Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

AAS21-01 Room:201B Time:May 27 15:15-15:30

Volume Integral Equation Method Optimized for Black Carbon-Containing Aerosol Particles

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We propose a robust scheme of volume integral equation method (VIEM) for light scattering and absorption by black carbon-containing aerosol particles: the fractal-like aggregates of absorbing black carbon (BC) spherules that may be mixed with non-absorbing (or weakly absorbing) compounds. Conventionally, a particle volume has been uniformly approximated as a collection of small volume elements (dipoles) on a cubic lattice (CL). In the proposed scheme, each BC spherule is considered as a spherical dipole with original size, while remaining particle volume occupied by non-absorbing compounds is approximated by a collection of dipoles on a CL. We call this as Spherule-Retained-Cubic-Lattice (SRCL) scheme. For several model BC-containing particles, positive absorption bias of ˜30% persistent in the CL scheme is success-fully eliminated in SRCL scheme. The interaction matrix (i.e., discretized volume integral operator) associated with the SRCL scheme has less simple structure compared with that for CL scheme. We propose some key strategies for mitigating memory and computational costs in solving the matrix equation in the SRCL scheme.

Keywords: Atmospheric Radiation, Light Scattering Theory, Aerosol, Black Carbon

AAS21-02 Room:201B Time:May 27 15:30-15:45

Improved Technique to Measure the Size Distribution of Black Carbon Particles Suspended in Rainwater and Snow Samples

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Black carbon (BC) aerosols strongly absorb visible solar radiation. Quantitative understanding of wet removal process, which strongly affects the spatial distribution of BC, is important to improve our understandings on climate change. For this purpose, a measurement technique for BC in rainwater and in snow samples has been developed, as a combination of a nebulizer and a single particle soot photometer (SP2) (Ohata et al. 2011, 2013; Mori et al. 2014). We show two important improvements in this technique: (1) We have introduced a pneumatic nebulizer and experimentally confirmed its high extraction efficiency (~50%) independent of particle-size up to 2 μm. (2) We have extended the upper limit of detectable BC size range by the SP2 from 0.9 μm to 4 μm by modifying a photo-detector for incandescence. Using this technique, we have measured the size-resolved mass concentration in air and in rainwater, simultaneously, during last summer in Tokyo. We observed significant amounts of BC particles with diameters larger than 1μm in rain samples. The correlation between BC mass concentration in air and in rainwater was high ($r^2 = 0.59$), suggesting that the major sources of BC in rainwater were BC in the atmospheric planetary boundary layer. The size distribution of BC in rainwater was shifted to larger size as compared with that in air, indicating that larger BC particles in the air were removed more efficiently by precipitation.

Keywords: Black Carbon, Measurement, Wet deposition

AAS21-03 Room:201B Time:May 27 15:45-16:00

Measurements of the hygroscopicity and wet removal of black-carbon-containing particles in Tokyo

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Megacities are very large, concentrated anthropogenic sources of black carbon (BC) aerosols. Freshly emitted BC particles inside megacities affect local air quality and regional and global climate. The microphysical properties (e.g., number size distribution, coating thickness, and hygroscopicity) of atmospheric BC-containing particles are important because their efficiency of wet removal from the atmosphere can be highly dependent on these properties. In this study, we conducted intensive observations of the hygroscopicity and wet removal of BC-containing particles in the urban atmosphere of Tokyo during summer 2014. The number size distribution and coating thickness of BC-containing particles were measured with a standard Single Particle Soot Photometer (SP2). The hygroscopicity of BC-free and BC-containing particles was measured with a modified (humidified) SP2. In addition, the number size distribution of BC cores in rainwater was also measured with a nebulizer?SP2 system during rain events.

Throughout the observation period, for BC-containing particles with a dry diameter of about 200 nm, the particles with smaller BC fractions tended to represent greater water uptake, and the number fraction of the less hygroscopic (Growth factor <1.2 at 85% relative humidity) BC-containing particles was more than 70% of the total BC-containing particles. The measured average number size distribution of BC cores in rainwater was larger than that in the surface air before precipitation began, and the dependence of the wet removal of BC-containing particles on their BC-core sizes was successfully explained by the measured microphysical properties of BC-containing particles in the air and an assumed maximum supersaturation that the particles would have experienced during rain events. These measurement data indicated that BC-containing particles in Tokyo, especially particles with small BC cores (or with high critical supersaturation), were efficiently transported upward without being removed by precipitation.

Keywords: black carbon, hygroscopicity, wet removal

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AAS21-04 Room:201B Time:May 27 16:15-16:30

Evaluation of Refueling emissions and its OFP

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Refueling emissions have been considered one of the main VOC sources in Japan. However there is only a few study which discuss the emission mechanism and its detailed effect on total VOC emissions in Japan. We performed the experiments using sealed housing evaporative determination (SHED) to evaluate the refueling emissions. For the measurement devices, we adopted not only total hydrocarbon, but also the composition analysis using proton transfer reaction plus switchable reagent ion mass spectrometry (PTR+SRI-MS) to estimate the ozone formation potential of refueling emissions. We also tested some provention devices of refueling emissions.

Keywords: Refueling emissions, VOC, Ozone formation potential, PTR-MS

AAS21-05 Room:201B Time:May 27 16:30-16:45

Evaluation of black carbon radiative effect using a mixing state resolved three-dimensional model

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This study evaluates the uncertainties in black carbon (BC) and its optical and radiative parameters over East Asia (spring 2009) using a BC mixing state resolved three-dimensional model that can explicitly calculate BC processes in the atmosphere such as emissions, aging processes by condensation and coagulation, the enhancement of absorption and CCN activity by the aging, activation to cloud, and dry and wet deposition. The focus of this study is the uncertainties in the size distribution and the mixing state in emissions. One base case simulation and 14 sensitivity simulations are conducted to understand the variability of BC mass concentrations in column, absorption aerosol optical depth, and the radiative forcing by BC absorption due to the uncertainties in emissions. The variability of BC optical and radiative parameters is estimated to be 39-59%. This variability corresponds to BC absorption forcing from -12.6 to 6.5 W m^{-2} at the surface and from 4.3 to 6.6 W m^{-2} at the top of atmosphere over East Asia, showing the importance of the treatment of the size and the mixing state in emissions. In contrast, the variability of BC mass concentrations is 17% and smaller than that of BC optical and radiative parameters. Therefore, BC optical and radiative parameters (BC mass concentrations) are more (less) sensitive to the size and the mixing state in emissions. This result shows that the following two points are important in the estimation of BC radiative forcing. The first is to reduce the uncertainties in the size and the mixing state in emissions. The second is to improve the representation of BC mixing state and the enhancement of BC absorption in aerosol models because most models do not treat them sufficiently. My analysis also shows that coagulation and lens effect (absorption enhancement due to the change in BC mixing state) play important roles to make the different variability between BC mass concentrations and BC optical and radiative parameters.

Keywords: aerosol, black carbon, mixing state, mixing state resolved three-dimensional model, absorption enhancement, radiative forcing

AAS21-06 Room:201B Time:May 28 09:00-09:15

Atmospheric Processing of Combustion Aerosols as a Source of Soluble Iron to the Open Ocean

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Atmospheric processing of combustion aerosols may promote transformation of insoluble iron into soluble forms. Here, an explicit scheme for iron dissolution of combustion aerosols due to photochemical reactions with inorganic and organic acids in solution is implemented in an atmospheric chemistry transport model to estimate the atmospheric sources of bioavailable iron. The model results suggest that deposition of soluble iron from combustion sources contributes more than 40% of the total soluble iron deposition over significant portions of the open ocean in the Southern Hemisphere. A sensitivity simulation using half the iron dissolution rate for combustion aerosols results in relatively small decreases in soluble iron deposition in the ocean, compared with the large uncertainties associated with iron solubility at emission. More accurate quantification of the soluble iron burdens near the source regions and the open ocean is needed to improve the process-based understanding of the chemical modification of iron-containing minerals.

Keywords: Global environmental change, Atmospheric deposition, Soluble iron, Biomass burning

AAS21-07 Room:201B Time:May 28 09:15-09:30

Adjoint of the coupled Eulerian-Lagrangian transport model

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We present the development of an inverse modeling system employing an adjoint of the global coupled transport model consisting of the National Institute for Environmental Studies (NIES) Eulerian transport model (TM) and the Lagrangian plume diffusion model (LPDM) FLEXPART. NIES TM is a three-dimensional atmospheric transport model, which solves the continuity equation for a number of atmospheric tracers on a grid spanning the entire globe. The Lagrangian component of the forward and adjoint models uses precalculated responses of the observed concentration to the surface fluxes and 3-D concentrations field simulated with the FLEXPART model. Construction of the adjoint of the Lagrangian part is less complicated, as LPDMs calculate the sensitivity of measurements to the surrounding emissions field by tracking a large number of particles backwards in time. Developing of the adjoint to Eulerian part required significant manual code modification owing to the structure and complexity of the NIES model.

The overall advantages of our method are follows:

1. No code modification of Lagrangian model is required, making it applicable to combination of global NIES TM and any Lagrangian model;
2. Once run, the Lagrangian output can be applied to any chemically neutral gas;
3. High-resolution results can be obtained over limited regions close to the monitoring sites (using the LPDM part), and at coarse resolution for the rest of the globe (using the Eulerian part), minimizing aggregation errors and computation cost.

The results are verified using a series of test experiments. These tests demonstrate the high accuracy of the NIES-FLEXPART adjoint when compared with direct forward sensitivity calculations. Adjoint of coupled NIES-FLEXPART model therefore combines the flux conservation and stability of an Eulerian finite difference of adjoint formulation with the flexibility, accuracy and high-resolution of a Lagrangian backward trajectory formulation.

The accuracy of the adjoint model is extensively verified by comparing adjoint to finite difference sensitivities. We show acceptable tolerance of agreement obtained. The potential for inverse modeling using the adjoint of NIES- FLEXPART coupled model is assessed in a data assimilation framework using simulated observations, demonstrating the feasibility of exploiting CO_2 measurements for optimizing CO_2 emission inventories.

Keywords: carbon cycle, atmospheric transport, adjoint model, inverse modeling

AAS21-08 Room:201B Time:May 28 09:30-09:45

Estimating source-receptor relationships of tropospheric ozone: On the importance of model horizontal resolution

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Ozone (O_3) near the surface is harmful to human health and to vegetation including crops. It is recognized that intercontinental transport of air pollutants affects air quality over a region. Task Force on Hemispheric Transport of Air Pollutants (TF HTAP) coordinated a multi-model inter-comparison of 21 chemical transport models (CTMs) for assessing source-receptor relationships (i.e., the change in pollutants over a receptor region produced by change in emissions in a source region). Typical horizontal resolution of HTAP models was about 300 km. A coarse-resolution model tends to overpredict ozone chemical production (e.g., Wild and Prather, 2006). However, it is unclear how model horizontal resolution affects source-receptor relationships of tropospheric ozone. We estimated source-receptor relationships of tropospheric ozone using the CHASER global CTM (Sudo et al., 2002) with medium-resolution (T42; 2.8 deg. x 2.8 deg.) and high-resolution (T106; 1.1 deg. x 1.1 deg.). The CHASER model is also developed as an atmospheric chemistry component of the MIROC-ESM-CHEM earth system model, and simulates detailed chemistry in the troposphere and the stratosphere with aerosols simultaneously. We conducted a 2010 control simulation and a sensitivity simulation with 20% reduced emissions in East Asia to estimate source-receptor relationships. The model results show that 20% East Asian emission reductions decrease surface O_3 by 0.94 ppbv and by 0.75 ppbv over East Asia in spring respectively in the medium-resolution and high-resolution models. The East Asian emission perturbations also reduced surface O_3 by 0.27 ppbv and by 0.24 ppbv in spring over North America respectively in the medium-resolution and the high-resolution models. Our results suggest that the high-resolution model tends to predict smaller decreases in surface O_3 over East Asia and North America in response to the East Asian emission reductions.

Reference

Wild and Prather (2006), J. Geophys. Res., 111, D11305, doi:10.1029/2005JD006605.
Sudo et al. (2002), J. Geophys. Res., 107, 10.1029/2001JD001113.

Keywords: tropospheric ozone, chemical transport model, source-receptor relationship, intercontinental transport

AAS21-09 Room:201B Time:May 28 09:45-10:00

Impacts of black carbon aging on its spatial distribution and radiative effect in the global scale

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KOIKE, Makoto[3] ; NOBUHIRO, Moteki[3] ; KONDO, Yutaka[3]

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Most aerosol components scatter 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. Freshly emitted hydrophobic BC particles become internally mixed with other water-soluble compounds through aging processes and they are converted to hydrophilic BC. Internal mixing with sufficient water-soluble compounds enhances the BC absorption efficiency of solar radiation, and the hydrophilic BC particles are able to serve as cloud condensation nuclei (CCN), which can be removed from the atmosphere by precipitation. Consequently, aging processes of BC influence its atmospheric lifetime and play an important role for the spatial distributions of BC and its radiative effects. However, a simple approach using constant values of the conversion rate from hydrophobic BC to hydrophilic BC (such as 24 hours) has been widely used in most global models and there were large uncertainties in estimating the spatial distribution of BC and its radiative forcing in previous studies. Recent studies pointed out the necessity of an advanced parameterization of BC aging processes to improve the quantitative estimation of the climate impacts of BC.

Recently, Oshima and Koike [2013] developed a new parameterization of BC aging based on the physical and chemical processes. In this parameterization, the conversion rate from hydrophobic BC to hydrophilic BC is expressed as a production rate of condensed materials normalized by the hydrophobic BC mass concentration. In this study, we applied this parameterization to the global-scale aerosol model MASINGAR-mk2 included in the MRI's earth system model [Yukimoto et al., 2012], which enables the representation of spatial and temporal variations of the conversion rate of BC aging depending on atmospheric conditions (the original approach assumed the constant conversion rate of 1.2 days).

We performed the model calculation with the BC aging parameterization for 2008-2009. We find that the conversion time scales from hydrophobic BC to hydrophilic BC exhibit distinct spatial variations and they were approximately one day and one week over the source regions in East Asia and the remote regions in the Arctic, respectively. We also performed the model calculation with the constant conversion rate (1.2 days) for the comparison. Over the source regions in East Asia, both calculations give small differences in BC mass concentrations and they reproduced the seasonal variations of BC mass concentrations observed by the surface measurements reasonably well. On the other hand, the both calculations give large differences in BC mass concentrations over the Arctic regions and the calculation with the parameterization improved the prediction of the BC mass concentration, which was underestimated in the constant-rate calculation.

The direct radiative forcing by BC (annually and globally averaged at the top of atmosphere) was approximately 0.3 W m^{-2} for the calculation with the parameterization (approximately 0.2 W m^{-2} for the constant-rate calculation). This result indicates that the aging process of BC in the micro-scale can significantly impact on the spatial distribution and radiative forcing in the global-scale through the parameterization. However, the calculations shown in this study do not take into account the enhancement of BC light absorption due to coatings and they may underestimate the direct radiative forcing. We will introduce model results including the enhancement effect in this presentation.

References

Oshima, N., and M. Koike (2013), *Geosci. Model Dev., 6*, 263-282, doi:10.5194/gmd-6-263-2013.
Yukimoto, S., et al. (2012), *J. Meteor. Soc. Japan, 90A*, 23-64, doi:10.2151/jmsj.2012-A02.

Keywords: Aerosol, Black carbon, Global aerosol model, Aging process, Transport, Radiative effects

AAS21-10 Room:201B Time:May 28 10:00-10:15

Interannual variabilities in tropospheric constituents during 2000-2013 simulated in a chemistry-aerosol coupled climate

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Global distributions and abundances of tropospheric constituents (O_3, CH_4, NOy, CO, VOCs, NHx, SOx and aerosols) interannually change under the influences of meteorology (transport, temperature, water vapor, clouds, rain, etc.) and emissions from anthropogenic/natural sources and biomass burning. In this study, we investigate interannual variability of tropospheric constituents during the years 2000 to 2013 in a chemistry-aerosol coupled climate model. The base chemical model used in this study is CHASER (Sudo et al., 2002, 2007) coupled with the aerosol model SPRINTARS (Takemura et al., 2006). The CHASER model, also developed in the framework of the MIROC earth system model (MIROC-ESM-CHEM), simulates detailed chemistry in the troposphere and stratosphere with an on-line aerosol simulation including production of particulate nitrate and SOA. We use the NCEP reanalysis data (FNL) for constraining the model's meteorology.Anthropogenic and biomass burning emissions are specified using the HTAP2 and MAC inventories, respectively. For biogenic VOCs emissions, we employ calculation by the land ecosystem/trace gas emission model VISIT (Ito et al., 2008). Our results show that temporal variability (anomaly) in surface and lower tropospheric ozone very clearly correlates with that in CO especially in NH, indicating principal importance of biomass burning emission in determining near-surface O3 variability; surface PM ($PM_{2.5}$) in NH also coincides with CO. Changes in middle to upper tropospheric O3, on the other hand, basically respond to variability in transport from the stratosphere and lightning NOx production. It is also demonstrated that temporal variability in tropospheric mean OH is largely controlled by tropospheric abundances of O_3, CO, and water vapor.

Keywords: tropospheric ozone, aerosol, PM2.5, methane, oxidation capacity, chemistry climate model

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AAS21-11 Room:201B Time:May 28 10:15-10:30

Numerical Analysis of total nitrate deposition over marginal seas of Japan

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In China, due to the expanded economy growth, anthropogenic NOx emissions increased more than twofold between 2000 and 2010. Aerosol nitrate and gas-phase nitrate produced from NOx deposite above ocean during long-range transport process, and the impacts on ocean-ecosystem are apprehensive. In this study, on the basis of regional chemical transport which can treat the detailed behavior of air pollutants, we investigated the deposition of total nitrate from atmosphere into marginal seas of Japan. Analyzed period was on the year from 2002 to 2004. Chemical transport model can well reproduce the atmospheric concentration and wet deposition amount by comparing the ground-based observation dataset of EANET. Above East China Sea (ECS), three-year averaged deposition amount of total nitrate was 252 Gg-N/year. Dry and wet deposition process respectively accounted 60% and 40%. Deposition amount of fine-mode nitrate and coarse-mode nitrate respectively attributed 22% and 50%, and the rest of 28% was gas-phase nitrate. During these period, anthropogenic NOx emissions from China was 5377 Gg-N/year, therefore, the deposition amount of total nitrate over ECS was corresponded to 4.7%. Taking into account that the deposition amount above China was 2039 Gg-N/year, the deposition amount over ECS was identified as 7.5% against to anthropogenic NOx emissions from China. In the conference presentation, we would like to present the analyzed results over Sea of Japan, Yellow Sea, and Pacific open oceans, and discuss the correspondence with anthropogenic NOx emissions from China.

Keywords: marginal seas of Japan, aerosol nitrate, gas-phase nitrate, deposition amount, chemical transport model

AAS21-12 Room:201B Time:May 28 10:30-10:45

Contribution of Siberian forest fires to PM2.5 pollution in Japan

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We examined the contribution from Siberian forest fires to PM2.5 pollution in Japan using a regional chemical transport model. In May 2003, several events resulting in PM2.5 concentrations exceeding Japan's air quality standard for daily mean value (35 μg/m^3) were observed at Rishiri in northern Japan. The model generally well reproduced the temporal variations of PM2.5 including the elevated events. The simulations demonstrated that the PM2.5 enhancements during the events were mostly attributed to biomass burning in Siberia, suggesting that the contribution from Siberian forest fires had a critical impact on the high PM2.5 days ($>$35 μg/m^3). The contributions from Siberian biomass burning to the monthly mean PM2.5 concentrations were estimated to be 64% at Rishiri and 45% at both Nonodake and Oki located in eastern and western Japan, respectively, suggesting that Siberian forest fires had a large impact on air quality for the whole of Japan. Especially at Rishiri, the observed PM2.5 concentrations and aerosol optical depth (AOD) from MODIS in May 2003 were much larger than those of the 10-year average in May from 2001 to 2010. The trend in horizontal distribution for May 2003 was opposite to the long-term average; PM2.5 and AOD in May 2003 were the highest in northern Japan.

Keywords: PM2.5, aerosol, forest fires, Siberia, transboundary pollution

AAS21-13 Room:201B Time:May 28 11:00-11:15

Observations of O3, CO, CO2 and CH4 concentrations at Happo and estimations of the source by chemical transport model

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A large increase in tropospheric O_3 concentrations was observed during spring for the period from 1998 to 2006 at Mt. Happo Observatory (36.7^{o}N, 137.8^{o}E, 1840 m asl), which is one of the Acid Deposition Monitoring Network in East Asia (EANET) stations (Tanimoto, 2009). The increase in the springtime O_3 reproduced by a regional chemistry-transport model incorporating the updated anthropogenic emissions inventory in East Asia can only explain about half of the observed O_3 increase (Tanimoto et al., 2009). On the other hand, previous source-receptor analysis by a global chemistry-transport model indicated that the contributions of local and regional sources can vary, depending on individual episodes (Wild et al., 2004). For better understanding of the discrepancies between the model prediction and observational evidence, it is necessary to better characterize air masses at Mt. Happo by simultaneous measurements of additional tracers like CO, CO_2, and CH_4.

Starting in July 2013, we have made continuous measurements of CO, CO2 and CH4 as well as O_3 at Mt. Happo. We found that the O_3 levels at Mt. Happo increased until 2007, and then the increase slowed down and now decreased to the same level as in 1990s. The CO concentrations observed for the period of 2013-2014 was found to be lower than those in 1990s. In particular, the current CO levels were 50 ppbv lower than in 1990s during summer. In total, 44 events associated with O_3 enhancement were identified for the period from July 2013 to August 2014. Correlations of CO with CO_2 and CH_4 with CO_2 were used to identify possible source regions for individual episodes. Emission ratios ($\Delta CO/\Delta CO_2$ and $\Delta CH_4/\Delta CO_2$) were calculated in each event, and compared with the ratios estimated by the regional emission inventory in Asia (REAS; Kurokawa et al., 2013). There is a discrepancy between two emission ratios. The$\Delta CO/\Delta CO_2$ indicated that most events except summer were affected by the emissions from East Asia. On the other hand, the $\Delta CH_4/\Delta CO_2$ indicated that most of events were caused by the emissions from Japan and Korea. It is difficult to identify the source regions by the ratios only.

We compared the observations with the model calculations by CMAQ v4.7.1, a regional chemistry-transport model, with the horizontal and vertical resolutions of 80 km and 37 layers, respectively. The model calculations well reproduced variability and seasonal changes of CO. For O_3, although the model prediction was higher than the observed, in particular during the summer season, the model reproduced the O_3 enhancement events reasonably well. The source regions inferred by the model will be discussed in the presentation.

Keywords: ozone, carbon monoxide, methane, carbon dioxide

AAS21-14 Room:201B Time:May 28 11:15-11:30

Long-term variations of atmospheric methane concentration over Siberia derived from aircraft and tower measurements

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Methane measurements over Siberia are crucial for estimating global CH_4 emissions since Siberia is estimated to contain over 100 million ha of wetlands. We have been acquiring long-term records of atmospheric CH_4 concentration in Siberia at 3 sites (Surgut, Novosibirsk, Yakutsk) using aircraft since 1993 and at a tower network since 2004 (JR-STATION: Japan-Russia Siberian Tall Tower Inland Observation Network, Sasakawa *et al.,* 2010, 2012). Observed CH_4 concentrations at the tower sites in West Siberia showed much higher than those observed at coastal background sites operated by NOAA in northern high latitudinal zone. They also exhibited clear seasonal cycle with double maxima in winter and summer. However increasing trend observed in background sites did not appear in tower data due to high variability in concentration during summer and winter. On the other hand, aircraft data did not have clear seasonal cycle but showed obvious increasing trend. Global stagnation in rise of CH_4 concentration around 2000-2006 was observed in aircraft data over taiga sites (Novosibirsk, Yakutsk) but not clear over wetland site (Surgut). In Surgut, vertical difference of CH_4 concentration in recent years between 1 km and 5.5 km altitude data decreased less than 2/3 of that in early 1990's. This weakening vertical gradient appeared in other altitude data (0.5-4 km) as well. Simulation results with a chemistry-transport model (ACTM; Patra *et al.,* 2009) suggested that transport influence on this trend could be small. A regional emission tagged tracer simulation with the ACTM (Umezawa *et al.,* 2014) indicated that the CH_4 emissions from West Siberia and Europe could produce most extent of the vertical gradient. This finding thus suggested that the sum of dominant emissions decreased in these 20 years.

References
Patra *et al., J. Meteorol. Soc. Jpn.,* **87**(4), 635-663, 2009.
Sasakawa *et al., Tellus,* **62**B, 403-416, 2010.
Sasakawa *et al., Tellus,* **64**B, 17514, doi:10.3402/tellusb.v64i0.17514, 2012.
Umezawa *et al, Tellus,* **66**B, 23837, 2014.

Keywords: Siberia, methane, tower network, aircraft observation

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AAS21-15 Room:201B Time:May 28 11:30-11:45

Variations of atmospheric methane concentration and its carbon and hydrogen isotopic ratios at Churchill, Canada

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Methane (CH_4) is the second most important anthropogenic greenhouse gas after CO_2. High-precision measurements of carbon and hydrogen stable isotopic ratios of CH_4 ($\delta^{13}CH_4$ and $\delta D\text{-}CH_4$) provide additional constrains to contributions of individual CH_4 sources to atmospheric CH_4 variations. Since 2007, we have conducted an air-sampling program at Churchill, Canada (58.44'N, 93.50'W) on the northern perimeter of the Hudson Bay Lowland, the second largest wetland area in the world i.e. one of the most important CH_4 source regions at northern high latitudes. In this study, we present temporal variations of CH_4, $\delta^{13}CH_4$ and $\delta D\text{-}CH_4$ at this site.

We observed long-term increase in the CH_4 concentrations at Churchill since 2007, which is consistent with the trend reported by the global observation networks such as NOAA/ESRL/GMD. The CH_4 concentration at Churchill is generally higher than that at Ny-Ålesund (78.55'N, 11.56'E), a northern high-latitude background station away from regional CH_4 sources. On the other hand, $\delta^{13}CH_4$ and $\delta D\text{-}CH_4$ at Churchill are lower than those at Ny-Ålesund, plausibly reflecting regional CH_4 emissions. Clear seasonal cycles of the CH_4 concentration and $\delta^{13}CH_4$ were observed; seasonal maximum and minimum of the CH_4 concentration take place in January-February and June-July, respectively, while those of $\delta^{13}CH_4$ were in May and October, respectively. Seasonal cycles of $\delta D\text{-}CH_4$ were obscure but observable. The seasonal phases of these variables were up to one month earlier than those at Ny-Ålesund. The cause of the difference could be attributable to wetland emissions in the surrounding region. Short-term variations of the CH_4 concentration were observed year around, but pronounced in summer. By inspecting relationships between the CH_4 concentration and the isotopic ratios, we found that the predominant CH_4 source of the short-term CH_4 variations is wetlands in summer but fossil fuels in winter.

Keywords: methane, carbon and hydrogen isotopic ratios, Hudson Bay Lowland, wetlands

AAS21-16 Room:201B Time:May 28 11:45-12:00

Temporal variation of methane profile observed with FTIR at Tsukuba

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The vertical profiles of CH_4 have been observed with high-resolution Fourier transform spectrometer at Tsukuba, Japan since 2001. SFIT2 spectral fitting program was used to derive the vertical profiles from 3 spectral regions in 3 micrometer region.

CH_4 is the second important contributor of the anthropogenically enhanced greenhouse effect but there are many uncertainties in the source variations.

Daily averaged CH_4 total column density kept a level from 2001 to 2006, then increased from 2007 to 2008, and again kept a level from 2009 to 2014. Tropopause height shows no significant change between before and after 2007, indicating stable dynamical situation. Derived CH_4 profiles show that the increase occurred mainly in the troposphere.

Keywords: FTIR, Greenhouse Gas, Methane

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

AAS21-17 Room:201B Time:May 28 12:00-12:15

Atmospheric methane measurement by open-path laser methane instrument at paddy fields in India

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Methane is the second important greenhouse gas after carbon dioxide, and increasing importance to the Earth's radiative budget. To better quantify methane emissions, their regional and temporal distribution, and attribution to the different methane sources is needed.Satellite observations offer the possibility of sensing methane globally and retrieving methane abundances in remote areas and can help with interpretation of sparse ground based measurement. In southeast and south Asia, the previous satellite observations suggest that the emission from rice paddies is significant and important source of methane during rainy season. However, there are large uncertainties in quantitative estimation of methane emission in these areas and there are needs for more certification between satellite and ground based measurements. In remote areas with insufficient infrastructure, air sampling and subsequently analysis are typical and reliable method for gas analysis. We developed the methane concentration measurement system which can make a continuous observation to interpolate the data of sampled air between each sampling period and we have operated the developed system at rural area in India.

The developed measurement system consists of gas sensor, power supply, data logger, remote control instruments and telecommunication equipment. The methane gas sensor is used a laser methane measurement instrument (LaserMethane, ANRITSU CORPORATION) which is a portable detector with low electric consumption, easy maintenance, and outdoor use. Remote sensing of methane is accomplished by means of infrared absorption spectroscopy with near-IR diode laser using reflected light from a reflector located at several tens meters away from the detector. High sensitivity is achieved by the second-harmonic detection of wavelength modulation spectroscopy. It can quickly and selectively detect the integral methane concentration on the optical path of the laser beam. To measure the methane concentration at paddy field in India, the methane measurement system was installed at rural area (Sonepat, Haryanea) on the north of Delhi and has been operated since the winter of 2014. The air sampling along with our measurement has been carried out once a weak currently. The methane concentration from the laser instrument can be corrected with the more precise value of the sampled air. To establish how to correct the data and calibrate the system, we performed both of laboratory experiment and field measurement. We will present about the development of the open-path laser methane measurement system and the recent results of field measurement in India.

Keywords: methane, open-path laser spectroscopy, paddy field, India

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

AAS21-18 Room:201B Time:May 28 12:15-12:30

Relationship between interannual variation in the changing rate of APO trend at Cape Ochi-ishi and PDO

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Since atmospheric potential oxygen (APO=O_2+1.1xCO_2) mainly reflects the air-sea gas exchange of O_2 and CO_2 by definition, the spatio-temporal variations in APO are expected to constrain the ocean biogeochemical process and dynamics. Here we examine the relationship between temporal variations in APO trend observed at Cape Ochi-ishi (COI; 43.2^{o}N, 145.5^{o}E) and the Pacific Decadal Oscillation (PDO) index to investigate the causes for the inter-annual variations in the APO trend. The PDO is a long-term Pacific climate variability, having two extreme phases which is classified by basin-scale patterns of the sea surface temperature (SST) anomaly. When the SST anomalies are cool in the northern North Pacific and warm in the tropical Pacific, the PDO index has positive value. And the opposite pattern of the SST anomalies correspond to the negative PDO index. The cool SST enhances the ocean vertical ventilation which brings deeper waters with depleted O_2 to the surface, causing the O_2 ingassing. The cool SST also enhances the ingassing flux by increasing gas solubility. To the contrary, the enhanced ocean vertical ventilation brings the subsurface nutrients to the surface, enhancing the O_2 outgassing through the increase in the ocean primary production. Thus, the correlation analysis between the changing rate of the APO trend (dAPO/dt) at COI and the PDO index would allow us to investigate how the SST anomaly in the northern North Pacific affect the air-sea gas exchanges. Unfortunately, there is no significant correlation between dAPO/dt and the POD index. However, when dAPO/dt and the PDO index are decomposed into the middle ($0.3<f<0.6$ cycle/yr) and low ($f<0.3$ cycle/yr) frequency domains by using a digital filtering technique, the scatter plots of the middle-term and long-term variations show significant negative and positive correlations, respectively. These results might suggest that the ventilation/thermal effect is dominant for the middle-term SST variation while the biotic effect exceeds it for the long-term SST variation.

Keywords: APO, atmospheric oxygen, PDO, atmospheric CO2, air-sea gas exchange

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

AAS21-19 Room:201B Time:May 28 12:30-12:45

Variations in the atmospheric Ar/N2 and APO observed at Tsukuba, Ochi-Ishi, Hateruma and Minamitorishima, Japan

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Atmospheric Ar/N_2 ratio is a unique tracer of spatiotemporally-integrated air-sea heat fluxes, and expected to be a new tool to validate changes in the global ocean heat content (e.g. Keeling et al. 2004; Cassar et al., 2008). The Ar/N_2 ratio is also useful to estimate thermal and biological components of Atmospheric Potential Oxygen (APO = O_2 +1.1xCO_2) separately, so that it will contribute to better understanding of the oceanic carbon cycle. Therefore, we have developed a high-precision measurement system of the atmospheric Ar/N_2 ratio and APO (Ishidoya and Murayama, 2014), which is applicable both for continuous observations and analyses of discrete flask air samples, and started systematic observations of the Ar/N_2 and APO at Tsukuba (36N, 140E) and Hateruma Island (24N, 124E), Japan since 2012 and at Cape Ochi-Ishi (43N, 146E) and Minamitorishima Island (24N, 154E), Japan since 2013. Clear seasonal cycles of the Ar/N_2 ratio were observed at all the sites, and the peak-to-peak amplitudes of the seasonal cycles were in the range of 15 - 50 per meg. The observed amplitudes were found to be significantly larger than those calculated using atmospheric transport models and the seasonal air-sea N_2 fluxes climatology (TransCom fluxes; Garcia and Keeling et al., 2001) with a scaling factor to convert changes in the atmospheric N_2 concentration to those in the Ar/N_2 ratio (Blaine, 2005). We will also present preliminary estimations of the thermal and the biological APO at our sites by using the observed seasonal Ar/N_2 and APO cycles.

Acknowledgements
We would like to acknowledge N. Oda and F. Shimano, Global Environmental Forum, and many staffs of Japan Meteorological Agency for their supporting the observations.

References

Blaine, T. (2005) Continuous Measurements of Atmospheric Argon/Nitrogen as a Tracer of Air-Sea Heat Flux: Models, Methods, and Data. PhD Thesis, University of California, San Diego.

Cassar, N. et al. (2008) An improved comparison of atmospheric Ar/N_2 time series and paired ocean-atmosphere model predictions. J. Geophys. Res., 113, D21122. DOI: 10.1029/2008 JD009817.

Garcia, H. & Keeling, R. (2001) On the global oxygen anomaly and air-sea flux. J. Geophys. Res, 106, 31155-31166.

Ishidoya, S. & Murayama, S. (2014) Development of high precision continuous measuring system of the atmospheric O_2/N_2 and Ar/N_2 ratios and its application to the observation in Tsukuba, Japan. Tellus B, 66, 22574, http://dx.doi.org/ 10.3402/tellusb.v66.22574.

Keeling, R. et al. (2004) Measurement of changes in atmospheric Ar/N_2 ratio using a rapid-switching, single-capillary mass spectrometer system. Tellus B, 56, 322-338.

Keywords: Atmospheric Ar/N2 ratio, Atmospheric Potential Oxygen (APO), Air-sea heat flux

Japan Geoscience Union Meeting 2015
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AAS21-20 Room:201B Time:May 28 14:15-14:30

Seasonal variations of nitrogen and oxygen isotopic signature of atmospheric nitrate in coastal Antarctica

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Nitrate (NO_3^-) is the end-product of oxidation of nitrogen oxides (NO_X=NO+NO_2) in the atmosphere and one of the major ions preserved in Antarctic snow and ice. Therefore, there has been great interest in using concentration and isotopic signature of nitrate in ice cores to reconstruct past atmospheric NO_X sources and their oxidation processes to nitrate. For interpretation of nitrate records in Antarctic ice cores, it is necessary to know the long-term changes of concentration and isotopic compositions ($^{15}N/^{14}N$, $^{17}O/^{16}O$ and $^{18}O/^{16}O$) of nitrate in the atmosphere which deposits on the surface snow. In this study, we present seasonal variation of nitrogen and triple oxygen isotopic composition of nitrate collected at French Antarctic Station Dumont d'Urville (66^{o}40'S, 140^{o}01'E) throughout the year 2011. The significant increase of nitrate concentration during spring and summer period was observed and ^{15}N were depleted in the nitrates, indicating that there was the substantial NO_X input to the atmosphere by photolysis of nitrate in the surface snow. In addition, relatively low ^{17}O excess in summer period suggests that NO_X oxidation to nitrate by OH radicals was increased. On the other hand, high ^{17}O excess with low concentration in fall and winter period suggests that OH oxidation pathway was depleted and other oxidation pathways related to O_3 were dominant. Additionally, the small nitrate increase in winter period might be attributed to the transport of stratospheric nitrate to troposphere due to the formation of polar stratospheric clouds. In the presentation, we will discuss the long-term change of the seasonal trends and compare the result with that of 2001 year-round isotopic analysis using nitrate aerosols at the same station.

Keywords: Antarctic, Aerosol, Nitrate, Stable isotopic analysis

AAS21-21 Room:201B Time:May 28 14:30-14:45

Determination on the triple oxygen isotopic composition of atmospheric nitrous acid (HONO)

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The photolysis of nitrous acid (HONO) has been recognized as a potentially important source of OH radicals, which is known as a major oxidant in the atmosphere removing reductive trace gases such as methane and NMHCs. There are two major formation pathways to produce atmospheric HONO, one is a process so-called “direct emission” in which HONO emits directly from various sources on the ground and the other “secondary formation” in which HONO is produced by chemical reaction of nitrogen compounds in the atmosphere. Their contributions to the production of atmospheric HONO, however, have not been well understood.

In order to quantify the contribution of HONO derived from secondary formation, we determined a triple oxygen isotope, $\Delta^{17}O$ value of atmospheric nitrous acid (HONO). $\Delta^{17}O$ value of HONO produced via secondary formation is expected to have highly positive values as those of O_3 ($\Delta^{17}O$ = +30 ±10 ‰), while no $\Delta^{17}O$ anomaly ($\Delta^{17}O$ = 0 ‰) should be observed for HONO which is emitted directly from various sources on the ground.

Atmospheric HONO was collected using filter-pack method (Noguchi et al., 2007) in which HONO accumulates on the K_2CO_3 impregnated filter as NO_2^-. Since HONO is collected as NO_2^-, we must be careful about oxygen exchange between NO_2^- and H_2O on the filter. If the sampling period becomes longer, $\Delta^{17}O$ of HONO could become smaller than the original value due to rapid oxygen exchange between NO_2^- and H_2O on the filter. Therefore, in order to decide appropriate sampling periods for $\Delta^{17}O$ measurement of HONO, we conducted a field sampling of atmospheric HONO during December 15-26, 2014, at Hokkaido Institute of Environmental Sciences, Sapporo, Japan. We arranged seven different periods (half a day, one day, two days, three days, four days, one week and two weeks) for atmospheric HONO collection. We also set two kinds of sampling flow rate for HONO sampling; faster flow rate (10 L/min) for shorter sampling periods (from half a day to three days) and slower flow rate (4 L/min) for longer sampling periods (from four days to two weeks). HONO-derived NO_2^- on the filter was extracted to pure water. After that, it was reduced to N_2O using HN_3 and then converted to O_2 via thermal decomposition and then introduced to IRMS for $\Delta^{17}O$ measurement. The concentration of NO_2^- and NO_3^- in the extracted water were measured by traditional ion chromatography to calculate NO_2^- yield (ratio of NO_2^- among the sum of NO_2^- and NO_3^-) on the filter.

We found clear difference on NO_2^- yield absorbed on the filter between the two sample flow rates. Low flow late (4 L/min) result in lower NO_2^- yield of around 79% on average which coincide well with those reported previously (76%, Ohyama et al., 2012). Very high NO_2^- yield of more than 98% were observed in the filter collected at high rates (10 L/min). We concluded that we could prevent NO_3^- formation via reaction of NO_2^- with O_3 by collecting HONO in the condition of higher sample flow rate.

The result of $\Delta^{17}O$ value of HONO ranged from +6 ‰ to +9 ‰ through the observation periods. We could not find any $\Delta^{17}O$ depletion due to oxygen exchange between NO_2^- and H_2O on the filter during the collection periods. Assuming that $\Delta^{17}O$ value of HONO derived from secondary formation is +35 ‰, the contribution of HONO produced via secondary formation to atmospheric HONO was estimated to be about more than 20% demonstrating its significance on the formation pathway of atmospheric HONO in the winter of urban area.

Keywords: HONO, nitrous acid, triple oxygen isotope, source, winter, Sapporo

AAS21-22 Room:201B Time:May 28 14:45-15:00

Determination of partitioning of alpha-pinene ozonolysis products between gaseous and aerosol phases

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Organic material accounts for a substantial fraction of atmospheric fine particulate matter, which directly and indirectly affects the global climate as well as human health. Many gas-phase organic compounds undergo oxidation in the gas phase to yield products, generally oxygenated, that have vapor pressures sufficiently low that they are partitioned between the gas and aerosol phases. Such compounds are often referred to as semi-volatile organic compounds (SVOCs) and, when present in the aerosol phase, as secondary organic aerosols (SOAs). 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. We use chemical ionization-mass spectrometry to identify SVOCs in both the gaseous and the aerosol phases and to estimate the gas-aerosol partitioning of each SVOC. By using the same technique to measure SVOCs in both the gaseous and the aerosol phases, we were able to determine the partitioning of each SVOC between the gaseous and aerosol phases from the ratio of ion signals, without knowing the concentration of each SVOC. This ability to partition each SVOC between the gaseous and aerosol phases is a strong point of this approach, because most chemical species in SOAs are thought to be multifunctional, and determining their concentrations seems to be impossible. In the present study, we used two proton transfer reaction-mass spectrometers for real-time measurements of SVOCs produced in α-pinene ozonolysis in both the gaseous and the aerosol phases and determined the partitioning of each SVOC between the gaseous and aerosol phases. Time profiles of the SVOCs in both the gaseous and the aerosol phases were compared. This work was supported by the Environmental Research and Technology Development Fund (5-1408) of the Ministry of the Environment, Japan.

Keywords: Secondary organic aerosol, Gas-particle partitioning, Chemical ionization-mass spectrometry, Proton transfer reaction-mass spectrometry, alpha-Pinene, Ozonolysis

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AAS21-23 Room:201B Time:May 28 15:00-15:15

Impact of oxidation processes on optical properties of isoprene SOAs

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Isoprene is the most abundant volatile organic compounds (VOCs) emitted from biosphere and is known as one of the precursors of secondary organic aerosols (SOAs) in the atmosphere. The formation yield of the isoprene-SOAs is considered to be enhanced in the presence of acidic seed particles such as sulfuric acid. Recently, it has been suggested that some organic aerosols, which is called “brown carbon” , can absorb solar radiation, especially at the ultraviolet (UV) and shorter visible wavelengths and contribute to the radiation balance and photochemical reactions in the atmosphere. However, no experimental study on complex refractive index (RI) of the SOAs generated from the isoprene has been reported. In this work, wavelength dependence of the complex RI values of the SOAs generated in the oxidation of isoprene with OH, NO_3, and O_3 in the presence or absence of SO_2 have been examined.

The SOAs were generated in a 6 m^3 Teflon coated stainless steel photochemical smog chamber. In the OH oxidation experiments, the reaction mixture of isoprene and NO in the presence or absence of SO_2 (sulfuric acid precursor) was continuously irradiated by UV light after the addition of a small amount of methyl nitrite as a source of OH radicals. In the ozonolysis experiments, isoprene was reacted with O_3 in the presence or absence of CO (OH scavenger) and SO_2. In the NO_3 oxidation experiments, ozone was added to the mixture of isoprene and NO_2 in the presence of SO_2. The optical properties of the SOAs were measured by two photoacoustic spectrometers (PASS-3 and PAX, absorption and scattering at 375, 405, 532, 781 nm) and a custom-built cavity ring-down spectrometer (CRDS, extinction at 532 nm). Chemical properties of aerosols were also measured by an Aerodyne aerosol mass spectrometer (ToF-AMS). The size distributions of SOAs were measured by a scanning mobility particle sizer (SMPS).

Absorption, scattering, and extinction efficiencies of SOAs are calculated by dividing the absorption, scattering, and extinction coefficients by total mobility cross sections measured with the SMPS. The RI of the SOAs is determined by comparing the size parameter dependence of extinction, scattering, and absorption efficiencies with Mie theory. The significant imaginary part values of RI at 405 and 532 nm are obtained for the SOAs generated in the OH oxidation of isoprene in the presence of SO_2, while the imaginary part values are negligible for the SOAs generated in the ozonolysis (in the presence of OH scavenger) and NO_3 oxidation of isoprene. In the presentation, relationship with chemical properties and the atmospheric implications of the results will also be discussed.

Keywords: Isoprene, Secondary organic aerosol, Aerosol optical properties, Complex refractive index, Brown carbon

AAS21-24 Room:201B Time:May 28 15:15-15:30

Effects of relative humidity on tetrol formation from isoprene/NO photo-oxidation

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2-Methyltetrols, molecular markers of isoprene secondary aerosol, are produced by the particle-phase hydrolysis of organonitrate esters (Sato, 2008; Szmigielski *et al*., 2010; Jacobs *et al*., 2014) and/or the particle-phase oxidation of isoprene epoxydiols (Jacobs *et al*., 2014) during the isoprene/NO_X photo-oxidation. The effects of relative humidity, acid and base on 2-methyltetrol formation from the isoprene/NO photo-oxidation were investigated. We used a 6-m^3 Teflon bag and a 6-m^3 stainless steel chamber for humid and dry conditions, respectively. 2-Methyltetrol formation under humid conditions (RH $\simeq$ 80%) was enhanced in the presence of sulfur dioxide and was also enhanced in the presence of ammonia. In contrast, 2-methyltetrol formation under dry conditions (RH $<$1%) was less catalyzed or suppressed in the presence of sulfur dioxide. The ratio of total 2-methyltetrol mass to total organic aerosol mass was 0.21 – 18 wt% under various present conditions. 2-Methyltetrol formation in the aqueous solution of aerosol sample was also investigated, and was found to be enhanced by both the acid and the base. The present results show that the presence of water is critical for acid-catalyzed 2-methyltetrol formation from isoprene/NO photo-oxidation. The ester hydrolysis will be a major pathway for 2-methyltetrol formation because it was enhanced by the base.

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References: Sato, K. (2008) *Atmos. Environ.* **42**, 6851 – 6861. Szmigielski, R. *et al*. (2010) *Atmos. Res.* **98**, 183 – 189. Jacobs, M. I. *et al*. (2014) *Atmos. Chem. Phys*. **14**, 8933 – 8946.

Keywords: biogenic volatile organic compound, secondary organic aerosol, organic nitrate, aqueous-phase reaction, environmental chamber

AAS21-25 Room:201B Time:May 28 15:30-15:45

Continuous observations of atmospheric HCHO by MAX-DOAS at Yokosuka, Japan: Verification and correlation with ozone

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Tropospheric ozone is an important greenhouse gas with the third largest global warming effect after CO2 and CH4. Its photochemical production in the atmosphere is not quantitatively understood, partly because of the large uncertainties in the amount and origins of the volatile organic compounds (VOCs) in the atmosphere serving as precursors of ozone. Accurate observations of formaldehyde (HCHO), formed from VOC oxidation simultaneously with ozone, would provide pivotal information of the VOC emission rates and ozone production mechanisms. This study focuses on the measurements of HCHO in the urban area, specifically at Yokosuka (35.32 degN, 139.65 degE), Japan. Appropriateness of the observations was verified and then the correlation with ozone concentrations was studied.

Differential slant column densities of HCHO were derived from MAX-DOAS spectrum observations (336.5 - 359 nm) at Yokosuka and then converted to the vertical column densities/profiles using aerosol information retrieved simultaneously. We obtained observational data from October 2007 to December 2013, and from 08H (0800-0900 JST) to 15H in winter and from 06H to 17H in summer. The HCHO concentrations at the lowest layer derived from MAX-DOAS agreed quite well with the monthly ground-based observations of HCHO conducted at Oppama site, 2 km west of our location. Although we showed that recent satellite observations of HCHO provided reasonable agreement with MAX-DOAS over a rural site near Moscow, Russia, poorer agreement was obtained at Yokosuka, potentially affected by the spatial inhomogeneity in the HCHO concentrations in or near the urban region.

Monthly averages of the tropospheric vertical column density of HCHO derived from MAX-DOAS at 13H showed clear seasonal variation with maxima during July-September ((1.4-2.0)x10ˆ16 molecules cmˆ-2) and minima during December-March. The temporal variation during summer was quite similar to that of ozone concentrations observed at Oppama, while the HCHO levels were quite low in April/May, when the ozone concentration was even higher. The HCHO partial column in the lowest 1 km altitude range at 13H during June-August showed tight positive correlation with the surface ozone concentrations. These analyses suggested that the MAX-DOAS observations of HCHO are successful in quantifying HCHO secondarily produced in the atmosphere by photochemistry and that the short-lived HCHO would be a useful tracer to differentiate in-situ ozone production from long range transport.

Keywords: Tropospheric photochemistry, Volatile organic compounds, Urban atmosphere, Ozone precursors

AAS21-26 Room:201B Time:May 28 15:45-16:00

Evaporation of aerosol particles upon heating in a transmission electron microscope

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Thermal property (e.g., evaporation temperature) of atmospheric aerosol particles is important to measure and classify their species using, for example, an aerosol mass spectrometer, a thermos denuder, and thermal method for elemental carbon/organic carbon (EC/OC). However, it is largely unknown about the thermal behavior of ambient aerosol particles especially organic aerosol particles and their mixture with inorganic materials. Therefore, evaporation temperatures of ambient aerosol particles with their compositions need to be determined.

This study uses a transmission electron microscope (TEM) and a heating holder, which can heat samples on TEM grids >1000 ℃ while observing their shapes. Thus, it is possible to observe particle evaporation process upon heating. The TEM chamber is in vacuum (~0.00001Pa) and lacks of oxygen. Thus, particle volumes on TEM grids changes through evaporation/sublimation at specific temperature. In general, an aerosol mass spectrometer uses 600 ℃ to vaporize aerosol particles, a thermos denuder uses 200-300 ℃ to remove volatile materials, and an EC/OC measurement use ~500 ℃ to distinguish OC and EC. Thus aerosol thermal properties were analyzed by heating from room temperature to 600 ℃.

This study mainly used ambient samples collected from biomass burning during Biomass Burn Observation Project (BBOP) in 2013. These samples were collected at North America using an aircraft. The results indicated that organic materials in biomass burning lost their volume while heating up to 600 ℃ but did not completely evaporate but remained residue, which is probably due to charring of organic matters. Especially, spherical brown carbon organic particles occurring in biomass burning (tar balls) left their volume by 30% at 600 ℃. The results imply that tar balls are difficult to measure their properties when assuming they are volatile materials even at 600 ℃.

Acknowledgements: The author acknowledges the BBOP campaign team, especially L I Kleinman, A, J Sedlacek, and P R Buseck, for their helps for the sampling and the analyses of BBOP samples.

Keywords: aerosol, heating, organic matter, transmission electron microscopy, biomass burning

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AAS21-27 Room:201B Time:May 28 16:15-16:30

Speciation of sulfate in aerosols for the precise estimation of its global cooling effect

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Global cooling effect by aerosol is one of causes which influence earth's climatic change (IPCC, 2013). In particular, sulfate aerosols are known to cool the earth indirectly by forming cloud condensation nuclei (CCN) because of their high hygroscopicity. However, the hygroscopicity can change depending on the sulfate species. For example, $CaSO_4\cdot 2H_2O$ is sulfate having low hygroscopicity. Therefore, determination of sulfate species in aerosols is necessary to interpret the degree of cooling effect by sulfate aerosols in environment.

In this study, aerosol sampling was conducted in Higashi-Hiroshima (34.40 N, 123.71 E), Hiroshima, Japan. In addition, the samples were collected using two methods as to particle size. One method collected non-size-fractionated aerosols for about a year from September 2012 to September 2013. The other method collected size-fractionated aerosol in various periods such as winter when concentrations of anthropogenic aerosols were high (PA sample; collected from January 31 to February 1, 2013), spring (March 4 to 9, 2013), summer (July 22 to August 5, 2013), and fall (November 11 to 25, 2013). For these samples, major ion composition was measured by ion-chromatography, while chemical species of sulfur and calcium in the aerosol samples were determined by X-ray absorption fine structure (XAFS) spectroscopy. Furthermore, to unravel the function of CCN by sulfate aerosols in more detail, samples for single particle analysis were collected on May 31, 2014 during a dust event, which was analyzed individually using scanning transmission X-ray microscopy (STXM).

Atmospheric concentration of each major ion in the atmosphere had seasonal variation. Sulfate ion ($SO_4{}^{2-}$) concentration was larger in PA, in which concentration of ammonium ion ($NH_4{}^{+}$) and nitrate ion ($NO_3{}^{-}$) were also larger than those in other seasons. Meanwhile, size distribution of aerosol is important to determine its origin, because it is widely recognized that aerosol larger than 1 μm diameter is of natural origin. On the other hand, particles finer than 1 μm is of anthropogenic origin. In general, concentrations of $SO_4{}^{2-}$ and $NH_4{}^{+}$ were larger in finer particles. Therefore, it is strongly suggested that the aerosol sample collected in this period was influenced by human activities. In spring, concentration of calcium ion (Ca^{2+}) increased particularly in the coarse particles, which suggests that its origin was from natural source.

Subsequently, sulfate species in the aerosol samples was determined using XAFS, where it was found that concentration ratio of calcium sulfate ($CaSO_4\cdot 2H_2O$) which has low hygroscopicity to total concentration of $SO_4{}^{2-}$ in the aerosol sample ($[CaSO_4\cdot 2H_2O]/[SO_4{}^{2-}]_t$) was larger in spring than that in PA. The abundance of $CaSO_4\cdot 2H_2O$ in atmosphere cannot be ignored because of its comparatively high $[CaSO_4\cdot 2H_2O]/[SO_4{}^{2-}]_t$ ratio, especially in spring. It was also found that indirect cooling effect by sulfate will be small in spring due to the larger ratio of $[CaSO_4\cdot 2H_2O]/[SO_4{}^{2-}]_t$. To provide further details of the effect by CCN function, Ca species of single particle samples in the dust period was determined using STXM. It was shown that there was $CaSO_4\cdot 2H_2O$ at the surface of the particle, which is the site of the chemical reactions with other species in aerosols. In addition, $Ca(NO_3)_2\cdot 4H_2O$, which was minor Ca species in the bulk analysis, was also detected in the particles. Individual analysis of single particle is important to determine minor species in aerosol samples, which leads to better understanding of chemical processes in the atmosphere.

In conclusion, it was suggested that the degree of indirect cooling effects of sulfate aerosol can change seasonally because concentrations of low hygroscopicity sulfate species in the atmosphere are variable.

Keywords: aerosol, speciation of sulfate, global cooling effect, X-ray absorption fine structure

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Interaction between oxalate aerosol and metal: stability and global cooling effect of aerosol

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Photoreaction contributes to the formation and removal processes of oxalic acid that is a major component of organic aerosols. Oxalic acid is formed by photooxidation of high molecular weight organic aerosols via glyoxylic acid, and decomposed into carbon dioxide. In addition, previous study showed that oxalic acid forms insoluble metal-oxalate complex, which suggested that global cooling effect of oxalic acid is lower than previous estimation because metal-oxalate complex does not work as cloud condensation nuclei. Interaction between oxalic acid and metal might affect photoreactivity like hygroscopicity. In this study, speciation of oxalic acid and measurement of reaction rate constant for photoreaction were conducted to evaluate the effect of metal for global cooling effect and photoreaction.

Size fractionated aerosol samples were collected at Higashi-Hiroshima in winter, spring, and summer. Speciation analysis of oxalic acid was conducted by X-ray absorption fine structure (XAFS) spectroscopy for zinc (Zn), lead (Pb), and Calcium (Ca). Photoreaction experiments were conducted by ultraviolet ray about oxalic acid and glyoxylic acid. Oxalic acid and glyoxylic acid were measured by Total Organic Carbon (TOC) Analyzer and colorimeter using Schiff base, respectively.

As a result of speciation, Ca and Zn oxalate complexes were found in fine particles (<1.7 μm), but Pb complex was hardly found. The ratio of metal-oxalate complexes to total oxalic acid was about 30% to 50% about each sample. This result showed that the cooling effect of oxalic acid might be smaller than previous estimation.

As a result of photolysis experiments, half-life time of oxalic acid, Mg complex, and Zn complex is 19 minutes, 71minutes, and 172minutes, respectively. This result showed that photoreactivity of oxalic acid was decreased due to the decrease of quantum yield by forming metal-oxalate complexes. In contrast, photoreactivity of glyoxylic acid was increased by coexisting with Zn. Photoreaction of glyoxylic acid to oxalic acid is addition reaction of oxygen, which differs that of oxalic acid to carbon dioxide by cutting carbon bond. It is thought that the reason why photoreactivity was improved is what Zn worked as catalyst.

Keywords: organic aerosol, oxalic acid, metal complex, photo reactivity, indirect effect

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Major ion composition in aerosol: As an new indicator of chlorine deficiency

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A large part of sodium and chlorine in aerosol particles are derived from surface seawater as sodium chloride (sea-salt; NaCl). Sodium chloride in aerosol is altered to sodium nitrate ($NaNO_3$) and sulfate (Na_2SO_4) by the reaction with nitric acid (HNO_3) and sulfuric acid (H_2SO_4) in atmosphere, respectively. In these reactions, gaseous HCl is emitted from sea-salt particles to the atmosphere, which is is called as chlorine deficiency. These are important chemical reactions to anthropogenic N, in the process of transport from continent to open ocean, and to H_2SO_4 as scavenging process in atmosphere (Akimoto, 2014). However, detail processes of the chemical reaction and size-dependence of aerosol particles on this reaction are not clear. In order to clarify these reactions/processes in aerosol, we employed mass fractions (MF) parameter to size-fractionated aerosol particles obtained from land/continent and ocean. Direct speciation of Na was also conducted by soft X-ray absorption fine structure (XAFS) spectroscopy to intercompare the abundance ratio of Na species to those estimated by MF.

Size-fractionated aerosol particles on land were collected by a high volume cascade impactor at Higashi-Hiroshima from December 2012 to March 2014. Marine total suspended particulate (TSP) and size-fractionated aerosol particles were collected in the *R/V Hakuho-Maru* research cruises of KH-12-4 (the North Pacific Ocean: from 23th August to 3rd October 2012) and KH-13-4 Leg. 4 (the Bay of Bengal: from 31th July to 14th August 2013), respectively. Major ionic concentrations (Na^+, ${NH_4}^+$, K^+, Mg^{2+}, Ca^{2+}, Cl^-, ${NO_3}^-$ and ${SO_4}^{2-}$) in aerosol samples were determined by an ion chromatography after appropriate pretreatment. MF parameters were calculated as $[X]_{eq}$/[total anion]$_{eq}$ (X: Cl^-, ${NO_3}^-$ and nss${SO_4}^{2-}$). Direct speciation of Na in continental size-fractionated aerosol particles were conducted by XAFS spectroscopy on BL-10, SR-center, Ritsumeikan University.

MF$[Cl^-]_{eq}$ was inversely correlated with both MF$[{NO_3}^-]_{eq}$ and MF[nss${SO_4}^{2-}$]$_{eq}$ in continental coarse aerosol particles. It can be said that the chlorine deficiency is explained by the reaction with ${NO_3}^-$ and/or nss${SO_4}^{2-}$. The regression line for MF$[Cl^-]_{eq}$-MF[nss${SO_4}^{2-}$]$_{eq}$ was -2.16. As for MF$[Cl^-]_{eq}$-MF$[{NO_3}^-]_{eq}$, the regression line shows -1.03, and this regression line satisfies the equation of y=1-x. Thus, HNO_3 has large contribution as a reactant of NaCl in the urban atmosphere. Furthermore, chemical reaction of NaCl with HNO_3 and H_2SO_4 preferentially occur on the small aerosol particles because further decrement of MF$[Cl^-]_{eq}$ was found in smaller size of aerosols compared with that of large aerosol particles. The speciation analysis with XAFS spectroscopy showed comparable results with that obtained from MF analysis using the high reacted aerosol samples from continent (MF$[Cl^-]_{eq}$: MF$[{NO_3}^-]_{eq}$: MF[nss${SO_4}^{2-}$]$_{eq}$ =18:56:23). As for marine aerosol samples from the North Pacific Ocean, dominant reactant of NaCl is H_2SO_4. On the other hand, the reaction of NaCl occurs with both ${NO_3}^-$ and ${SO_4}^{2-}$ above the Bay of Bengal.

As a consequence, MF is very useful tools to find dominant reactant of NaCl and Na chemical species as a result of chlorine deficiency in both continental and marine aerosol particles.

Keywords: atmospheric chemistry, aerosol, Na, XAFS spectroscopy