is a powerful method for investigating the sources of atmospheric CO₂. Recently, the laser absorption spectroscopy has been applied to the measurements of the stable isotopes. Using this technique, the isotopomers are easily recognized without interference of other species. Therefore, since the sample gas is just introduced into the sample gas cell, the real-time measurements are able to be performed. In the 2-um near infrared region, the continuous measurements of the stable carbon isotopes have been performed. However, the measurements of the stable oxygen isotopes are not performed in this wavelength region. Accordingly, we developed the new system that enables the sensitive measurements of atmospheric CO₂ stable oxygen isotope ratio in the 2-um near-infrared region.

2. Experimental

We applied wavelength modulation spectroscopy (WMS) to CO₂ stable oxygen isotope measurement. A 2.045-um distributed feed-back (DFB) diode laser was used as a light source. The laser wavelength was sinusoidally modulated at 11 kHz. After the beam was passed through a Herriott-type multi-pass cell, it was focused onto a photodiode detector. The second harmonic (2f) signal was demodulated by a digital lock-in amplifier, and the data was acquired to a personal computer. CO₂ stable oxygen isotope ratio was determined from the measurements of ¹²C¹⁸O¹⁶O/¹²C¹⁶O¹⁶O spectrum signal ratio. A premixed diluted gas of 424.5 ppm, d¹⁸O = 30.8 per mill in air was used as a sample gas.

3. Results and Discussion

The influence of a pressure, temperature, and the intensity of neighbor peaks on the stable oxygen isotope measurements were simulated. From the result of the spectrum simulation, it was found that the ¹²C¹⁸O¹⁶O line, which is the 20012 - 00001 of the P(18) at 4890.586 cm⁻¹, and the ¹²C¹⁶O¹⁶O line, which is the 20013 - 00001 of the R(56) at 4890.819 cm⁻¹, are suited for stable oxygen isotope measurement. The signal was averaged over 100 consecutive scans at 0.77 Hz for the continuous measurement of the stable oxygen isotopes. In 2-hours measurement, the obtained precision was 0.07 per mill. The limit of detection for CO₂ using our apparatus was 47.4 +- 16.1 ppb.

4. Conclusions

Using WMS with a 2.045-um DFB laser diode and a Herriott-type multi-pass cell, the CO₂ stable oxygen isotope ratio was measured. The precision of the 2-hours measurements and the limit of detection using our apparatus were achieved to be 0.07 per mill and 47.4 +- 16.1 ppb, respectively. It was showed that the measurements of the CO₂ stable oxygen isotopes ratio are able to be performed by using our apparatus.

Keywords: Measurements of stable oxygen isotope, Carbon dioxide, Wavelength modulation spectroscopy, Multi-pass, DFB laser