

Data composite of airborne sulfur dioxide measurements in the upper troposphere

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Sulfur dioxide (SO₂) is a key aerosol precursor gas, however, only during recent years high-precision in-situ data could be obtained for the upper troposphere (UT) using airborne chemical ionization mass spectrometry. Data summaries of SO₂ will be presented from a large number of campaigns performed with the research aircraft Falcon and HALO during the years 2005 to 2015 covering a geographical region from 83°N to 65°S and 105°W to 135°E and altitudes up to 15 km. The SO₂ data were gridded onto a 5° latitude by 5° longitude horizontal grid with a 1-km vertical resolution. The data composites provide information about the SO₂ distribution at mid-latitudes, tropical and polar regions. Median SO₂ background mixing ratios in the UT range between 10-25 ppt, however, also areas with strongly enhanced SO₂ mixing ratios in the UT were observed, associated with events of new particle formation. The SO₂ sources and transport pathways for these specific observations will be discussed.

Keywords: sulfur dioxide, aircraft measurements, new particle formation

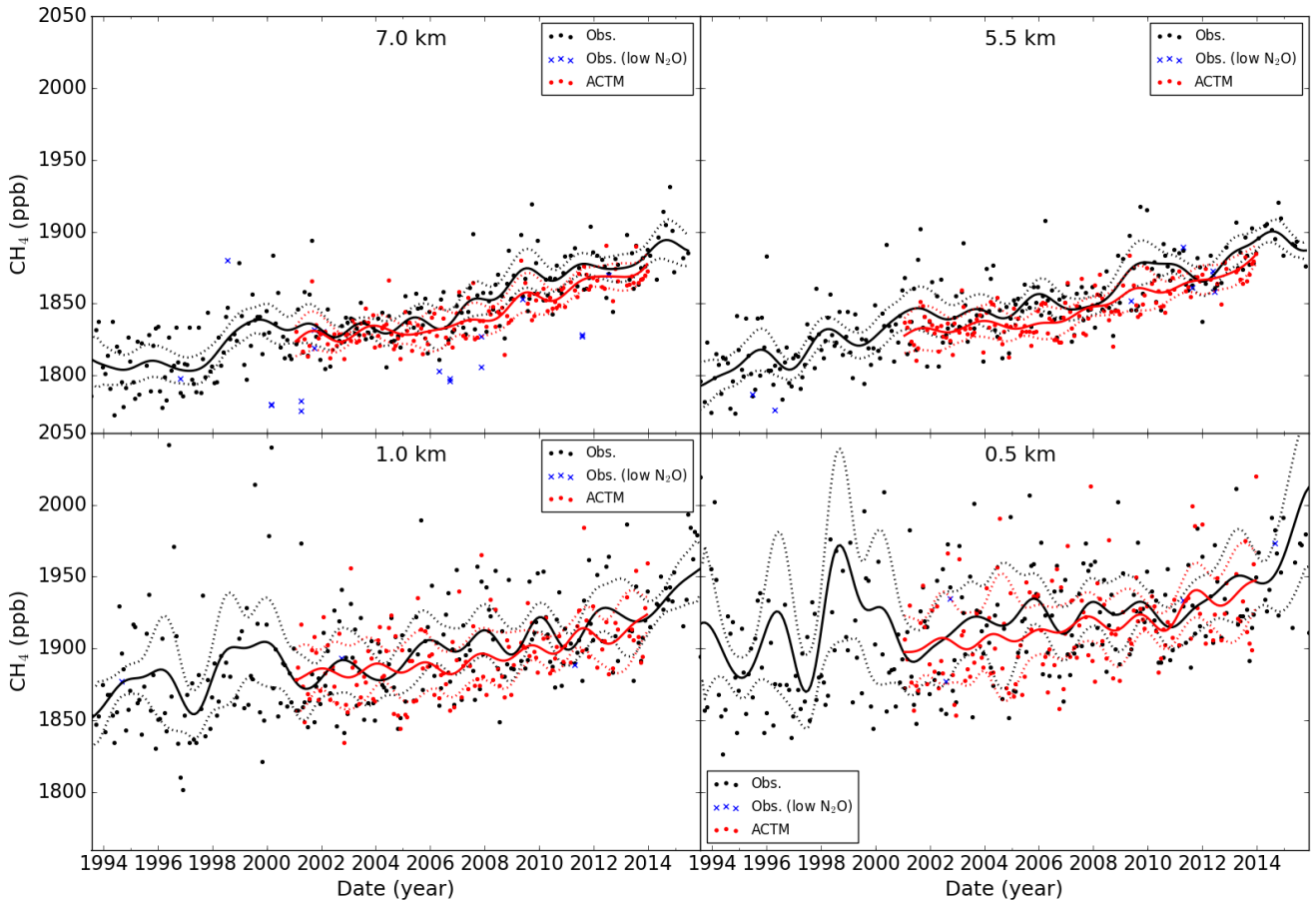
Temporal characteristics of CH₄ vertical profiles observed over Surgut (Novosibirsk) from 1993 (1997) to 2014 in West Siberian Lowland

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We have carried out monthly flask sampling with aircraft over the boreal wetlands in Surgut and a pine forest nearby Novosibirsk, both located in West Siberian Lowland (WSL). Vertical profiles of methane (CH₄) concentration were measured up to about 7 km since 1993 at Surgut and 1997 at Novosibirsk. Temporal variation at each altitude of both sites exhibited increasing trend with stagnation during 2000-2006 as observed globally from ground-based measurement network (Figure). In addition to winter maximum as seen at other remote sites in northern mid to high latitudes, a maximum was observed in summer, particularly in lower altitudes over the WSL. Large CH₄ emissions from the wetlands in the WSL likely have exceeded zonal-mean CH₄ loss by reaction with OH radical during summer, leading to the summer maximum. Methane emissions from different parts of the Earth's surface, atmospheric transport, and chemical loss produce the vertical CH₄ gradient and its variability. The vertical gradient at Surgut has been decreasing; the annual mean CH₄ difference between 5.5 km and 1.0 km decreased from 63±9 ppb during 1994-2000 to 37±8 ppb during 2009-2013. On the other hand, no clear decline in CH₄ vertical gradient appeared at Novosibirsk. An atmospheric chemistry-transport model simulation captured the observed decrease in the vertical CH₄ gradient at Surgut, when CH₄ emission from Europe was decreased but increased from the regions south of Siberia, e.g., the populated Asian nations and tropical land. At Novosibirsk, the influence of the European emission was relatively small. Our results also suggest that the regional emissions around the WSL did not change significantly over the period of our observations. Long-term monitoring of CH₄ vertical profile over West Siberia enabled us to detect variation in its emissions from the WSL and the surrounding land regions.

Keywords: Methane, Aircraft observation, West Siberian Lowland



Climatological variations of tropospheric CO₂ over the Asia-Pacific region observed by the CONTRAIL commercial airliner measurements

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We present spatial and temporal variations of tropospheric CO₂ over the Asia-Pacific region analyzed from 10 years of the CONTRAIL commercial airliner measurements. The CONTRAIL flights with the high-frequency CO₂ measurements have covered large part of the Asia-Pacific region. Here we address climatological variations of CO₂ from the boundary layer to the upper troposphere across the Asia-Pacific region toward comprehensive understanding of influence of Asian surface fluxes under the varying seasonal meteorology. Highlights of this study are summarized as follows. (1) Seasonally elevated and highly variable CO₂ is observed in East Asia to the North Pacific in spring. This is likely explained by active passage of eastward-tracking synoptic systems that sweeps the continental East Asia and uplifts the region's CO₂ emissions up to the free troposphere. (2) The region-wide CO₂ decrease is obvious across the Asia-Pacific region and it is principally composed of CO₂ drawdowns originating in two distinct regions: boreal Eurasia and South Asia. We observed seasonally largest variability of CO₂ in the UT north of 40° N, likely due to heterogeneous spatial distributions of biospheric fluxes combined with sporadic convective vertical transport over the continent. Our observations also characterized distinct CO₂ depletion in the upper troposphere over South Asia as a result of strong South Asian biospheric uptakes and confinement in the Asian summer monsoon anticyclone. The development and decay of the anticyclone remarkably contributes to distributing CO₂ over the Asia-Pacific region. (3) As the cyclonic activity decays and the monsoon anticyclone develops from spring to summer, CONTRAIL measurements with highest data density over East Asia to the North Pacific serve as better constraints to CO₂ fluxes in East Asia in spring and those in South Asia in late summer.

Keywords: Carbon dioxide, Aircraft observation, Asian monsoon

Recent trend of atmospheric nitrous oxide isotopocules in the Northern Hemisphere

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Nitrous oxide (N₂O) is one of the increasing greenhouse gases in the troposphere and is the most important stratospheric ozone-depleting gas emitted in the 21st century. In the Northern Hemisphere, sources of atmospheric N₂O include human activity in Europe, Russia, Asia, and North America (e.g., agriculture), biomass burning (forest fires), oceans, and future climate change might cause substantial change in such sources. Isotopocule ratios of N₂O, which include not only elemental ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios but also site-specific ¹⁵N/¹⁴N ratio in asymmetric NNO molecule, are regarded as useful parameters to infer the origin and production-consumption mechanisms of N₂O, and to estimate its global budget. Previous studies on N₂O trapped in the firn in polar ice sheet revealed the secular trend of isotopocule ratios, but there have been only a few reports on long-term monitoring of atmospheric N₂O isotopocule ratios in the Northern Hemisphere.

We have been measuring mixing ratio and isotopocule ratios of N₂O at one site in the low latitude and two sites in the high latitude of the Northern Hemisphere. At Hateruma, a southwestern island of Japan (24°N, 124°E), monthly air samples are collected into glass flasks at 46 m above sea level, and N₂O isotopocule analysis has been conducted since 1999. At Novosibirsk in the western Siberia, Russia (55°N, 83°E), monthly samples are collected at altitudes of 500 m and 7000 m by aircraft, and N₂O isotopocule data have been obtained since 2005. At Churchill, northern Canada (59°N, 94°W), surface air samples are collected biweekly, and N₂O isotopocule analysis has been conducted bimonthly since 2011.

Results show that the bulk nitrogen isotope ratio ($d^{15}\text{N}^{\text{bulk}}$) are decreasing at the similar rate (about -0.04‰ yr⁻¹) as reported by firn-air analysis while the N₂O mixing ratio are increasing (about 0.8 ppbv yr⁻¹) at the three sites. This suggests isotopically light N₂O sources such as agriculture are still contributing to the increase in the atmospheric N₂O. Detailed analysis of the time series reveals that year-to-year variation of the mixing ratio and $d^{15}\text{N}^{\text{bulk}}$ has been enhanced since around 2010 at all the three sites, and that vertical gradient of the mixing ratio and $d^{15}\text{N}^{\text{bulk}}$ over Novosibirsk has been also variable recently. Cause of these findings will be discussed with respect to temporal change in N₂O flux and isotopic signature of surface sources and change in atmospheric circulation including troposphere-stratosphere exchange, with the aid of atmospheric model simulation.

Keywords: Greenhouse gas, Troposphere, Stable isotope analysis

Emissions of CO₂, CO, and CH₄ from peat forest fires on Sumatra Island in non El-Niño year 2013

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We observed substantial enhancements of atmospheric trace gases and aerosols (CO₂, CH₄, CO, PM2.5, PM10, and black carbon) in summer of 2013, with continuous instruments onboard the NIES voluntary observing ships sailing in the Southeast Asia region. The enhancements were observed off the east coast of the Malay Peninsula and in the straits of Malacca along the shipping route, associated with prominent enhancements in CO. The 6-year climatology (2008 –2013) of the monthly mean CO mixing ratios in these areas shows the maximum in June, followed by moderate but relatively high values in following months of July and August. Our analysis combining in-situ measurements, satellite observations, and an air trajectory analysis showed that the observed enhancements were due mainly to the intensive biomass burnings that occurred in the central Sumatra. We examined the quantitative relationships between the observed CO₂, CO, and CH₄ during the CO enhancement events. Strong correlation was found between these gases, and the calculated emission ratios of CO/CO₂ suggested large contribution of peat forest fires to the observed enhancements (CO/CO₂ = 135 ppb/ppm). We determined the emission factors (EF) of CO₂, CO, and CH₄ from the peat forest fires using the emission ratios of CO/CO₂ and CH₄/CO₂, showing the EFs of 1722, 132.0, and 6.27 (g/kg) for CO₂, CO, and CH₄, respectively. These EFs were compared with those calculated from the current emission inventory (GFED version 4S), which are 1671, 144.5, and 11.95 (g/kg) for CO₂, CO, and CH₄ respectively. These EFs were consistent with each other except CH₄, suggesting that the EF used in GFED4S is overestimated for CH₄ from peat fires.

Keywords: Greenhouse gases, Southeast Asia, Biomass burning

Individual Particle Analysis of Marine Aerosols Collected over the North Pacific and its Marginal Seas

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Atmospheric aerosol particles can play a vital role in the climate change, because they can absorb and scatter solar radiation, and form clouds by working as cloud condensation nuclei. However, scientific understanding of atmospheric aerosol behavior is not sufficient (IPCC, 2013) due to the lack of knowledge. In this study, chemical compositions and morphology of marine aerosol particles were characterized based on individual particle analysis collected over the North Pacific and its marginal seas.

Samplings of atmospheric aerosol particles were carried out during KH-13-7 cruise (the Pacific Ocean: 2013/12/11-2014/2/12), KH-14-3 Leg2 cruise (the Pacific Ocean: 2014/7/17-8/11), KS-16-8 cruise (the sea near Japan: 2016/7/5-7/13) and MR16-06 (the Bering Sea and the Arctic Ocean: 2016/8/22-10/5). Individual particles were analyzed using a transmission electron microscope and an energy dispersive X-ray spectrometer.

Sea-salt particles without apparent reactions with other components accounted for more than 80% in the samples collected over the open seas. On the other hand, one sample out of the two samples collected near Hachijo-jima was accounted about 90% by modified sea-salt particles and sulfates. This result indicates that the pollutants from the Asian continent were transported to the observed area by the transition of the Baiu front. In the presentation, we are planning to report on the samples collected over the Arctic Ocean as well.

Keywords: Atmospheric aerosol, Sea-salt, Sulfate, Nitrate, TEM, EDX

Evaluation of satellite-based tropospheric NO₂ vertical column density using MAX-DOAS observations and their integrated analysis

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Tropospheric NO₂, a major component of nitrogen oxides (NO_x) emitted from anthropogenic sources (cars and power plants) and also from forest fires and lightning, is now regarded as a pollution marker detectable from space with a highest sensitivity. Temporal and spatial variations in the NO₂ density have been depicted by satellite observations and even their long-term trend is discussed. However, the tropospheric NO₂ vertical column density (TropoNO₂VCD) reported from satellite observations may be biased low; they can be only half of the true value near the urban region (Kanaya et al, 2014). As such, accurate understanding of the TropoNO₂VCD values derived from satellites is still poor. In this study, we re-examined the TropoNO₂VCD product from OMI/Aura satellite derived with DOMINOv2 algorithm in terms of the influence from assumptions in the vertical profile and co-existing aerosol effect. Here, ground-based MAX-DOAS observations of TropoNO₂VCD made at Yokosuka (35.32°N, 139.65°E) during 2007-2014 were regarded as true values and were compared with satellite values. Applying averaging kernels from satellite observations to the MAX-DOAS profiles removed most of the low bias, suggesting that the assumption in the vertical profile shape was critical. In the DOMINOv2 algorithm, NO₂ vertical profile shapes were borrowed from TM4 model simulations with a coarse spatial resolution; it tended to underestimate weight of NO₂ present near the surface in urban regions and this fact was overlooked when the tropospheric air mass factor (AMF) was determined, resulting in the low bias. When AMF was re-determined by borrowing MAX-DOAS based vertical profile shape, instead of that of TM4, the OMI-based TropoNO₂VCD increased by as much as a factor of 2.2 in average and showed better agreement with MAX-DOAS observations. Similarly, the corresponding near-surface concentrations increased and showed better consistency with the values from ground-based monitoring. In summary, utilizing correct vertical profile shapes enabled reasonable estimation of TropoNO₂VCD and surface-level concentrations from satellite. On the other hand, shielding effect from co-existing aerosols was found important when cloud fraction was 0.03 or lower. The tendency was consistent with the analysis results of OMI using POMINO algorithm, taking aerosol effect into account explicitly.

Keywords: air pollution, nitrogen dioxide, algorithm

Deployment of the 4AZ-MAXDOAS system at Chiba, Japan: the potential to investigate the spatial inhomogeneity of atmospheric components

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Ground-based observation data utilized for the model evaluation have been often obtained at sites, where target physical parameters, such as concentration of trace gas, are thought to be homogeneously distributed on a model grid spatial scale. However, the spatial distribution should depend on the physical parameter. More importantly, there tends to be the lack of sufficient test regarding the spatial homogeneity, particularly around sites, which are usually categorized as urban or suburban sites. Here, we present the new observation system, the 4-different-azimuth-viewing Multi-Axis Differential Optical Absorption Spectroscopy (4AZ-MAXDOAS) system. The continuous observation by the 4AZ-MAXDOAS system has been conducting in Chiba University, Chiba, Japan (35.63N, 140.10E) since November 2014, to investigate spatial distributions of atmospheric components such as nitrogen dioxides (NO₂), formaldehyde (HCHO), glyoxal (CHOCHO), and water vapor (H₂O) on a spatial scale of about 10 km. We found that daily 4AZ-MAXDOAS data for a 0-1 km layer show the significant spatial inhomogeneity, even for H₂O. However, the observed spatial inhomogeneity as well as the temporal inhomogeneity can be lowered by taking averages over longer time. We found that the differences among monthly-mean NO₂ volume mixing ratios for 4 different viewing directions were as small as ~2 ppbv. Similarly, those differences for HCHO, CHOCHO, and H₂O were estimated to be as small as ~1 ppbv, 60 pptv, and ~0.2%, respectively. It is suggested that for measurements made at a single site, averaging data over time can lower effects of both spatial and temporal inhomogeneities on the estimate of the representative values for a grid adopted by a model and for a pixel measured by a satellite instrument.

Keywords: MAX-DOAS, NO₂, HCHO, CHOCHO, H₂O

Characterization of aerosols and trace gases in Phimai, Thailand using MAX-DOAS measurements.

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We present the Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) aerosol and trace gas measurements performed in Southeast Asia, at Phimai, Thailand (15.18°N, 102.56° E). Our MAX-DOAS instrument has been operating there since September 2014. Aerosol and trace gas vertical profiles were retrieved using the Japanese MAX-DOAS profile retrieval algorithm version 2 (JM2), a multi-component profile retrieval algorithm based on the optimal estimation method. The components retrieved are Aerosol Extinction Coefficient (AEC) at 357 and 476 nm and 6 trace gases (NO₂, SO₂, O₃, CHOCHO, HCHO and H₂O). The MAX-DOAS data of AEC and its vertically-integrated quantity, i.e., the Aerosol Optical Depth (AOD), were compared to those of the co-located AD-Net (Asian Dust and aerosol lidar observation network) LIDAR (Light Detection and Ranging) and SKYNET sky radiometer measurements, respectively. Aerosol measurements from all the three platforms showed similar seasonal variations with enhanced aerosol loading during the dry season (October-May). This enhancement was associated with biomass burning, which is a pronounced event in this region according to literature reports. This was further supported by satellite observations (MODIS), which show high correlations with MAX-DOAS data with an R^2 of 0.71. The seasonal variation of trace gases (NO₂, SO₂, O₃, CHOCHO, and HCHO) showed similar patterns with enhanced concentrations during the dry season, consistent with the influence of biomass burning. In the dry season, the CHOCHO/HCHO ratio was estimated to be 0.025 ± 0.017 , which is in the range of the literature values reported for rural sites. The Ozone Monitoring Instrument (OMI) tropospheric NO₂ data also showed similar seasonal variations but tended to be biased high by 27%. It is thus expected that such unique results from multi-component observations with MAX-DOAS will be useful for evaluating satellite data and models for the Southeast Asia region.

Keywords: MAX-DOAS, Aerosols, AOD

Estimation of atmospheric ammonia distribution from GOSAT-TIR

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Atmospheric ammonia has the various sources such as food production, wastes, and biomass-burning and their emissions are increasing rapidly with human activities. It is reported that it has the large impacts for the environments, for instance, the formation of particulate matter or CCN, and the eutrophications. However, the accurate estimation of its behavior is difficult because their life-time in the atmosphere is not so long. Space-borne hyper-spectral TIR sounders enable to monitor them globally. Clarisse et al. (2009) had reported the global concentration distribution using the brightness temperature difference at the ammonia absorption band. The similar studies are also reported using the other sounders, TES, AIRS, and CrIS. Although they had captured the seasonal variations of the concentrations, the smaller time-scale events can be hardly detected because of their revisit cycle of 16 days. In addition, it also reported that there are some differences between the results from the satellites and the numerical simulations based on the inventories (Shephard et al., 2011). GOSAT which has the shorter revisit cycle of 3 days has the potential to reveal short time-scale events. The retrieval algorithm was developed based on non-linear Maximum a Posteriori (MAP) method (Rogers, 2000) and the scaling factor to the U. S. standard ammonia profile is estimated as the parameter. The large error causes, temperature and water vapor profiles are pre-estimated from GOSAT-TIR data. The preliminary results show the high concentrations in the northern India and the eastern China consistently with the previous researches and the global distribution will be presented.

Keywords: satellite remote sensing, thermal infrared radiation, atmospheric minor constituents

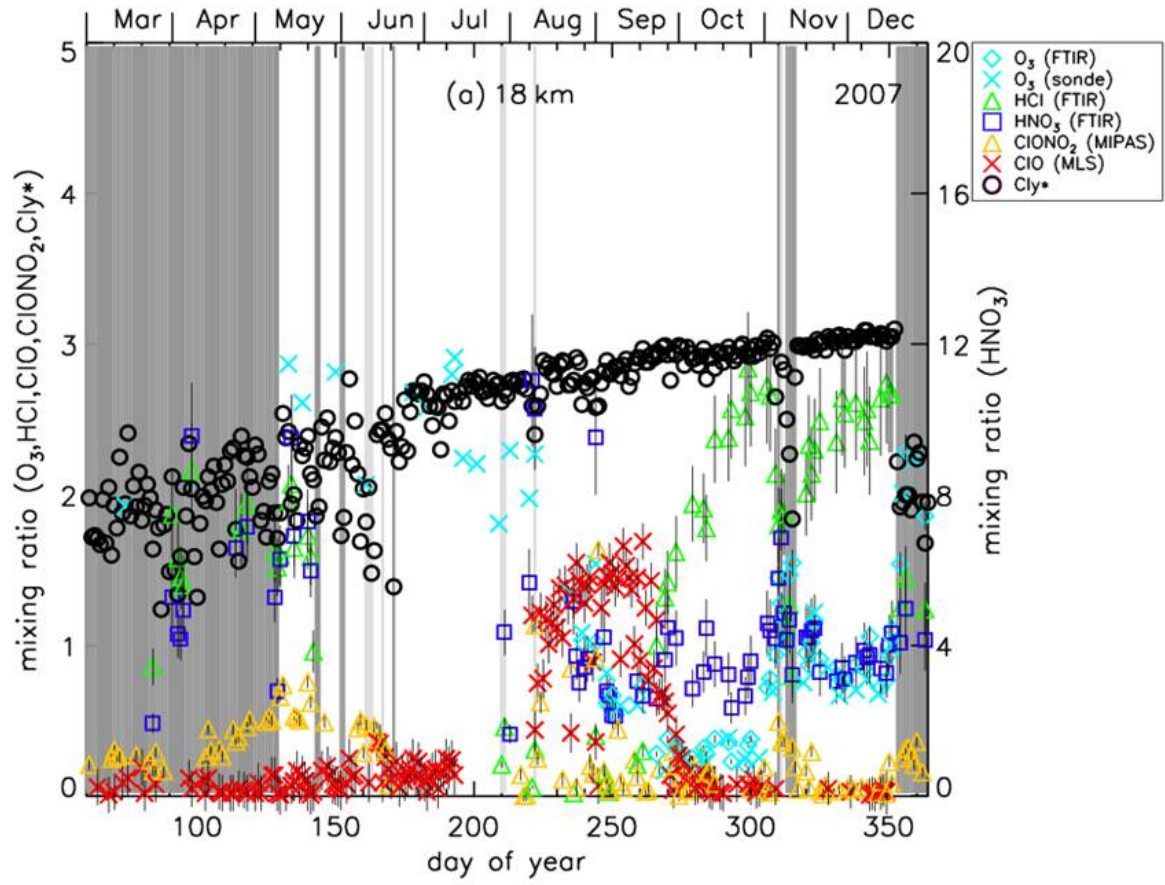
Temporal evolution of minor species observed with ground-based FTIR at Syowa Station, Antarctica in 2007, 2011, and 2016

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Vertical profiles of O_3 , HNO_3 , HCl , and $ClONO_2$ were retrieved from solar spectra taken with a ground-based Fourier-Transform infrared spectrometer (FTIR) installed at Syowa Station, Antarctica (69.0S, 39.6E) from March to December, 2007, September to November, 2011, and October to December, 2016. We analyzed temporal variation of these species combined with ClO data taken by Aura/MLS, and $ClONO_2$ data taken by Envisat/MIPAS satellite sensors at 18 and 22 km over Syowa Station. In early July, polar stratospheric clouds (PSCs) started to be formed over Syowa Station. With the return of sunlight at Syowa Station in early July, $ClONO_2$ and HCl showed depleted values while ClO showed enhanced values. At all three altitudes (18 and 22 km), when ClO concentrations started to decline in early September, HCl started to increase rapidly, while the increase in $ClONO_2$ was gradual. The Cl partitioning between HCl , $ClONO_2$, and ClO showed difference at different altitudes. At the altitudes of 18 km, where ozone was almost depleted, ClO and HNO_3 amounts are low, so conversion to HCl was favored rather than $ClONO_2$. Whereas, at 22 km, sufficient ozone still remained, at an amount that $ClONO_2$ formation from ClO and NO_y species continued to occur at this altitude. This is the first in the world to observe O_3 destruction and recovery process of reservoir chlorine (HCl and $ClONO_2$) after disappearance of PSCs using ground-based FTIR in the Antarctic.

Keywords: FTIR, Syowa Station, Cl , ozone, ozone hole



Theoretical Studies of Spectroscopic Line Mixing in Remote Sensing Applications

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The phenomenon of collisional transfer of intensity due to line mixing has an increasing importance for atmospheric monitoring. From a theoretical point of view, all relevant information about the collisional effect on line shapes is contained in the relaxation matrix whose diagonal elements are the half-widths and shifts of individual lines while the off-diagonal elements correspond to line interferences. For simple systems such as those consisting of diatom-atom or diatom-diatom, accurate fully quantum calculations based on sophisticated and realistic interaction potentials are feasible. However, fully quantum calculations become unrealistic for more complex systems. Meanwhile, due to relying on the isolated line approximation, the semi-classical Robert-Bonamy formalism, which has been widely used to calculate half-widths and shifts for decades, fails in calculating the off-diagonal matrix elements. As a result, in order to simulate atmospheric spectra where effects from line mixing are important, semi-empirical fitting or scaling laws such as the energy corrected sudden (ECS) and infinite order sudden (IOS) models are commonly used. Recently, we have found that in developing semi-classical line shape theories, to rely on the isolated line approximation is not necessary [1]. By eliminating this assumption, we have developed a more capable formalism that enables one not only to reduce uncertainties of calculated half-widths and shifts, but also to calculate the whole relaxation matrix. Thanks to this progress, one can address the line mixing based on interaction potentials between two interacting molecules. We have applied this formalism for Raman and infrared spectra of linear molecules [1-4], asymmetric-top molecule [5], and symmetric tops with inversion symmetry such as the NH₃ molecule [6-8]. Our calculated half-widths of NH₃ lines in the parallel and perpendicular bands match measurements very well. Furthermore, the method has been applied to the calculation of the shape of the Q branch and of some R manifolds in the nu₁ band of NH₃, for which an obvious signature of line mixing effects has been experimentally demonstrated. Similarly, the formalism very well reproduces off diagonal elements measured in some of ^PP doublets in the nu₄ band. In summary, comparisons with measurements show that predictions from the new formalism accurately match the experimental line shapes.

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Keywords: Line mixing, relaxation matrix, line shape parameters, pressure broadened half-widths and shifts

Seasonal and decadal variations in stable carbon isotope ratios of low molecular weight dicarboxylic acids and related compounds in the remote marine aerosols from the western North Pacific

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Oxalic and other dicarboxylic acids comprise an important fraction of water-soluble organic aerosols in various environments. To better understand long-term atmospheric changes in the western North Pacific, we collected marine aerosol samples in 2001-2014 on weekly basis at a remote island, Chichijima (27° 04'E; 142° 13'N), which is located in the boundary of westerly and easterly wind regimes. Here we present seasonal and decadal trends in stable carbon isotopic compositions ($\delta^{13}\text{C}$) of diacids dicarboxylic acids ($\text{C}_2\text{-C}_{11}$), oxoacids ($\text{C}_2\text{-C}_9$) and α -dicarbonyls ($\text{C}_2\text{-C}_3$) in the Chichijima aerosols. These compounds were determined using gas chromatography (GC) and GC/MS techniques after BF_3 /n-butanol derivatization and using a GC/isotope ratio/MS technique.

Concentrations of total diacids fluctuated in a range of 10-600 ngm^{-3} with winter/spring maxima and summer minima. The maximum concentrations in winter/spring can be explained by a combination of enhanced emissions of polluted aerosols and their precursors in the Asian Continent and enhanced atmospheric transport to the North Pacific due to the intensified westerly winds in winter/spring. The concentrations of diacids seemed to increase from 2001 to 2008 and then decrease toward recent years, as supported by major ion analyses. Recent decline of diacids concentrations may be associated with the changes in the anthropogenic emissions due to the air quality improvement in Asian countries.

Stable carbon isotopic compositions determined for 2006 showed relatively high $\delta^{13}\text{C}$ values of oxalic acid (-22‰ to -4‰). The isotopic ratios were found to increase from winter to summer. Significant enrichment of ^{13}C in oxalic acid in summer should be associated with photochemical aging of organic aerosols in the marine atmosphere, caused by kinetic isotopic fractionation during the photo degradation of oxalic acid. We will discuss the decadal changes in the stable carbon composition of oxalic acid in relation to the atmospheric oxidation capability in the western North Pacific.

Keywords: Marine aerosols, Oxalic acid, Stable carbon isotope ratio, Seasonal and decadal trends

Aggregated, iron-oxide nanoparticles as a major metal atmospheric aerosol

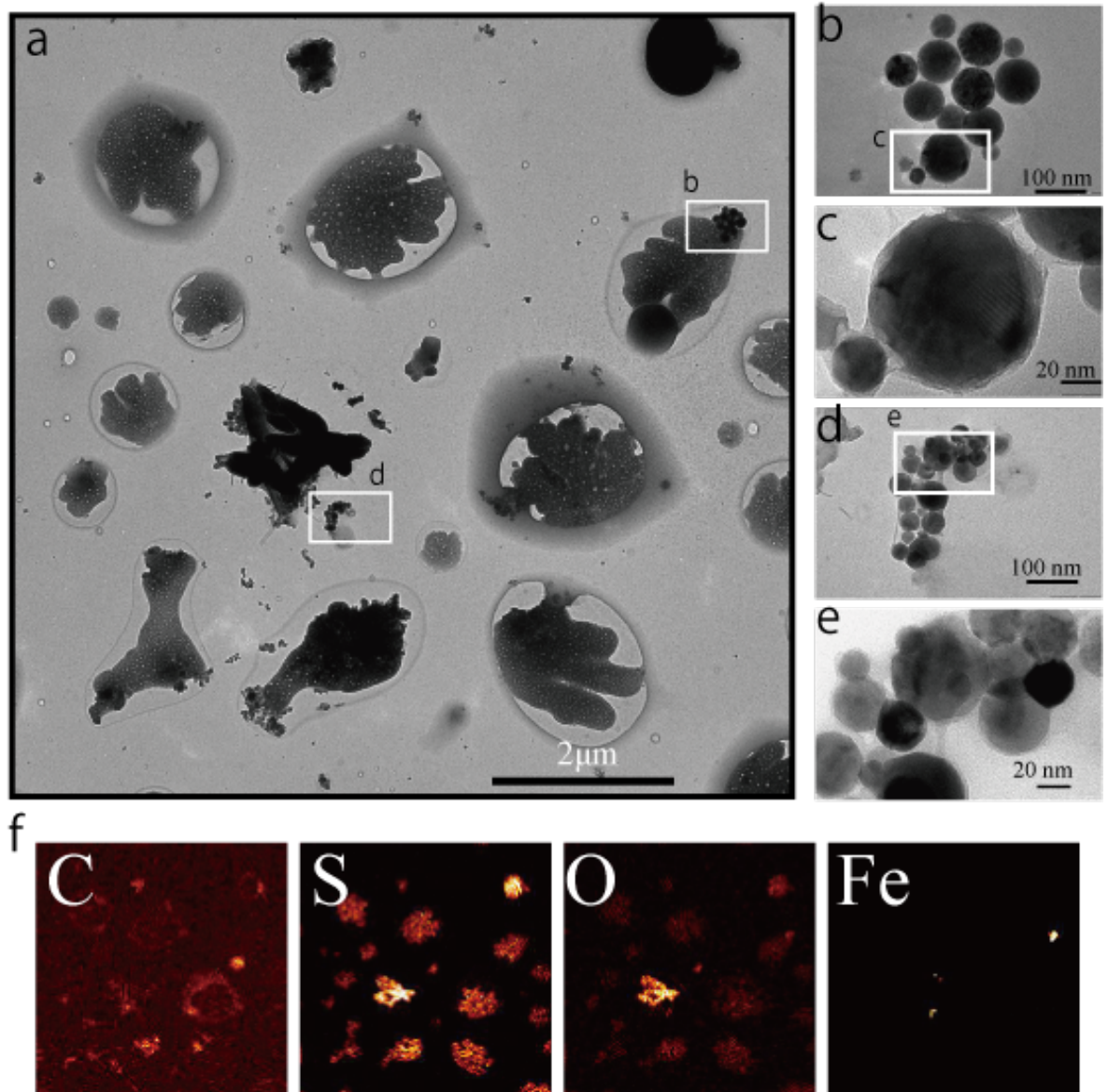
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Iron-oxide particles possibly contribute to climate, if they absorb light; marine environment, if they dissolve to water; and human health, if they have toxicity. However, little is known about the influences of iron-oxide particles in atmosphere to these important issues. This study examines iron-oxide particles by using transmission electron microscopy (TEM) and single-particle soot photometer (SP2) from samples collected from Tokyo, Japan as well as those from other locations. TEM and SP2 use fundamentally different detection techniques for the iron-oxide particles. TEM allows characterization of the morphological, chemical, and structural features of individual particles, whereas SP2 optically measures the number, size, and mixing states of iron-oxide particles. By using both techniques, we aim to understand the occurrence, abundance, and chemical and physical properties of iron-oxide particles in atmosphere.

In this presentation, we mainly focus on the results by using TEM. TEM revealed that there are substantial amount of iron-oxide particles in aerosol samples with smaller than one micrometer, consistent to the results from SP2. These iron-oxide particles are mostly aggregates of iron-oxide particles with less than one hundred nanometer, similar to soot particles, suggesting that they are emitted from anthropogenic sources. They mainly consist of iron oxide although manganese, chromium, nickel, and other elements are occasionally detected. Electron-energy loss spectroscopy (EELS) analysis shows that these iron-oxide particles are magnetite, which absorbs light and has potential toxicity. Our results suggest that iron-oxide particles could be abundant in the aerosols having anthropogenic sources and may have an important contributions to climate, marine environment, and human health.

Keywords: Transmission electron microscope, Single-particle soot photometer, Magnetite, Tokyo



PAHs in PM_{2.5} at high altitude in southern China: Meteorology, Emissions and Transport

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PM_{2.5} samples were collected for polycyclic aromatic hydrocarbons (PAHs) analysis from March 18 to May 20 in 2012 at Mount Lushan (1165m), where is located in southern China. The sampling site was located between the boundary layer and troposphere, an ideal site for learning the influences of long-range transport on PAHs distributions. The volume concentrations of the measured PAHs were 6.98 ng/m³ ranged from 1.47-25.17 ng/m³ during the sampling time. The PAHs level at Mount Lushan was at a medium level comparing to other sites around the world. PAHs mass in PM_{2.5} were 160.24 ug/g ranging from 63.86 to 427.97 ug/g. The predominant compounds were BbF (benzo[b]fluoranthene), Pyr (pyrene) and BP (benzo[g,h,i]perylene). In terms of aromatic-ring PAHs distributions, 6-ring and 4-ring were predominant, accounting for 27.9% and 24.2% of the total. It is due to that high molecular weight (HMW) PAHs have lower volatility and easier to attach in the particles comparing to low molecular weight (LMW) PAHs.

Meteorological conditions including temperature and humidity could affect the PAHs distributions. Temperature had a negative correlation with PAHs concentrations, i.e. when the temperature was higher, the PAHs concentrations become lower. This is due to the volatility of PAHs. Humidity had no significant relationship with PAHs concentrations. When the wind is strong, PAHs concentrations were lower. Strong wind would accelerate air motion, therefore PAHs were not easy to attach to particulates. Foggy and rainy weather occurred during the sampling campaign. Selected samples before and after the special weather were analyzed. The concentrations of LMW PAHs were much higher than the HMW PAHs before fog or rain. For the PAHs concentrations, they are lower obviously after fog and rain. This suggested that foggy and rainy day lower pollutant levels and played a role in cleaning air.

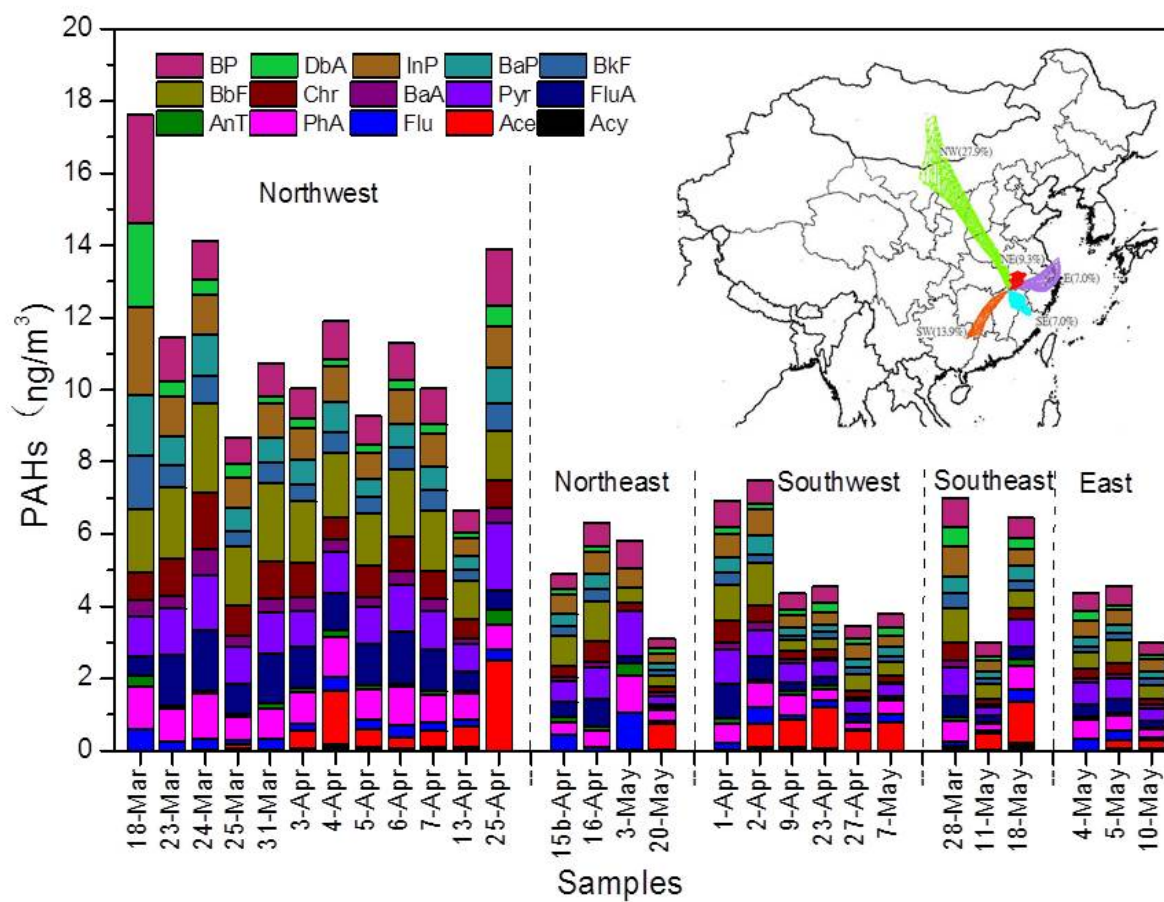
The backward trajectories simulated by HYSPLIT (the Hybrid Single Particle Lagrangian Intergrated Trajectory) model were mainly originated from five directions. The air mass from northwest, northeast, southwest, southeast and east accounted for 27.9%, 9.3%, 13.9%, 7.0% and 7.0%, respectively. Figure 1 suggested that Mount Lushan was mainly influenced by air mass from northwest during the sampling. The total concentration of PAHs were highest (11.31 ng/m³, 6.65-17.60 ng/m³) under the influence of northwestern air mass. The PAHs levels were similar when air mass from northeast (5.08 ng/m³) and southwest (5.03 ng/m³). When sample were originated from the sea in the east, the PAHs concentrations were at lowest level (3.97 ng/m³). In addition, when Mount Lushan was mainly affected by northwestern air mass, most of the PAHs species were much higher except for AnT (anthracene) and Flu (fluorene). The concentration of AnT was similar (low level) in every sample during the sampling time and Flu concentration was the highest when affected by air mass from northeast. Thus, the air mass from northwest carried large amounts of pollutants to Mount Lushan and the long-range transport influenced the PAHs distributions.

Another important factor that affected PAHs distributions was the emissions. Ratio analysis AnT/(AnT+PhA), FluA/(FluA+Pyr), BaA/(BaA+Chr) and InP/(InP+BP) and PCA (principal components analysis) were used to identify the emission sources of PAHs in PM_{2.5}. It is suggested that the main emission sources were mainly from pyrolysis of petroleum fuel (vehicle exhaust) and biomass (coal) combustion. Many factories and highways existing in the north and southwest of Mount Lushan can well explain the main source of the PAHs. The PAHs distributions were mainly influenced by long-range

transport and emission sources. Temperature, wind, fog and rain could also affect PAHs distributions in $PM_{2.5}$.

We gratefully acknowledge the National Natural Science Foundation of China (21177073) and Mount Lushan Meteorological Station.

Keywords: PAHs distributions, Transport, Meteorology, Mount Lushan



Variability of Mixing State of Aerosols observed at a Surface Site in Korea in the Spring of 2016

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Aerosols have large influence on the radiative balance of the Earth's atmosphere by scattering or absorbing solar visible radiation (direct effect) and by altering cloud microphysical properties (indirect effect) (IPCC, 2013). These effects can significantly depend on the chemical composition and mixing state of aerosol particles. Specifically, the mixing state of sulfate, nitrate, and organics with black carbon (BC) is a key parameter for estimating the aerosol direct and indirect effects (Bond and Bergstrom 2006, Adachi et al. 2010). However, there have been few studies on real-time measurements of chemical compositions mixed with BC in the atmosphere. The purpose of this study is to investigate the chemical composition of aerosol particles classified by the mixing state with BC in Asian outflow.

Ambient measurements were conducted in Korea from March 1 to April 7, 2016. A laser induced incandescence-mass spectrometric analyzer (LII-MS, Miyakawa et al. 2014) was used for the measurements. The LII-MS consists of a series of laser induced incandescence (LII) and mass spectrometric (MS) detectors. In the LII section, BC containing particles can be efficiently vaporized and emit incandescence signals by rapid heating in a near-infrared laser cavity. The sample air is subsequently introduced into the MS section to quantify chemical compositions of aerosol particles. The classification of aerosol particles with respect to the mixing state with BC (internal and external mixture) can be achieved by turning on and off the LII laser.

Nitrate, sulfate, and organics were the major species of PM₁ aerosols. On average, nitrate was most abundant and the fraction of internal mixture for sulfate was higher than that for the others. We found no systematic difference exceeding experimental errors between external and internal mixtures for nitrate and sulfate. Details of the temporal variation of chemical composition will be presented and discussed.

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Keywords: Aerosol, Chemical composition, BC mixing state

Spatial distributions and radiative effects of black carbon with MRI Earth System Model

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Most aerosol components have only the scattering property of solar radiation; however, black carbon (BC) aerosols efficiently absorb it and lead to heating of the atmosphere. Because of these effects, the role of BC particles in the climate system has been recognized to be particularly important. However, there remain large uncertainties in estimates of the spatial distributions of BC and its radiative effects in current climate models.

Recently, Meteorological Research Institute (MRI) developed a new version of MRI Earth System Model (MRI-ESM2) for participating in the Coupled Model Intercomparison Project Phase 6 (CMIP6). In this study, we modified treatments of BC in MRI-ESM2. We applied a new BC aging parameterization, which enables the representation of variations of the conversion rate from hydrophobic BC to hydrophilic BC depending on atmospheric conditions, although the original approach assumes the constant conversion rate of 1.2 days. We developed a new treatment of wet removal of aerosols in cumulus parameterization scheme, which enables a simultaneous treatment of vertical transport and wet removal of aerosols in cumulus convection in a consistent manner, although the original approach does not. We represented enhancement of BC light absorption due to coatings assuming internal mixing with sulfate, although the original approach does not take into account the coatings on BC.

We performed the MRI-ESM2 calculations for 2008-2015 with nudging towards the meteorological data (JRA-55) and sea surface temperature (not coupled with the ocean model in this study). Comparisons with the surface measurements showed that MRI-ESM2 improves the predictions of seasonal variations of BC over the Arctic, although the original constant-rate aging approach underestimates the BC concentrations and does not reproduce the seasonal variations. Comparisons with several aircraft measurements showed that MRI-ESM2 improves the vertical profiles of BC in the upper and middle troposphere, although the original wet removal approach largely overestimates BC mass concentrations. These results suggest that the seasonal variations of BC over the Arctic were primarily controlled by aging processes and wet removal by cumulus convection played an important role for BC concentrations in the upper and middle troposphere.

The annually and globally averaged direct radiative forcing by BC at the top of atmosphere was estimated to be approximately 0.2 W m^{-2} in this study. Comparisons with calculations using the original approaches suggest that the forcing increased by 40% due to enhancement of BC light absorption with coatings and increased by 20% due to improvement in representations of BC aging processes.

Keywords: Aerosol, Black carbon, Climate model, Aging process, Wet deposition, Radiative effects

Frost flowers and sea-salt aerosols over seasonal sea-ice areas in north-western Greenland

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Sea-salts and halogens in aerosols, frost flowers and brine play an important role in atmospheric chemistry in polar regions. Sea-salt fractionation proceeds on new and young sea ice. For that reason, sea-salt ratios in sea-salt particles (or aerosols) released from sea-ice areas differ from those of bulk seawater ratio, because of sea-salt fractionation on frost flower and in brine. Sea-salt fractionation can engender modification of aerosol hygroscopicity, which is closely related to phase transformation, heterogeneous reactions, and abilities of cloud condensation nuclei and ice nuclei. To elucidate the atmospheric impact of fractionated sea-salt particles, and their relation between sea-salt particles in the atmosphere and frost flowers on sea ice, one must ascertain their (1) chemical properties (e.g., concentrations, ratios, and pH) of frost flowers and brine, and (2) the physical and chemical properties of aerosols (e.g., size distribution, constituents, and mixing states) above seasonal sea ice with frost flowers. In spite of the importance, simultaneous observations and measurements of aerosols and frost flowers over seasonal ice areas with frost flower appearance have not been reported for polar regions.

Simultaneous sampling and observations of frost flowers, brine, and aerosol particles were conducted on several types (fresh - aged) of sea-ice and frost flowers around Siorapaluk in north-western Greenland during December 2013 - March 2014. Sea-salt constituents in frost flowers were determined with ion chromatograph (IC). Br⁻ and iodine (I⁻ + IO₃⁻) were analyzed with IC-MS and ICP-MS, respectively. Individual aerosol particles were observed and analyzed using SEM-EDX.

Results show that water-soluble frost flower and brine constituents were sea salt constituents (e.g., Na⁺, Cl⁻, Mg²⁺, and Br⁻). Concentration factors of sea-salt constituents of frost flowers and brine relative to seawater were 1.14-3.67. Sea-salt enrichments of Mg²⁺, K⁺, Ca²⁺, and halogens (Cl⁻, Br⁻, and I) in frost flowers were associated with sea-salt fractionation by precipitation of mirabilite (Na₂SO₄ 10H₂O), hydrohalite (NaCl 2H₂O), and sylvite (KCl). Comparison between sea-salt ratios in brine and frost flower implied that precipitation of mirabilite and hydrohalite proceed in slush layer and then the residual brine were migrated vertically onto frost flowers in our research conditions. Molar ratios of sea-salts (Mg²⁺/Cl⁻, K⁺/Cl⁻, Ca²⁺/Cl⁻, and Br⁻/Cl⁻) changed gradually with aging and growth of frost flowers and sea-salt fractionation under colder conditions. Furthermore, sea-salt fractionation was associated with not only surface air temperature but also sea-ice thickness which related to heat conduction from seawater. In contrast to Br⁻ enrichment in frost flower with the aging, changes of I/Cl⁻ ratio in frost flowers, however, were not clear. Iodine release from frost flowers might be more likely to proceed relative to Br⁻ release. Aerosol number concentrations, particularly in coarse mode, were increased considerably by release from the sea-ice surface under strong wind conditions. Sulphate depletion by sea-salt fractionation was found to be slight in sea-salt aerosols because of heterogeneous SO₄²⁻ formation on sea-salt particles. Mg was enriched in coarse and fine sea-salt particles collected on sea-ice area. Mg in sea-salt particles was in the form of MgCl₂ and MgSO₄. Strong Mg enrichment might be more likely to proceed in fine sea-salt particles. Mg enrichment in sea-salt particles was enhanced under colder conditions. In addition, ikaite-like and mirabilite-like particles identified in the atmosphere only near new sea ice are close to the sea-ice margin. Thus, Ikaite-like and mirabilite particles might be released from initial sea-ice before freezing over, and Mg-rich sea-salt particles might be released from sea-ice surface with frost flowers.

Keywords: Sea-salt aerosols, Halogens, Frost flower

Estimation of sulfate aerosol sources during an intensive field campaign in October–November, 2015 at Cape Hedo, Okinawa

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Air quality in Asia is a major regional-to-global environmental problem, and under such circumstances, several collaborative international experiments have been conducted over the western Pacific region. To investigate the transformation of aerosols during long-range transport (LRT) is necessary for promoting our understanding of regional air pollution and climate change. An intensive observation campaign at Cape Hedo, Okinawa, Japan (CHAAMS) was conducted from late October to early November 2015. The location of CHAAMS is suitable for capturing the atmospheric pollutants via LRT. During this period, sulfate (SO_4^{2-}) was the dominant aerosol component, and the air quality model can capture the observed meteorological conditions and SO_4^{2-} variation. By using the air quality model with the tagged tracer method, the sources of high SO_4^{2-} concentration were estimated. On October 27, when the westerly wind was dominant, the main source was anthropogenic SO_2 emissions in China. On November 1, when the northerly wind prevailed, the impact of volcanoes in western Japan was significant and the conversion ratio from SO_2 to SO_4^{2-} was lowest, at less than 70%, due to the faster transport. During the latter part of the campaign, the northerly to easterly winds were prominent, and the impacts of Korea, Japan, and ship to SO_4^{2-} observed at CHAAMS were also obvious. On November 4, when the contributions from Korea, Japan, and ship were the highest, the conversion ratio was also the highest, at greater than 95% due to long-range transport. The modeled sources of volcanoes and ship emissions corresponded well with the observed coarse-mode SO_4^{2-} and V/Mn ratio, respectively. It was demonstrated that the mutual evaluation of sources from model and observations enable to estimate SO_4^{2-} sources with higher confidence.

Keywords: Sulfate Aerosol, Source contribution, Air quality model, Long range transport

Modeling the Long-Range Transport of Particulate Matters During Winter in East Asia using NAQPMS and CMAQ

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Two regional chemical transport models (NAQPMS and CMAQ) were used to simulate several episodes of high PM_{2.5} concentration observed in January 2015 over China and Japan. Simulation results from both models reasonably explained observed PM_{2.5} levels, as well as the variation observed within three sites in both China and Japan. Some bias existed between these models due to differences in frameworks, including model domains, horizontal resolution, vertical layers, and emissions.

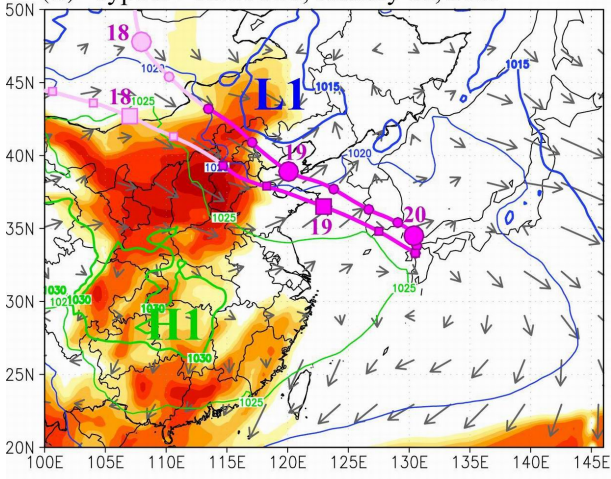
Based on the model results and the synergetic aerosol observations in Fukuoka, Japan, three types of LRT of air pollutants were observed. The first episode showed increased fNO₃⁻ concentrations relative to fSO₄²⁻ (type N), indicating the importance of NO₃⁻ LRT in winter. The second episode showed fSO₄²⁻ concentrations, which were ~3.4-fold greater than fNO₃⁻ (type S). The third episode showed high dust concentrations mixed with anthropogenic pollutants (type D), indicating that the LRT of dust was also important in winter, as well as spring.

Both models reasonably explained variations in aerosol components during episodes N and S. Simulated spatial distribution variations indicated the outflow of fSIA from continental Asia to western Japan, consistent with the corresponding PM_{2.5} peak at Qingdao and over Japan. During episode S, RH was significantly higher than episode N, therefore, SO₄²⁻ formed quickly due to aqueous-phase reactions under high RH conditions.

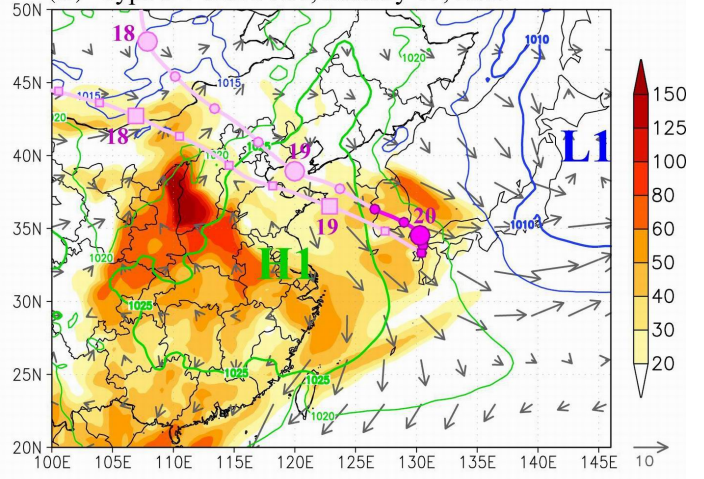
During episode D, mineral dust transported from continental Asia was quickly transported to downwind regions, stagnating over the south of Japan for three days (See Figure). Measurements showed high cNO₃⁻ concentrations and high cNO₃⁻/fNO₃⁻ ratio during episode D. These findings were well reproduced by the NAQPMS model after considering heterogeneous reactions on dust particles, which indicates the importance of heterogeneous processes for the LRT of dust and anthropogenic pollutants over East Asia. During this period, both models underestimated fSO₄²⁻ levels, indicating that current models may miss certain emissions of SO₂ and mechanisms promoting the conversion of SO₂ to SO₄²⁻.

Keywords: Secondary inorganic aerosol, Dust, Air quality model, Long-Range Transport, East Asia

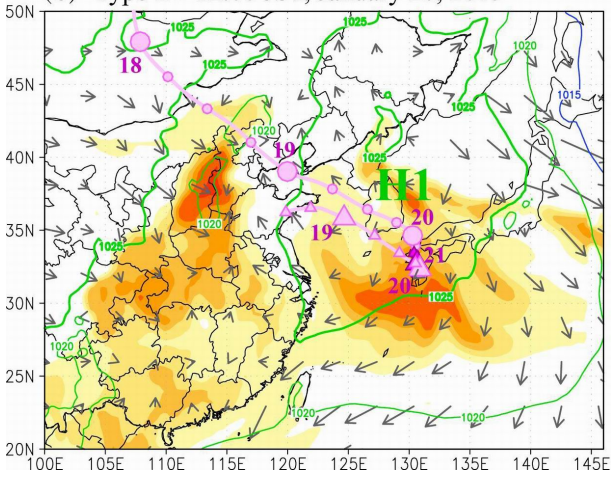
(a) Type D: 12:00 JST, January 18, 2015



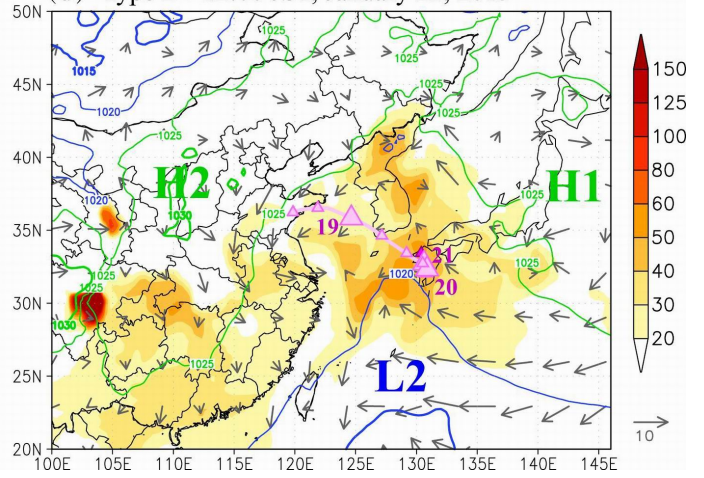
(b) Type D: 12:00 JST, January 19, 2015



(c) Type D: 12:00 JST, January 20, 2015



(d) Type D: 12:00 JST, January 21, 2015



Joint retrieval of aerosol optical depth and surface reflectance over land using geostationary satellite data

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The Advanced Himawari Imager (AHI) aboard Himawari-8 geostationary satellite provides high-frequent observations with big coverage, multiple spectral channels, and high spatial and spectral resolution. With these characteristics, the AHI data have significant advantages to monitor the air quality and estimate the aerosol properties. In this study, AHI data were used to develop an algorithm for the joint retrieval of aerosol optical depth (AOD) over land and land surface bidirectional reflectance. Instead of constructing a Look-Up-Table (LUT) and pre-estimating the surface reflectance to retrieve the AOD, the atmosphere properties and surface bidirectional reflectance were retrieved simultaneously using an optimal estimate method. The algorithm uses an Earth-atmosphere model, which couples the atmospheric radiative transfer model and surface bidirectional reflectance factor (BRF) model. Utilizing the character that the surface reflectance properties are much more stable than atmosphere aerosol, our retrieval is based on the two basic assumptions: the surface bidirectional reflective properties is invariant during a short time window while aerosol properties (e.g. AOD, AE) change. Optimal estimate method is employed to calculate the AOD and surface BRF. Detailed analysis and validation about the retrieval results were conducted using ground-based measurements (Aerosol RObotic NETwork (AERONET) sites) and satellite product (MODIS C6 aerosol product). The validation of the AOD with AERONET measurements shows a high correlation coefficient: $R^2=0.81$, $RMSE=0.13$, and about 80% AOD retrieval results within the Expected error (EE) of $(0.20 \cdot AOD_{AERONET} \pm 0.05)$. The retrieved AOD were also compared with MODIS Collection 6 AODs and it shows high consistency. All comparison and validation demonstrated that the algorithm has the ability to estimate hourly aerosol optical depth with high accuracy over land.

Long-term trend of springtime tropospheric ozone at Mt. Happo, Japan, 1998–2016

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Tropospheric ozone is one of the most important trace gases in the Earth's atmosphere because it plays a central role in global warming, oxidizing capacity of the troposphere, and air quality at local, regional and global scales. During the past decades the emissions of pollutants from East Asia have been rapidly increasing. In particular China is the largest and dominant contributor to the Asian emissions. However, recent several studies based on the analysis of satellite tropospheric nitrogen dioxides data inferred possible peaking out of nitrogen oxides emissions in China. Along with the emissions, climate plays an important role in controlling the variations in tropospheric ozone. Some studies suggested that interannual to decadal climatic variations modulate the airflow from polluted regions. We revisited and updated the long-term trend of tropospheric ozone at Mt. Happo, Japan, based on continuous measurements for the period from 1998 to 2016. We focused on the springtime ozone concentration and possible influences by the continental outflow from East Asia. Since 1998 the springtime ozone concentration has shown a large increase until 2007, very likely caused by the increase in the emissions of ozone precursors associated with economic growth in eastern China, as evidenced from satellite observations of nitrogen dioxides. After the monotonic increase until 2007, the ozone level has been flattened associated with substantial drops in 2008 and 2012. And the recent ozone levels have been sustained until 2016. We concluded that two decreases were induced by two different factors. One is the decrease of contribution from central eastern China because of the changes in meteorological fields. When the anomaly of pressure over the Pacific Ocean east of Japan decreases and the anomaly surrounding the Tibetan Plateau increases, polluted air masses from central eastern China tend to be transported to Mt. Happo by the strong westerly component. The other factor is the decrease in emissions of ozone precursors from eastern China, which is the phenomenon observed by satellite.

Keywords: ozone

Sources and effects of atmospheric nitrous acid in the marine boundary layer

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Nitrous acid (HONO) is an important reservoir of hydroxyl (OH) radicals in the atmospheric boundary layer. However, its sources are still not well understood. As few HONO observations have been performed in marine areas, we conducted measurements at two coastal sites, Tuoji Island in North China and Hong Kong, to investigate the sources and effects of HONO in the marine boundary layer. Compared with urban sites, HONO concentrations were low in marine sites. However, they were still significantly larger than that could be explained by the mechanisms in photostationary state (PSS). Through case study, results have indicated an interesting phenomenon that HONO may be produced faster on sea surface than on land surface. And further studies should be carried out to confirm this finding. In addition, HONO plays an influential role in atmospheric oxidative capacity and air quality in coastal regions.

Keywords: Nitrous acid (HONO), Sources, Effects, Marine boundary layer

Assessment of Sensitivity of Tropospheric Ozone Production to NO_x and VOCs Emissions Using WRF/Chem Model for Megacity Delhi

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An increase in ozone build up in the recent years has been witnessed in Delhi, the capital city of India which is a cause of alarm due to the detrimental effects of ozone on public health. Regular monitoring of ozone concentrations revealed that an increase of $6 \mu\text{g m}^{-3}$ from 2009 ($35.3 \mu\text{g m}^{-3}$) to 2012 ($41.5 \mu\text{g m}^{-3}$) was recorded (Gupta and Mohan, 2015) in Delhi and in summer 2015, exceedance of O₃ levels ranged from 92% - 97%. Tropospheric ozone is produced by a cycle of reactions involving two basic pollutants NO_x and VOCs. Chemical regional transport models such as WRF/Chem are used extensively for modeling of ozone concentration. As ozone production has distinctive daytime and nighttime chemistry, Gupta and Mohan (2015) recommended that for Delhi model implementation shall be made for policy decisions cautiously with due consideration to the magnitudes of ozone levels. In order to implement control strategies it is conducive to understand whether the study area is NO_x or VOC limited. This study focuses on the WRF/Chem model to simulate ozone concentration for megacity Delhi during summer conditions for three consecutive years. To understand the role of VOC and NO_x in ozone formation model simulated VOC to model simulated NO_x ratios were studied through scatter plots. Ozone production is considered to be VOC limited at low VOC to NO_x ratio i.e. less than about 4 to 1 and for high ratio greater than about 15 to 1 the region is classified as NO_x limited. There are various sources that contribute to VOC emissions such as vehicular pollution, refueling stations, industrial hubs, diesel generator sets etc. In Delhi overall about 26 to 54% of VOCs are due to the emissions from diesel internal combustion engine (Srivastava et al., 2005). Srivastava et al. (2005) reported source contribution to total VOC for a traffic junction in Delhi as 43% from diesel exhaust, 24% from gasoline, 19% from evaporative and 14% from other sources. As the ozone production is VOC limited for megacity Delhi, WRF/Chem model can be further used to apply control strategies. The response of reduction in VOC emissions from transport sector on ozone production can be modeled in order to formulate effective mitigation measures involving both VOC and ozone reduction.

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Keywords: Ozone, VOC to NO_x ratio, WRF/Chem, Megacity Delhi

Seasonal and interannual variations in the atmospheric Ar/N₂ ratio observed at five ground based stations in Japan

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Atmospheric Ar/N₂ ratio is a unique tracer to detect the spatiotemporally-integrated air-sea flux or ocean heat content (OHC), since the variations in surface Ar/N₂ ratio are driven by air-sea Ar and N₂ fluxes principally due to changes in solubility in seawater. The relative temperature dependence of the solubility of Ar is larger than that of N₂, so that the atmospheric Ar/N₂ ratio increases with increasing ocean temperature. We have started systematic measurements of the Ar/N₂ ratio by using a mass spectrometer (Ishidoya and Murayama, 2014) at Tsukuba (36°N, 140°E) and Hateruma Island (24°N, 124°E), Japan since 2012 and at Cape Ochi-ishi (43°N, 146°E), Takayama (36°N, 137°E) and Minamitorishima Island (24°N, 154°E), Japan since 2013. Not only clear seasonal Ar/N₂ cycles with summertime maxima were found at all stations, but also clear interannual variations were seen from the 5-years data at Tsukuba and Hateruma; gradually increased from 2012 to the beginning of 2015 and did not show a significant increase/decrease since then. The seasonal amplitudes and appearances of maxima and minima of the Ar/N₂ cycles were larger and earlier, respectively, at coastal stations at Hateruma, Ochi-ishi and Minamitorishima than those at inland sites at Tsukuba and Takayama. The peak-to-peak seasonal amplitudes were in the range of 15-45 per meg, which were comparable to or larger than those reported by past studies (Keeling et al., 2004; Cassar et al., 2008). The interannual variations of Ar/N₂ ratio at Tsukuba and Hateruma were generally in phase with those in the global OHC reported by NOAA/NODC (updated from Levitus et al., 2012), which suggests our observational results reflect wide-area averaged information of ocean temperature.

Acknowledgements

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Keywords: atmospheric Ar/N₂ ratio, ocean heat content, seasonal variation, interannual variation

Estimation of CO₂ contributions from fossil fuel consumption based on the atmospheric O₂ and CO₂ continuous measurements

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Atmospheric carbon dioxide (CO₂) concentrations observed in urban areas and the surroundings often show short-term elevations on a time scale ranging from several hours to a few days. These variations are considered to be attributed to the CO₂ emissions from biotic activities and burning of fossil fuels. Partitioning the contribution rate between the individual CO₂ sources would be useful to reduce the uncertainty of the CO₂ emissions estimated from atmospheric inversion calculations. The ratio of oxygen (O₂) consumption to CO₂ emission for fossil fuel burning ($-O_2/CO_2$) ranges from 1 to 2, depending on the elemental composition of the fossil fuel. The average $-O_2/CO_2$ exchange ratio for the fossil fuel consumed in Japan is more than 1.4 while that for land biotic process is 1.1. Therefore, the difference in the exchange ratios could allow us to determine the contributions from the individual sources. In this study, we started a continuous observation of the atmospheric CO₂ and O₂ concentration at Tsukuba in February 2015, and evaluated the individual contributions of the biotic and fossil fuel-derived emissions to the short-term CO₂ variations based on the observed $-\Delta O_2/\Delta CO_2$ changing ratios. The observed $-\Delta O_2/\Delta CO_2$ changing ratios show clear seasonal variation with minimum in summer and maximum in winter, ranging from 1.0 to 1.6. Taking into account of the average $-O_2/CO_2$ exchange ratio of 1.58 for the fossil fuel consumption in Tsukuba, we obtained the contribution ratios of fossil fuel burning to the CO₂ variations were more than 70% in winter and 0–30% in summer. To validate the above estimations based on the $-O_2/CO_2$ exchange ratio, we conducted flask samplings of air 6 times at the different months during the observation period and measure ¹⁴CO₂, which is known as good indicator of the burning of fossil fuels. Note that 5 flask samples were usually collected for each sampling at an interval of 3 hours to detect the diurnal variations. The contribution rates of the fossil fuel CO₂ estimated from $-O_2/CO_2$ ratios and ¹⁴CO₂ agree each other within the uncertainties.

Heterogeneous reactions of gaseous ozone with aqueous sesquiterpenes: The roles of Criegee intermediates

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We report the detection of intermediates/products generated on fresh surfaces of alpha-humulene and beta-caryophyllene solutions in water/acetonitrile mixtures exposed to gaseous ozone for ~ 10 microsecond. We focus on the identification of intermediates/products and their mechanisms of formation via negative ion online electrospray mass spectrometry complemented with the use of (1) H/D and ¹⁶O/¹⁸O isotopes, (2) a OH-radical scavenger, (3) variable O₃ number densities, and (4) n-alkyl carboxylic acid additions. We will discuss how our results provide direct evidence on the distinct reactivity of Criegee intermediates at air/aqueous interfaces.

Keywords: Criegee, Terpenes, BVOC, ozone, surface, interface

Inhaled ozone reactions with endogenous antioxidants and surfactants on the surface of lung lining liquid films

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We report the detection, via online electrospray ionization mass spectrometry, of the intermediates/products generated on the surface of surfactant protein B aqueous solutions exposed to gaseous ozone for 10 microseconds in the presence/absence of ascorbic acid/ascorbate as antioxidant. These experiments simulate how inhaled ozone reacts with typical components of the air-aqueous interface of human respiratory tract lining fluids. We found dramatic changes in the species detected at pathological acidic pH ~4 vs normal physiological pH 7 conditions. We will provide clues on the identity of the species generated in each case and on their mechanisms of formation. We will discuss the implications of our findings on the adverse health effects induced in healthy and diseased subjects.

Keywords: Inhaled ozone, Surfactant protein B , Health effects of air pollution on healthy and diseased subjects

Surface melting on ice surfaces visualized by advanced optical microscopy

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Ice is one of the most abundant crystals on the earth, and hence its phase transitions exert enormous influence on the global environment. Surface melting of ice crystals is one of such phase transitions: ice crystal surfaces are covered with thin liquid layers, so called quasi-liquid layers (QLLs), even below the melting point (0°C). Since QLLs enhance various chemical reactions in ice clouds, presence or absence of QLLs is also important for atmospheric chemistry.

Recently, we and Olympus Engineering Co., Ltd. have developed laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM) by which we succeeded in the direct visualization of 0.37-nm-thick elementary steps [1] and QLLs [2] on ice for the first time. The direct visualizations revealed that QLLs with two types morphologies partially cover the ice surface [2,3] although QLLs had been thought to cover the whole ice surface uniformly. And we found that the appearance of QLLs depended on not only the temperature but also water vapor pressures [4,5] and species of ambient gases [6].

For example, we found that hydrogen chloride (HCl) gas strongly induced the appearances of QLLs. The droplet shape QLLs were observed in the temperature range of -15.0 ~ -1.5°C, where no QLL appears in the absence of HCl gas [6]. These results indicate that HCl gas adsorbed on ice crystal surfaces probably changed the surface structure of ice crystals and then induced the subsequent melting of ice surfaces. The long-term (one-hour) existence of the droplet QLLs under the undersaturated conditions and their behaviors strongly suggest that the droplet QLLs were thermodynamically-stable HCl solutions. In addition, we found that the HCl induced droplets were embedded into ice crystals by growth of ice crystals and the embedded droplets appeared again by evaporation of ice crystals. These results show the possibility that ice crystals can store large amount of gas components as fluid inclusions.

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[2] Sazaki et al. (2012) *PNAS* **109**, 1052.

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[4] Asakawa et al. (2015) *PNAS* **113**, 1749.

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Keywords: Ice, Surface melting, Quasi-liquid layer, Hydrogen chloride gas, Advanced optical microscopy

Evaluation of ice nucleating activity of mineral aerosols: importance of mineralogy and aging process

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Ice crystals may be formed in the super-cooled liquid phase clouds with the aid of aerosol particles that act as ice nuclei. Among various aerosol particles that act as ice nuclei, mineral dusts are considered most ubiquitous due to their abundance in the earth's atmosphere. However, the mechanism by which mineral dusts act as efficient ice nuclei is not well understood. The purpose of this study is to narrow down the mineralogical factors that determine their initial ice nucleation activity. This study employed a cold-float technique to evaluate ice nucleation activity of mineral dusts with various mineralogical compositions. We show that there are potentially three major mineralogical factors controlling the ice nucleating activity of feldspar mineral group, namely, the cation type, solid solution state and ordering structure. In addition, we found that the ice nucleating activity of feldspar drops and shows similar activity as the clay minerals following treatment by sulfate acid, suggesting atmospheric aging may slow down the ice nucleation by the most efficient mineral types (e.g. K-feldspar). These results have important implications in the ice nucleating activity of mineral dusts in the actual atmosphere.