Response of total ozone reactivity analyzer to mixture of gaseous isoprene and NO

*Jun Matsumoto[1], Roberto Sommariva[2]

1. Faculty of Human Sciences, Waseda University, 2. School of Geography, Earth and Environmental Sciences, University of Birmingham

Biogenic volatile organic compounds (BVOCs) have been focused on as precursors of tropospheric ozone (O_3) and secondary organic aerosols. Various species of BVOCs have C=C double bonds and can react with O_3. To capture BVOCs comprehensively, a total ozone reactivity (R_{O3}, the sum of $k_i[VOC_i]$) analyzer has been developed [1-4]. R_{O3} of sample BVOCs can be determined when decrease of O_3 due to BVOCs+O_3 is precisely monitored. In our previous studies, the detection limit of the analyzer reached 6.3×10^{-5} s^{-1} (S/N=3, 60-s average, 50-s reaction) [4]. To apply the analyzer to field observations where the samples consist of multiple compounds, characteristics of the analyzer should be explored further. For example, nitric oxide, NO, which exists significantly everywhere in the troposphere, can react with ozone rapidly. When BVOCs are captured as R_{O3}, NO can be detected simultaneously. A model study reported that, even when R_{O3} in the forest atmosphere is focused, contribution of NO to R_{O3} can be critical [5]. Generally, NO concentration can be captured easily utilizing an NO analyzer. Thus, if dependence of the output of R_{O3} analyzer on NO concentration is understood, contribution of NO to observed R_{O3} can be separated and R_{O3} due to BVOCs can be accurately quantified. In this study, mixtures of isoprene and NO standard gases were prepared and response of R_{O3} analyzer to the mixtures was experimentally captured in order to explore the possibilities of the standard addition method of NO to BVOCs samples. As a result, among the isoprene standard sample (A) and NO-added isoprene samples (B, C, D), a strong correlation was observed between the concentration of NO and the measured R_{O3} as shown in Fig.1. The intercept of the regression line agreed well with the observed R_{O3} of isoprene standard sample (A). It was experimentally confirmed that, when NO addition was conducted, the contribution of BVOCs (isoprene in the figure) to R_{O3} could be determined as the intercept of the regression line between NO concentration and measured R_{O3}. Consequently, the method of standard addition to separate the contribution of NO from observed R_{O3} was established. Evaluation of BVOCs as R_{O3} is possible even when NO coexists in the sample. As a next step, application of this method to R_{O3} observations for studying BVOCs emission from real plants and/or ambient samples is promising.

[1] Matsumoto, J., AGU Fall Meeting 2011, USA, A51A-0232 (2011).
[2] Matsumoto, J., Aerosol Air Qual. Res., 14, 197-206 (2014).
[3] Matsumoto, J., 1st OH Reactivity Specialists Uniting Meeting, Germany (2014).
[4] Matsumoto, J., Chem. Lett., 45, 1102-1104 (2016).
[5] Mogensen et al., Atmos. Chem. Phys., 15, 3909-3932 (2015).

Keywords: biogenic VOCs, nitrogen oxides, standard addition method

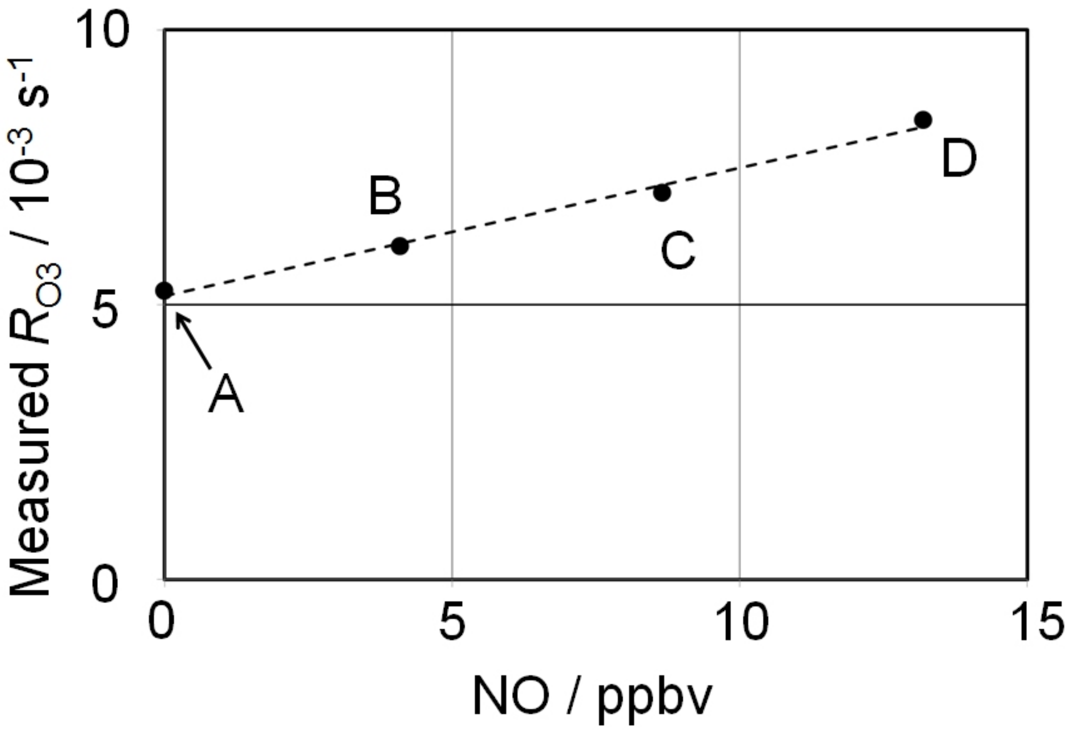


Fig.1 Observed relationship between NO mixing ratio and measured ozone reactivity.
A: isoprene standard sample. B, C, D: NO-added isoprene samples.
Regression line (dashed line): slope $2.3\text{x}10^{-4}$ s^{-1} $ppbv^{-1}$, intercept $5.2\text{x}10^{-3}$ s^{-1}.

Analyses of trends, seasonal variations, and short-term variations of atmospheric N_2O concentrations observed at Hateruma Island and Cape Ochi-ishi

*Yasunori Tohjima[1], Keiichi Katsumata[1], Toshinobu Machida[1], Kentaro Ishijima[2]

1. National Institute for Environmental Studies, 2. Japan Agency for Marine-Earth Science and Technology

Nitrous oxide (N_2O) is one of the important anthropogenic greenhouse gas in the atmosphere, having a GWP 265 times that of CO_2 for a 100-year timescale. To enhance understanding of the global N_2O cycle, the National Institute of Environmental Studies (NIES) has been carrying out in-situ observations of the atmospheric N_2O at Hateruma Island (HAT; lat. 24.1°N, long. 123.8°E) since March 1996 and at Cape Ochi-ishi (COI; lat. 43.2°N, long. 145.5°E) since June 1999 by using gas chromatographic systems. In this study, the trends, the seasonal variations, and the synoptic-scale variations of the atmospheric N_2O observed at both sites are examined. The N_2O concentrations at both sites steadily increased at an almost same rate of about 0.8 ppb/yr. Although the interannual variations in the growth rates seem to be rather small, relatively large increasing rates larger than 1.1 ppb/yr were observed for HAT in 1999-2000 and for HAT and COI in 2014-2015. The average seasonal cycles show the maxima in April for both sites and the minima in July for HAT and in September for COI. The peak-to-peak amplitudes of the average seasonal cycles are about 0.5 ppb and 0.8 ppb for HAT and COI, respectively. It should be noted that the seasonal amplitude for HAT seems to increase temporally at a rate of 0.012 ± 0.007 ppb/yr ($p=0.1$) although that for COI doesn’t show a significant long-term change. In addition to the seasonal variations, synoptic scale variations are often observed especially at HAT during a period from November to March, when the polluted air masses are predominantly transported from the continental regions. The standard deviations of the detrended and deseasonalized time series of N_2O for the winter 5-month period for HAT show significant temporal increase. The EDGAR inventory estimation (v4.2, FT2012) shows that the anthropogenic N_2O emissions from China increase about 40% during 1996-2012. Therefore, the increasing trends in the amplitudes of the seasonal and short-term variations at HAT may reflect the anthropogenic emission increase in China.

Keywords: atmospheric N2O, greenhouse gas, seasonal variation, short-term variation

Short-term variations of N_2O and CO mixing ratios observed at suburb of Sendai from November to December 2016

*Yoichi Inai[1], Wei Li[1], Hideki Nara[2], Shinji Morimoto[1], Shuji Aoki[1]

1. Tohoku Univ., 2. NIES

Nitrous oxide (N_2O) is one of the most important greenhouse gas, and carbon monoxide (CO) has a significant role in atmospheric chemistry through reactions with hydroxyl radical (OH) in the atmosphere. The both gases are released from anthropogenic and natural origins and should be monitored with high accuracy to understand their dynamics. Atmospheric N_2O and CO mixing ratios over Aoba-yama, suburb of Sendai, Japan had been observed from November to December 2016 by a continuous measurement system for N_2O and CO, that was a newly developed in Tohoku University using Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS). The baseline mixing ratios of N_2O and CO mixing ratios were ˜331 ppb and ˜150 ppb, respectively, during the measurement period. Further, short-term and sporadic increases of N_2O and CO were also frequently observed. By means of meteorological analyses including backward trajectory calculations, those short-term variations are interpreted as being affected by local emissions near the observation site in some cases, or by regional-scale transport of air masses in other cases. The overall tendency for trajectories suggests that air masses transported from northeast China have relatively low mixing ratios of N_2O and CO, while those from near Japan have relatively high mixing ratios of them.

Keywords: N2O CO, trajectory analysis, transport, lower troposphere, northeast Asia

Real-time measurement of atmospheric carbon monoxide combined with mid-infrared wavelength modulation spectroscopy

*Chikara Hashimoto[1], Kenichi Tonokura[1]

1. Graduate School of Frontier Science, University of Tokyo

Carbon monoxide (CO) is emitted from incomplete combustion of fossil fuels and biomass. It affects the concentration of CO_2 and CH_4 through the reactions with hydroxyl radicals. The major method of the measurements of CO is NDIR. This method is highly sensitive and highly stable. There are a lot of data of the concentration of CO measured with NDIR, but they show only hourly average. In this study, we observed CO concentration in the atmosphere with a mid-IR laser absorption spectrometer that uses a 4.69 μm quantum cascade laser with wavelength modulation spectroscopy (WMS).
The absorption line for the measurements of CO was at 2131.63 cm^{-1}. The laser was scanned at 1.10 Hz. The beam was collimated with CaF_2 lens and introduced into the cell. The optical path length was 29.91 m. The signal from a photodetector was processed by the lock-in amplifier.
To assess signal stability and detection limit, 1.02 ppm CO gas was introduced into the WMS system. The precision (1 σ) of the measurement for 7 hours was 4.18 ‰.
For the measurement of the detection limit of this instrument, we collected the signal of different CO mixing ratio and made the calibration curve. From the slope and the averaged baseline deviation, the detection limit (SNR = 2) was found to be 10 ppb.
Measurements of outside air were conducted on the Kashiwa campus of The University of Tokyo over February 8-11, 2017. During the measurements of ambient air, the calibration was performed every 6-9 hours.
Outside air measurements were conducted over February 8-11, 2017. The CO mixing ratio during the measurements ranged from 0.11 ppm to 0.60 ppm. In the daytime of February 10, the wind brew from northwest. There are no big industrial areas in that direction. So the CO concentration was low and steady. There are some spikes in CO concentration. These may be attributed to cars passing near the observation point.
We performed in situ measurements of CO mixing ratios in ambient air with a near-IR laser absorption spectrometer using WMS. We successfully detected CO mixing ratio change in the ambient air instantly.

Continuous measurement of CO_2 and CH_4 concentration from a tower network (JR-STATION) over Siberia

*Motoki Sasakawa[1], Toshinobu Machida[1], Akihiko Ito[1], Noritsugu Tsuda[2], Mikhail Arshinov[3], Denis Davydov[3], Alexandrov Fofonov[3]

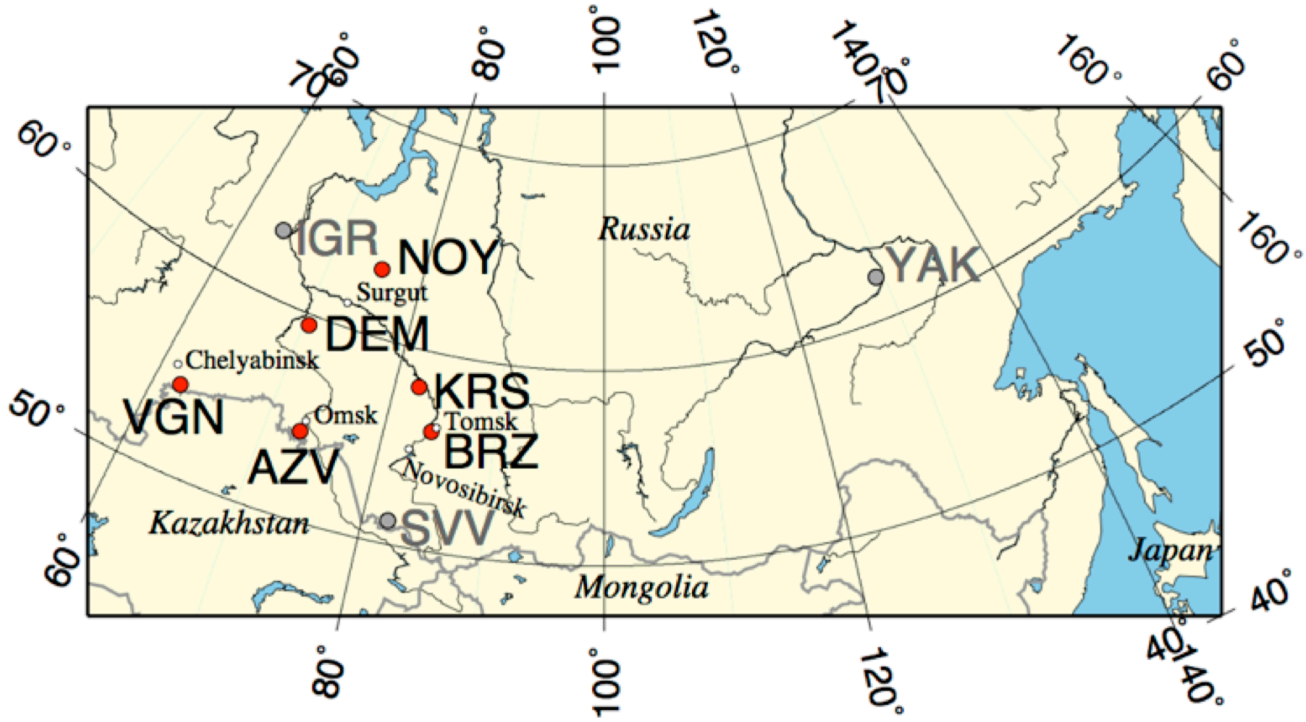
1. NIES National Institute of Environmental Studies, 2. Global Environmental Forum, 3. V.E. Zuev Institute of Atmospheric Optics, Russian Academy of Sciences

Continuous measureements of CO_2 and CH_4 concentration have been carried out with a tower network in Siberia (JR-STATION: Japan–Russia Siberian Tall Tower Inland Observation Network) in order to study the spatial and temporal variations of CO_2 and CH_4 and estimate the distribution of the flux over this vast area (Sasakawa *et al.,* 2010, 2012, 2013) where only a few atmospheric investigations were made.
The JR-STATION consists of 6 towers (Figure) located at Berezorechka (BRZ) since 2002, at Karasevoe (KRS) since 2004, at Demyanskoe (DEM) and Noyabrsk (NOY) since 2005, at Azovo (AZV) since 2007, and at Vaganovo (VGN) since 2008. Air samples taken at two heights (5-85 m) on each tower were analyzed with an NDIR (LI-COR, LI-820) for CO_2 and a SnO_2 semiconductor sensor (Suto *et al.,* 2010) for CH_4 after passing through the line with a glass water trap, a Nafion membrane dryer (PERMA PURE, MD-050-72F-2), and a magnesium perchlorate. Measurement precision was ±0.3 ppm for CO_2 and ±5 ppb for CH_4.
We will discuss the long-term variations in CO_2 and CH_4 observed with the present system. From the year of 2015, we installed a Cavity Ring-Down Spectroscopy (CRDS; Picarro inc.) at KRS, DEM, and NOY. We thus validate the recent data with the data by the CRDSs.

References

Sasakawa, M. *et al.,* Tellus **62B,** 403-416, 2010.
Sasakawa, M. *et al.,* Tellus **64B,** doi:10.3402/tellusb.v64i0.17514, 2012.
Sasakawa, M. *et al.,* J. Geophys. Res. **118,** 1-10, doi:10.1002/jgrd.50755, 2013.
Suto, H. *et al.,* J. Atmos. Ocean. Tech. **27,** 1175-1184, 2010.

Keywords: Cabon Dioxide, Methane, Tower measurement, West Siberian Lowland


IGR
NOY
Surgut
DEM
Chelyabinsk
KRS
VGN
Omsk
Tomsk
BRZ
AZV
Novosibirsk
Kazakhstan
SVV
Russia
YAK
Mongolia
Japan
60°
70°
80°
100°
120°
140°
160°
50°
40°

Estimating vertical fluxes of ozone within the atmospheric boundary layer

*Sergey Borisovich Belan[1], Pavel Antokhin[1], Ol'ga Antokhina[1], Mikhail Arshinov[1], Boris Belan[1], Denis Davydov[1], Alexsei P[2], Denis Savkin[1], Tatyana Sklyadneva[1], G Tolmachev[1]

1. V.E. Zuev Institute of Atmospheric Optics Russian Academy of Sciences, Siberian Branch, 2. Institute of Computational Mathematics and Mathematical Geophysics SB RAS

Investigation of the vertical distribution of ozone within the atmospheric boundary layer (ABL) was carried out by use of AN-2 light aircraft as a research platform. Vertical fluxes of ozone and their direction from the ground to the free-tropospheric level were calculated based on the in situ measurement data. Research flights have been performed over the greenhouse gas monitoring station located in a background area (56.1–56.4 N, 84.2–84.8 E) in the vicinity of abandoned village of Berezorechka (West Siberia). The schedule of diurnal flights was as follows: the first one just after the sunrise; the second one at noon; the third one 2-3 hours after noon, when a well-developed turbulence is observed; and the last one just before the sunset. A total of 10 diurnal cycles of measurements were undertaken.

Analysis of the obtained data showed that the rate of ozone influx from upper layers of the atmosphere is 3-10 times less than the ozone production rate in the ABL. Average rate of ozone influx from the free troposphere was about 1 mg m^{-3} h^{-1}, but ozone production rate in the ABL was about 5 mg m^{-3} h^{-1}, so the major part of ozone is formed by photochemical reactions that occur within the ABL and only 20 % of its content is determined by the influx from the free troposphere. The vertical profiles of the ozone fluxes have shown that their maximum values are observed at heights from 200 to 600 m AGL. The height of the maximum depends on the season: in winter it is lower than 200-300 m, and in summer the maximum is observed at 500-600 m. The value of the ozone flux maximum also depends on the season and varies from 1 μg m^{-2} s^{-1} in winter to 4.2 μg m^{-2} s^{-1} in spring.

This work was supported by the Russian Foundation for Basic Research (grant No 17-05-00374).

Keywords: Atmosphere, Ozon, Distribution

THE RELATIONSHIP BETWEEN OZONE FORMATION AND AIR TEMPERATURE IN THE ATMOSPHERIC SURFACE LAYER

*Sergey Borisovich Belan[1], Mikhail Arshinov[1], Boris Belan[1], Denis Savkin[1], Gennadii Tolmachev[1]

1. V.E. Zuev Institute of Atmospheric Optics Russian Academy of Sciences, Siberian Branch

Studying the formation and dynamics of ozone in the atmosphere is important due to several reasons. First, the contribution of tropospheric ozone to the global greenhouse effect is only slightly less than that of water vapor, carbon dioxide, and methane. Second, tropospheric ozone acts as a strong poison that has negative effects on human health, animals, and vegetation. Third, being a potent oxidizer, ozone destroys almost all materials, including platinum group metals and compounds. Fourthly, ozone is formed in situ from precursors as a result of photochemical processes, but not emitted into the atmosphere by any industrial enterprises directly.

In this work, we present some results of the study aimed at the revealing relationship between ozone formation rate and surface air temperature in the background atmosphere. It has been found that this relationship is nonlinear. Analysis of the possible reasons showed that the nonlinear character of this relationship may be due to a nonlinear increase in the reaction constants versus air temperature and a quadratic increase in the concentration of hydrocarbons with increasing temperature.

This work was supported by the Russian Foundation for Basic Research (grant No 17-05-00374).

Keywords: Atmosphere, Ozon, Temperature

Characteristics of atmospheric wave-induced laminae observed by ozonesonde at the southern tip of South America

*Hirofumi Ohyama[1], Akira Mizuno[1], Félix Zamorano[2], Takafumi Sugita[3], Hideharu Akiyoshi[3], Elian Wolfram[4], Jacobo Salvador[4], Gerardo Carbajal Benitez[5]

1. Nagoya University, 2. University of Magallanes, 3. National Institute for Environmental Studies, 4. Laser Application and Research Center, 5. National Meteorological Service

We have performed ozonesonde measurements at Punta Arenas (53.14°S, 70.88°W) in Chile and Río Gallegos (51.61°S, 69.29°W) in Argentina since 2014 to investigate vertical structures in the edge region of polar vortex as well as to validate ozone profiles measured by a differential absorption lidar and a millimeter-wave radiometer located at Río Gallegos. In such a southern part of South America (Patagonia area), the National Meteorological Service of Argentina also has made regular ozonesonde measurements at Ushuaia (54.85°S, 68.31°W) in Argentina since 2008. In these ozone concentration profiles, small-scale fluctuations of the ozone volume mixing ratio with a layer of a few kilometers are frequently found. The lamina structure is formed by vertical displacement of isopleths due to gravity waves and by isentropic advection of a filament of vortex air due to Rossby wave breakings. In the Patagonia area, notable gravity waves are generated on the leeward of the Andes. The polar vortex could contribute to both the generation of the gravity waves by a spontaneous adjustment mechanism and the formation of large meridional ozone gradient associated with lamina due to the horizontal advection. To distinguish between the effects of the vertical displacement and the horizontal advection, we investigated correlation between the ozone and potential temperature fluctuations [Pierce and Grant, GRL, 1998; Thompson et al., JGR, 2011], which were obtained by applying a high-pass filter of 3 km to the ozone and temperature profiles. Monthly fractions of the ozone fluctuation resulting from the gravity waves and Rossby waves were derived for the altitude ranges of tropopause height to 15 km, 15–20 km, and 20–25 km. Additionally, we investigated the effects of the ozone fluctuation on total ozone column for the outer side, the edge region, and the inner side of the polar vortex.

Keywords: Ozone, Stratosphere, Gravity wave, Rossby wave

Comparison of ozone profiles from DIAL, MLS, and chemical transport model simulations over Río Gallegos, Argentina in the 2009 spring

*Takafumi Sugita[1], Hideharu Akiyoshi[1], Hirofumi Ohyama[2], Elian Wolfram[3], Jacobo Salvador[3], Akira Mizuno[2]

1. National Institute for Environmental Studies, 2. Nagoya Univ., 3. Laser Application Research Center, UNIDEF

This paper evaluates the agreement of ozone profiles from the ground-based DIfferential Absorption Lidar (DIAL), the satellite-borne Aura Microwave Limb Sounder (MLS), and the 3-D chemical transport model simulations (CTM) over the South Patagonian Atmospheric Observatory (OAPA, 51.6°S, 69.3°W) in Río Gallegos, Argentina for the period from September to November 2009. We focus on this period, because a persistent ozone decrease for three weeks was found over the area around the southern tip in South America. Such the long-lasting decrease over the area was unusual (e.g., de Laat et al., GRL, 2010; Wolfram et al., Ann. Geophys., 2012). To compare the ozone profiles from DIAL with MLS retrievals, the averaging kernel matrix of MLS and the a priori profiles are used for converting the high-resolution DIAL profiles to the retrieval pressure levels of MLS. The comparison was done for pressure levels between 86 hPa and 5 hPa with the coincidence criteria of <500 km spatially and <24 hrs temporally. CTM used here incorporates a chemical module into MIROC3.2-GCM using horizontal winds and temperature nudged toward ERA-Interim data (e.g., Akiyoshi et al., JGR, 2016). The result shows a good agreement between DIAL and MLS with mean differences of ±0.1 ppmv (n=180), except for the 86 hPa level. CTM also agrees to DIAL with the mean differences of ±0.3 ppmv (n=23) between 56 hPa and 10 hPa. The root-mean-square differences increase with increasing altitudes from ˜0.5 ppmv at the 32-56 hPa levels to 1.3 ppmv at the 5 hPa level for both the two comparisons. Both of the two comparisons give mean differences of 0.5 to 0.7 ppmv at the 83 hPa level. It seems that DIAL tends to underestimate the ozone values only for this lower altitude region or some small scale differences in the ozone field cause the biases.

This research was supported by Science and Technology Research Partnership for Sustainable Development (SATREPS), Japan Science and Technology Agency (JST)/Japan International Cooperation Agency (JICA).

Keywords: stratosphere, ozone, DIAL, MLS, MIROC, CTM

A long-term monitoring of trace gases in troposphere and stratosphere retrieved from high-resolution FTIR measurements at Rikubetsu in Hokkaido, Japan

*Tomoo Nagahama[1], Isamu Morino[2], Kazuki Sunada[1]

1. Institute for Space-Earth Environmental Research, Nagoya University, 2. National Institute for Environmental Studies

The Institute for Space-Earth Environmental Research (ISEE) of Nagoya University had carried out measurements of solar absorption spectra using a ground-based Fourier Transform InfraRed Spectroscopy (FTIR) instrument (Bruker IFS120M) at Rikubetsu observatory (43.46°N, 143.77°E, 380 m a.s.l.) in Hokkaido since 1995. In 2014, the National Institute for Environmental Studies (NIES) installed another high-resolution FTIR instrument (Bruker IFS 120/5HR), and started the cooperative measurements with ISEE. The spectrum is obtained in mid-infrared band with a resolution of 0.0035 cm^{-1}. The vertical distribution of trace gases in troposphere and stratosphere is retrieved from the measured spectrum by using the SFIT4 (version 0.944) software with uniform retrieval parameters recommended by the Infrared Working Group of the Network for the Detection of Atmospheric Composition Change (NDACC/IRWG). This is for the purpose of obtaining the homogeneous retrievals at the NDACC measurement sites. We use an initial profile of pressure and temperature taken from the NCEP Reanalysis dataset and those of the molecular species except for water vapor taken from the results of the WACCM V6 40-yrs run. The vertical profile of water vapor is retrieved from the spectrum before the retrievals of the other species. Using SFIT4, we have retrieved the total column amounts and vertical profiles of O_3, HCl, HF, HNO_3, $ClONO_2$, CH_4, C_2H_6, N_2O, CO, HCN, CCl_4, and find the various temporal variations and the long-term trends from 1995 to 2016. Although the observed partial column of stratospheric O_3 does not show any trend with significance, that in the troposphere seems to decrease in 2000s. In addition, after 2000, we find negative trends in the time series of HCl and $ClONO_2$ total columns, being consistent with the global results.
In the presentation, we report the features of temporal variations of the species in stratosphere and troposphere as well as the details of the retrieval.

Keywords: Atmospheric composition, Infrared spectroscopy, Trends

Detection and analysis of the short-term increases of column-averaged dry air mole fraction of CO (XCO) observed at Rikubetsu, Hokkaido in 2015 early winter

*Kazuki Sunada[1], Tomoo Nagahama[2], Isamu Morino[3]

1. Institute for Space-Earth Environmental Research, Nagoya University, 2. ISEE, Nagoya University, 3. National Institute for Environmental Studies

The National Institute for Environmental Studies (NIES) has observed solar absorption spectra in near-infrared region with a high-resolution FTIR (Bruker IFS120/5HR) set up at Rikubetsu in Hokkaido (43.46°N, 143.77°E, 380 m a.s.l) as a site of the Total Carbon Column Observing Network (TCCON) since 2014, and retrieved the column-averaged dry air mole fractions of various species such as CO_2, CH_4 and CO. Although seasonal and short-term variations of the their species were observed, we focus on the short-term events that CO column-averaged mixing ratio (XCO) increased and decreased. In 2015 early winter, the observed XCO started increasing on 13 November, and became about 4.5 times larger than the seasonal mean value on 30. After that, on 9 December, it returned to the mean value. The same features also appear in CO_2 (XCO_2) and CH_4 (XCH_4), suggesting that this was caused by an air mass inflow from combustion sources. In order to understand the relation between the XCO enhancement and emission sources, we made trajectory analysis during the period of this event by using FLEXPART (Stohl et al. 2005) and NCEP CFSv2-6hour analysis dataset. In each day, we made the back-trajectory calculations in 2 weeks at the height of 1, 5 and 7 km, respectively. The results show that the air mass mainly comes from the North-east China and far distant regions. To evaluate influence on XCO in each region, we picked up the hotspots in the regions estimated above from the MODIS hotspot dataset, and made the forward-trajectory calculations from them. The result is that influence of the emission from the North-east China region was about 10 times larger than those in other regions. Thus, the observed increase of XCO is like to be the effect of air mass inflow from combustion source of the North-east China.

In this presentation, we discuss the comparison with other XCO-increasing events during the observation period and the relation among the species as well as the details of trajectory analysis.

Keywords: near-infrared solar absorption spectra, tropospheric carbon monoxide, trajectory analysis

Recent increase and subsequent decrease of the total column of ethane observed with FTIR at Tsukuba

*Isao Murata[1], Hideaki Nakajima[2], Isamu Morino[2]

1. Graduate School of Environmental Studies, Tohoku University, 2. National Institute for Environmental Studies

The total columns of C_2H_6 have been observed with a high-resolution Fourier transform spectrometer at Tsukuba, Japan since 2001. SFIT4 spectral fitting program was used to derive the total column from 2 spectral windows in 3 micrometer region.

C_2H_6 is the second major hydrocarbon and contribute to global warming and air pollution indirectly. The main sources are anthropogenic ones such as natural gas, biofuel, and biomass burning.

Temporal variation of retrieved total column of C_2H_6 shows a little bit decrease (-0.4%/year) from 2001 to 2008, increase (2.2%/year) from 2009 to 2013, and again decrease (-0.6%/year) from 2014 to 2016. The last trend from 2014 may due to decrease in emission (natural gas and biofuel) related to the increase in the production of fossil fuel due to the fall of the price.

Keywords: FTIR, Greenhouse Gas, ethane

Causes leading to enhancements in sulfur dioxide concentration observed by MAX-DOAS in Kyusyu

*Takaya Okuzaki[1], Hitoshi Irie[2]

1. Graduate School of Advanced Integration Science, Chiba University, 2. Center for Environmental Remote Sensing, Chiba University

We performed continuous observations of sulfur dioxide (SO_2) using the Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) at Kasuga in Kyushu, Japan. Spectra measured at 310-320 nm were analyzed with the DOAS method to retrieve mean SO_2 concentrations for a 0-1 km layer with a horizontal scale of about 10 km. This spatial scale is expected to provide useful inputs for data assimilation. First, we focused on data acquired in July-August 2014. In the period, seven days were identified as the SO_2 level was high (>5 ppbv). Back trajectory analysis indicates that there were two categories; the one from a volcanic origin (the Aso volcano and the Sakurajima volcano) and the other from a continental origin (China and Korea). Based on these results, we performed quantitative analysis using data obtained from January 2014 to September 2016. The mean and the median of the daily maximum SO_2 concentrations in the period were 3.3 and 2.1 ppbv, respectively. We investigated the dependence of the observed SO_2 level on the size of the range to judge whether the observed air masses passed over volcanoes and found that the higher SO_2 concentrations were observed in air masses that passed closer to volcanoes. The mean of the daily maximum SO_2 values affected by the Aso volcano was about 6 ppbv, which is larger than that for the Sakurajima volcano (4 ppbv), suggesting that the influence of the Aso volcano was larger. To consider the continental effect, we analyzed relations between SO_2 and the length of residence time over China or Korea and between SO_2 and the time required for reaching Kasuga from China or Korea. However, no significant correlation was observed. In this case, the mean of the daily maximum SO_2 values was about 2.4 ppbv. The results were unchanged even if only influences of urban areas in China or Korea were considered. These results suggest that the impact of long-range transport of air pollution from China or Korea on enhancements in SO_2 concentration was smaller than that of volcanoes in Kyusyu. In this presentation, we will also discuss results of analysis including the explosive eruptions of the Aso volcano occurred on 8 October, 2016.

Keywords: SO2, MAX-DOAS, valcano

Comparisons of column-averaged dry-air mole fractions of greenhouse gases among GOSAT/TANSO-FTS SWIR, TIR, and NICAM-TM data

*Hiromichi Hatta[1], Naoko Saitoh[2], Yosuke Niwa[3], Ryoichi Imasu[4], Kei Shiomi[5], Yukio Yoshida[6]

1. Chiba university Graduate School of Advanced Integration Science, 2. Center for Environmental Remote Sensing, Chiba University, 3. Meteorologocal Research Institute, 4. Atmosphere and Ocean research Institute, 5. Japan Aerospace Exploration Agency, 6. National Institute for Environmental Studies

Greenhouse gases Observing SATellite (GOSAT) was launched on 23 January, 2009. Thermal and Near-infrared Sensor for Carbon Observation Fourier Transform Spectrometer (TANSO-FTS) on board the GOSAT has SWIR and TIR bands and can observe column-averaged dry-air mole fractions of CO_2 and CH_4 (XCO_2 and XCH_4) in the SWIR bands [Yoshida et al., 2011] and CO_2 and CH_4 vertical profiles in the TIR band [Saitoh et al., 2009]. In this study, we calculated XCO_2 and XCH_4 values from the TIR CO_2 and CH_4 profiles, and then compared them with XCO_2 and XCH_4 data of the SWIR bands and Nonhydrostatic ICosahedral Atmospheric Model-based Transport Model (NICAM-TM) [Niwa et al., 2011]. Before calculating the TIR XCO_2 values, we applied bias-correction values evaluated based on the comparisons of aircraft CO_2 data.

We compared latitudinal distributions of XCO_2 among TANSO-FTS TIR, SWIR, NICAM-TM, and a priori (NIES-TM05) data [Saeki et al., 2013]. TIR XCO_2 data over the land in the Northern Hemisphere except the Sahara desert were slightly smaller than SWIR XCO_2 data and, in contrast, slightly larger over the land in the Southern Hemisphere. Over the Sahara desert, TIR XCO_2 data in the daytime were considerably smaller than SWIR and NICAM-TM XCO_2 data, which suggests that surface parameters used in the TIR retrieval had some problems. Over Hawaii where there is no strong CO_2 source, TIR XCO_2 data agreed with SWIR XCO_2 data to within 1% on average.

Keywords: GOSAT, XCO2, XCH4

Simultaneous estimate of surface temperature and surface emissivity from GOSAT/TANSO-FTS TIR spectra

*TOMOYUKI ITATSU[1], Naoko Saitoh[3], Ryoichi Imasu[2], Kei Shiomi[4], Akihiko Kuze[4]

1. Chiba University Graduate School of Advanced Integration Science, 2. Atmosphere and Ocean Research Institute, The University of Tokyo , 3. Center for Environmental Remote Sensing, 4. Japan Aerospace Exploration Agency

Thermal and Near-infrared Sensor for Carbon Observation Fourier Transform Spectrometer (TANSO-FTS) on board Greenhouse gases Observing SATellite (GOSAT) can observe column amounts and vertical profiles of CO_2 and CH_4 from short-wave infrared (SWIR) and thermal infrared (TIR) bands, respectively [Yoshida et al., 2011; Saitoh et al., 2009]. Uncertainties in surface parameters could affect retrieved CO_2 concentrations in the TIR retrieval [Saitoh et al., 2009]. In this study, we tried to estimate surface temperature and surface emissivity simultaneously from TIR spectra of GOSAT/TANSO-FTS, following the method proposed by Matsui and Moriyama [2008]. Their method utilized the relatively moderate wavelength dependence of surface emissivity compared to atmospheric gas absorption lines, and was applied to thermal infrared spectra with a high wavelength resolution obtained with Atmospheric Infrared Sounder (AIRS). We modified their method for the application to TANSO-FTS TIR spectra, and applied it to the spectra obtained over the oceans where the wavelength-dependence of surface emissivities is relatively known to examine the utility of the method.

We here defined wavelength channels with a transmittance above 0.95 without considering any continuum as a “smooth part” in the spectral range between 800 and 1000 cm^{-1}, and then estimated surface parameters on the basis of the “smooth part” channels. First, we applied the method to a TIR spectrum obtained over the ocean in mid-latitudes. We calculated surface emissivities by changing a surface temperature by 1 K in the range from 286 K to 310 K, and adopted the surface temperature when the calculated surface emissivities became smoothest with respect to wavelength. The estimated surface temperature was 294 K, which was close to the nearby MODIS sea surface temperature (SST) value (293.4 K). The simultaneously-estimated surface emissivity at 900 cm^{-1} was 0.97, which was also close to the sea surface emissivity of Aster Spectral Library, 0.99.

Furthermore, we applied our developed method to several TANSO-FTS TIR spectra obtained over the ocean (10–20°N, 160–170°E) on 1–3, January, 2013. We compared surface temperatures estimated by our method and nearby MODIS SST data. When their differences were small, the simultaneously-estimated surface emissivies were quantitatively close to the sea surface emissivities of Aster Spectral Library. However, when their differences were relatively large, the structures of the simultaneously-estimated surface emissivies were far from those of the sea surface emissivities. In the presentation, we will discuss the accuracy of our estimates of surface parameters, results of other seasons and regions, and the effect of changing several parameters in our method on estimated surface parameters.

Keywords: GOSAT, thermal infrared band, surface temperature, surface emissivity

Size-dependent wildfire occurrences in the boreal Eurasia and driving factors

*Chunmao Zhu[1], Yugo Kanaya[1], Hideki Kobayashi[1], Masahiko Saito[1]

1. Japan Agency for Marine-Earth Science and Technology

Large areas are burned every year in the boreal Eurasia. Pollutants emitted from fires in the Boreal Eurasia could be transported to the Arctic and the consequential deposition could accelerate the Arctic warming. However, there are so far limited knowledges on the wildfire pattern in the boreal Eurasia and the causes. Our purposes are to clarify the temporal and spatial pattern of wildfire and to investigate the factors affecting wildfire occurrence in the boreal Eurasia during 2005-2014.
Focusing on a domain in 50–75°N, 30–180°E, we divided the boreal Eurasia into 15 sub-regions and investigated the wildfire occurrences based on the Moderate Resolution Imaging Spectroradiometer MCD64A1 burned area product. Lands were burned mainly (96%) in >100ha size, although with large small fires (<100ha) counts (58%). Interannually, large land losses (>30 million hectares) occurred in 2008, 2010, 2012 and 2014 over the whole domain. Seasonally, wildfires occurred since April, peaked in July to August, and continued until October. Spatially, six high fire-prone regions were identified locating at the southwestern Russia, Kazakhstan, southwest Siberia, central Siberia, eastern Siberia and the Far East. Furthermore, we investigated the relations of burned area with climatic indices such as temperature, precipitation and soil drought index (Palmer Drought Severity Index, PDSI) in each sub-region. It was found that the burned area in southwest Russia, Kazakhstan, west Siberia had positive relation with temperature ($p < 0.05$). On the other hand, burned area had negative relations with precipitation and PDSI ($p < 0.05$) in most of the fire-prone regions. These results indicate that wildfire occurrence were fostered by the dry soil and air conditions. Furthermore, burned area is likely related to snow melting date, to which early snow melting date caused larger burned area. Our study implies that under a warmer world, wildfires in the boreal Eurasia tend to be severer and mega-fires more frequent.

Time-resolved measurements of organic compounds in particles during heterogeneous reaction of volatile organic compounds with primary and secondary aerosols

*Satoshi Inomata[1], Jun Hirokawa[2], Hiroshi Tanimoto[1], Fujitani Yuji[1]

1. National Institute for Environmental Studies, 2. Hokkaido Univ.

Volatile organic compounds (VOCs) undergo oxidation in the gas phase to yield semi-volatile organic compounds (SVOCs) and secondary organic aerosols (SOAs), which directly and indirectly affect the global climate as well as human health. Quantification of the impacts of SOAs requires understanding their chemical composition and processes of formation as well as mass yields. In particular, because a systematic underestimation of simulated SOA production increases with air mass ageing, speciation of the SVOCs produced by gaseous oxidation is essential. In addition, information about the partitioning of each SVOC between the gaseous and condensed phases as well as the reactions of the condensed SVOCs within the particulate phase is important for the description of SOA formation. Recently, we succeeded in a time-resolved measurement of organic compounds in particles by using proton transfer reaction mass spectrometry. In this study, changes of organic compounds in diesel exhaust particles and SOAs by an addition of some kinds of VOCs through heterogeneous reaction were investigated.

Keywords: Proton transfer reaction-mass spectrometry, Oligmer, Heterogeneous reaction, Secondary organic aerosol, Diesel exhaust particle

Hygroscopic characterization of individual cloud condensation nuclei with atomic force microscope

*Furuya Masaki[1], Atsushi Matsuki[1], Ayumi Iwata[1]

1. Kanazawa University

Majority of atmospheric aerosols takes up water and can eventually act as cloud condensation nuclei (CCN). How these particles interact with water therefore, regulates the climate and hydrological cycle. The hygroscopicity parameter κ is a single parameter that represents hygroscopicity of aerosol particles (Petters and Kreidenweis., 2007). In order to physically derive κ, it is necessary to obtain precise measure of the relative humidity, dry CCN size, hygroscopic growth factor (gf) and surface tension of the solution/air interface. Previously, κ of a given aerosol population has been derived using a hygroscopic tandem differential mobility analyzer (HTDMA).Although HTDMA has been widely accepted as a powerful tool to measure aerosol hygroscopic behavior, the measurement reflects an overall average of numerous particles and does not necessarily preserve extremes of the distribution. Therefore, it is also important to carefully examine particle hygroscopic growth at an individual particle level (Morris et al., 2016). Another limitation is that, previous works mainly assumed the surface tension of pure water or bulk solution, since there was no conventional method for directly measuring the surface tension of the droplets. Here, we present our attempts to combine methods to directly measure the surface tension and gf of a single droplet by atomic force microscopy (AFM), which in principle allow us to directly derive κ of individual particles. In this study, we measured gf and surface tension of sodium chloride (NaCl). The gf (80% RH) derived in this experiment (1.73±0.35) coincides with the value of the previous work (Morris et al., 2016) within the standard deviation. In terms of the surface tension, the retention force required for deriving the surface tension was found to be 19±3 nN, which is slightly smaller than the reported value of 30 nN (Morris et al., 2015), the difference can be attributed to the different shape of the cantilever used in both studies. Hygroscopicity parameter κ was derived from gf, dry particle diameter and surface tension obtained in this experiment and found to be 1.10. The fact that current value coincided with the values obtained in the previous study (Koehler et al., 2006; Clegg and Wexler., 1998), supports the validity and potential of this new method. In the future, other substances having various surface activities and mixing states (mineral salt and organic species) will be tested using this method, and further applied to actual atmospheric aerosol particles.

Impact of aerosol composition on the oxidation of bisulfite during the reactive uptake of nitrogen dioxide on aqueous aerosols

Lijie Li[1], *Agustin J Colussi[1], Michael R Hoffmann[1]

1. California Institute of Technology

Multiphase chemistry plays a vital role in global atmosphere. The importance of multiphase chemistry in the lower troposphere has been recently underscored by the severe haze-fog pollution episodes experienced over China megacities. A key finding is that despite reduced photochemistry under the haze, the oxidation of sulfur dioxide (SO_2) into sulfate aerosol remains unabated in the presence of low levels of ozone. The main oxidant under such conditions is the nitrogen dioxide (NO_2) emitted by motor vehicles and other combustion sources. The dark conversion of bisulfite (HSO_3^-) into bisulfate (HSO_4^-) by NO_2 has been ascribed to a heterogeneous process taking place on the neutral aerosol prevalent in Northern China. Previous studies in our laboratory, however, have shown that anions catalyze the disproportionation of NO_2 into NO_2^- + NO_3^-.This suggests that coexisting anions in aerosol and aerosol acidity could impact the heterogeneous oxidation of bisulfite during the gaseous NO_2 uptake on aqueous aerosols.

This work explores the contribution of aerosol composition to the oxidation of HSO_3^- during the reactive uptake of NO_2 on the surface of aqueous solutions. The aqueous aerosol surface is generated by microjets containing chloride ion (Cl^-) or formic acid (HCOOH) as proxies of ambient inorganic and organic components. The surface is instantaneously exposed to NO_2(g) followed by in situ anion analysis via online electrospray ionization mass spectrometry. The heterogeneous reaction occurs in ~1nm interfacial layers of the aqueous aerosol under NO_2 exposures similar to atmospheric conditions. The competition between the disproportionation process controlled by aerosol anion compositions, and the oxidation of bisulfite will be followed by the HSO_4^-/NO_3^- ratio. We will review other significant pathways for the oxidation of bisulfite under atmospherically relevant condition. This work addresses how the reactive uptake of gaseous pollutants affects the aerosol composition, thereby contributing to understand the mechanisms underlying urban pollution in haze-fog episodes.

Keywords: Haze-fog pollution, nitrogen dioxide, sulfate, sulfur dioxide, China megacities

Characteristics of Cloud Condensation Nuclei over the Urban Areas Measured at Tokyo Skytree

*Asato Maeda[1], Konosuke Sato[1], Kazuhiko Miura[1], Yoko Iwamoto[3], Ryohei Misumi[2]

1. Tokyo University of Science, 2. National Research Institute for Earth Science and Disaster Resilience, 3. Hirosuma University

Atmospheric aerosols influence the Earth' s radiation budget directly through absorption and scattering of solar radiation, and indirectly by modifying the properties of clouds. However, climate models still face large uncertainties as a result of insufficient understanding of aerosol-cloud interactions[1]. Thus, further studies on aerosol-cloud interaction are needed to improve climate models and to make better predictions of climate change. To investigate cloud condensation nuclei (CCN) characteristics over the urban areas, where few fixed-point observations are conducted in the world, CCN properties of atmospheric aerosols were observed at the Tokyo Skytree (TST) in Tokyo.

Measurements were carried out at TST (35.71°N, 139.81°E, 458m,a.g.l), from 3 to 30 June 2016. In this study, aerosol number size distribution, condensation nuclei (CN) number concentrations (N_{CN}), CCN number concentrations (N_{CCN}) with four supersaturations (SS%) were measured. Fog droplet size distributions and fog droplet number concentrations (N_{Fog}) were also measured. Using these data, we obtained the hygroscopic parameter (κ) and the effective radius (R_{eff}) of fog droplets.The results obtained at TST were compared with observation data of the summit of Mt. Fuji[2] where similar observations were made.

The average value of N_{CCN} at TST was larger than that of the summit of Mt. Fuji.[2]. The average value of κ at TST was smaller than that of the summit of Mt. Fuji . The CCN properties of aerosols did not vary significantly with air mass origins. As a result of the CCN characteristics of the period covered with clouds without drizzle, there was no positive correlation between the N_{Fog} and N_{CCN}. Also, there was no negative correlation between R_{eff} and N_{CCN} like the microphysical relationship known as the Twomey effect[3]. This is considered to be due to the small variation of N_{CCN} at TST. The relationship between R_{eff} and N_{CCN} under SS0.12% could be regarded as part of the negative correlation between R_{eff} and N_{CCN} obtained at the summit of Mt. Fuji .

References
[1] IPCC 2013, http://ipcc.ch/
[2] Watanabe A. (2015), *Tokyo University of Science Master's thesis*
[3] Towmey, S. (1959), *Geofis .Pura Appl.*, 43, 243-249

Keywords: cloud condensation nuclei number concentration, condensation nuclei number concentration, effective radius, fog droplet number concentrations

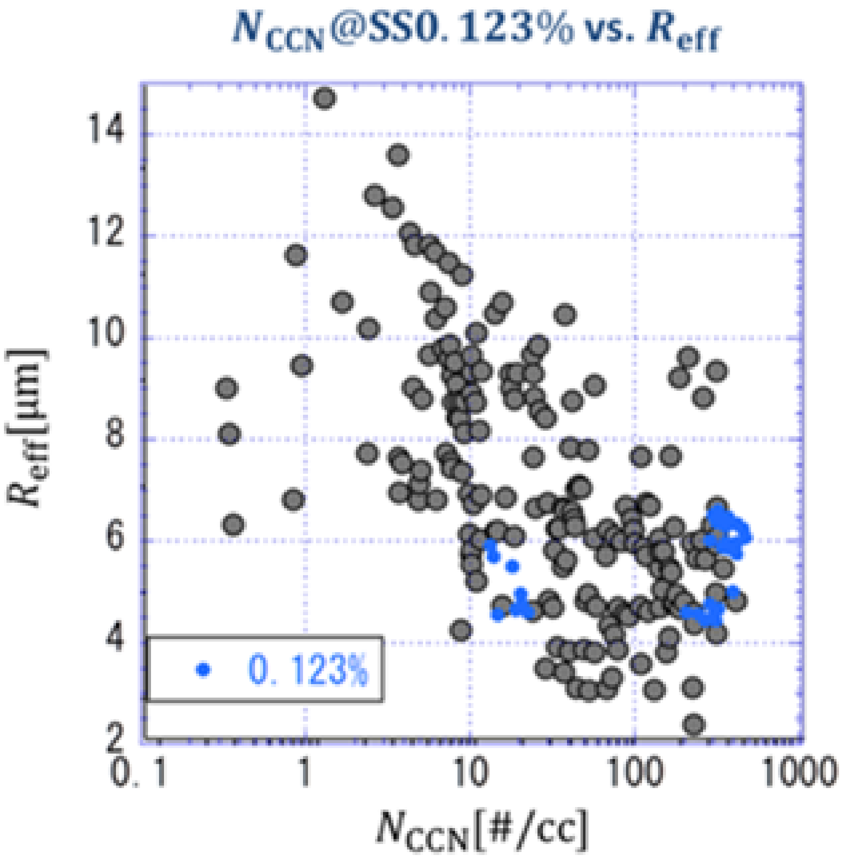


図　R_{eff}とN_{CCN}@SS0.123%（青）、N_{CCN}@SS0.15%（渡辺, 2015）（黒）の関係

Wet removal mechanisms of black carbon observed in Tokyo and Okinawa

*Tatsuhiro Mori[1], Moteki Nobuhiro[2], Sho Ohata[2], Makoto Koike[2], Yutaka Kondo[3]

1. Tokyo University of Science, 2. Graduate School of Science, The University of Tokyo, 3. National Institute of Polar Research

Quantitative understanding of wet removal process of black carbon (BC) is important because it controls temporal and spatial distribution of BC in the atmosphere. There are two categories of wet removal mechanisms: nucleation scavenging and impaction scavenging. Theoretically, the removal efficiencies of both mechanisms depend on microphysical properties (size(D_{BC}), coating thickness, and hygroscopicity) of BC. However, the relative contribution of these mechanisms to the removal of BC and the key BC microphysical property controlling the wet removal efficiency of BC have never been tested by direct observation. In this study, we conducted ground-based observations of BC in air and in rainwater in Tokyo and Okinawa, using a new observational method (Mori et al., 2016). We compared the observed size-dependent wet removal efficiency of BC particles ($RE(D_{BC})$, defined as the ratio of the measured size distributions of BC in rainwater to that of BC in ambient air) with the size-dependent number fractions of BC particles scavenged by nucleation ($F_{ccn}(D_{BC})$) and impaction ($F_{imp}(D_{BC})$) mechanisms. The $F_{ccn}(D_{BC})$ and $F_{imp}(D_{BC})$ were estimated from the observed microphysical properties of BC in the air before precipitation starts and the observed droplet size and intensity of precipitation.
The size dependence of $RE(D_{BC})$ showed remarkable differences for the observed 42 precipitation events (31 events in Tokyo and 11 events in Okinawa). The size dependence of $RE(D_{BC})$ for BC-containing particles with $D_{BC} > 100$ nm was successfully explained by the size dependence of $F_{ccn}(D_{BC})$, whereas the contribution of impaction mechanism can be dominant for particles with $D_{BC} < 100$ nm. For $D_{BC} > 100$ nm, when BC particles have relatively thick coating (shell/core ratio > 1.2), the $RE(D_{BC})$ depended little on D_{BC} and the major fraction of BC were removed via nucleation scavenging. On the other hand, when BC particles are nearly bare or have less coating, the $RE(D_{BC})$ highly depended on D_{BC}, and RE (i.e. F_{ccn}) is more sensitive to the hygroscopiticy of coating materials and the maximum supersaturation of water vapor that BC particles would experience during moist convection process. Our results show that the coating thickness of BC is the key parameter controlling wet removal of BC, and indicate that for accurate simulation of vertical transport of BC from the boundary layer to the free troposphere, detailed modeling of microphysical properties of BC and atmospheric supersaturation is required especially for BC particles with thin coatings.

Keywords: Black carbon, Wet removal mechanism, Field observation

Ship-based observation of black carbon at North Pacific Ocean: Analysis of transportation event at January on 2016

*Fumikazu Taketani[1], Takuma Miyakawa[1], Yuishi Komazaki[1], Hisahiro Takashima[1,2], Yugo Kanaya[1]

1. Japan Agency for Marine-Earth Science and Technology, 2. Fukuoka Univ.

Ship-based measurement for black carbon (BC) and carbon monoxide (CO) was conducted on board the R/V Mirai from 18 at North Pacific Ocean (12.9 °N, 130.5 °E) to 24 at Yokohama Port (35.4°N, 139.7°W) January 2016. Measurements of atmospheric BC particles and CO were conducted using a single particle soot photometer (SP2) instrument and CO analyzer, respectively. Ambient particles and gases were sampled on the flying bridge, ~18m above sea level. From 18 to 19 January 2016 (around 20°N and 135° E), high concentrations of BC and CO were observed. It was suggested the contribution from the Asian continent air mass by backward trajectory analysis. In spite of almost same source, it was indicated that different BC size distribution and mixing state at air mass in 18 and 19 January plumes, suggesting the air masses would undergo different removal processes. In the presentation, we are going to discuss the comparison with CO and other event cases in the cruise.

Keywords: Black carbon, single particle, Ship-based measurement