Session 1: AMS study (13:10-13:35)

Investigating the sources and chemical composition of aerosol along water vapor channel in the Southeastern Tibetan Plateau

Xinghua Zhang, Jianzhong Xu*, Miao Zhong, Lixiang Zhai

Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

Corresponding author: Jianzhong Xu (jzxu@lzb.ac.cn)

The contribution of ambient aerosols to atmospheric radiative forcing over the Tibetan Plateau (TP) has been increasing in recent years. Nevertheless, the physical and chemical characteristics, as well as their sources, remain poorly understood. An intensive field study was conducted from March 26 to May 21, 2021 in Motuo County (29.30°N, 95.32°E; 1305 m a.s.l.), situated in the Yarlung Tsangpo River valley of the southeastern TP which is the primary water vapor pathway of the TP. The study aimed to investigate the transboundary transport and formation mechanisms of aerosols originating from polluted regions in South Asia to the Tibetan Plateau during the pre-monsoon season in this area. The average submicron aerosol (PM_1) mass concentration, including organics, sulfate, nitrate, ammonium, and chloride characterized by an high resolution time-of-flight aerosol mass spectrometer, and black carbon measured by a photo-acoustic extinctiometer (PAX), was 5.7 µg m^{-3} on average with organic aerosol (OA) accounting for 57.9% and sulfate 21.1%, nitrate 2.3%, ammonium 7.3%, BC 12.1%, and chloride 0.2%. Multiple polluted episodes with maximum PM_1 mass reached 30 µg m^{-3} and increased contributions from secondary species were also observed. Regional transportation and secondary formation have been revealed to be the dominant aerosol sources in this remote site. Significantly increased contributions from secondary species, particularly the more-oxidized oxygenated OA (MO-OOA) containing a higher proportion of nitrogen-containing species, were predominantly observed during the initial half of the study period. The high MO-OOA exhibited a strong correlation with elevated aerosol liquid water content and biomass burning related aerosols, suggesting the significant role of aqueous aerosol processes on aerosol formation during the transport from South Asia along the transmission of water vapor in. In contrast, relatively stable concentrations were observed throughout the entire period for the less-oxidized oxygenated OA (LO-OOA), another secondary OA (SOA) component that might be associated with the oxidization of biogenic volatile organic compounds. However, significantly elevated contributions from LO-OOA were observed during the latter half period of the study. The variances in chemical compositions, sources, and formation processes during the different periods were further confirmed by the molecular-level analysis on filter samples. The results of this study highlighted the significance of aqueous formation of SOA components derived from the long-transported biomass aerosol and biogenic precursors within the forested regions in the southeastern TP.

Session 1: AMS study (13:35-14:00)

Enhancing characterization of organic nitrogen components in aerosols and droplets using high-resolution aerosol mass spectrometry

Xinlei Ge[1,2], Yele Sun[2,3], Justin Trousdell[2], Mindong Chen[1], Qi Zhang[2]

[1] *Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CICAEET), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China*

[2] *Department of Environmental Toxicology, University of California at Davis, One Shields Avenue, California 95616, United States*

[3] *State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China*

This study aims to enhance the understanding and application of the Aerodyne high-resolution aerosol mass spectrometer (HR-AMS) for comprehensive characterization of organic nitrogen (ON) compounds in aerosol particles and atmospheric droplets. To achieve this, we analysed seventy-five N-containing organic compounds, representing a diverse range of ambient ON types, including amines, amides, amino acids, N-heterocycles, protein, and humic acids. The ON here does not include organonitrates, therefore is denoted as non-organonitrate ON (NOON). Our results show that NOON compounds can produce significant levels of NH_x^+ and NO_x^+ ion fragments, which are typically recognized as ions representative of inorganic nitrogen species. We also discovered the presence of CH_2N^+ at m/z = 28.0187, an ion fragment that is rarely quantified in ambient datasets due to substantial interference from air-related N_2^+. As a result, we determined that an updated calibration factor of 0.79 for NOON quantification is necessary by using AMS. We also assessed the relative ionization efficiencies (RIEs) for different NOON species and found that the average RIE of NOON compounds (1.52 ± 0.58) aligns with the commonly used default value of 1.40 for organic aerosol (OA). Moreover, through a careful examination of the HR-AMS mass spectral features of various NOON types, we propose fingerprint ion series that can aid the NOON speciation analysis. The presence of $C_nH_{2n+2}N^+$ ions is closely linked with amines, with CH_4N^+ indicating primary amines, $C_2H_6N^+$ suggesting secondary amines, and $C_3H_8N^+$ representing tertiary amines. $C_nH_{2n}NO^+$ ions (especially for n values of 1-4) are very likely derived from amides. The co-existence of three ions, $C_2H_4NO_2^+$, $C_2H_3NO^+$, and CH_4NO^+, serves as an indicator for the presence of amino acids. Additionally, the presence of $C_xH_yN_2^+$ ions indicates the occurrence of 2N-heterocyclic compounds. Notably, an elevated abundance of NH_4^+ is a distinct signature for amines and amino acids, as inorganic ammonium salts produce only negligible amounts of NH_4^+ in HR-AMS. Finally, we quantified the NOON contents in submicron particles (PM_1) and fog water in Fresno, California and PM_1 in New York City (NYC). Our results revealed the substantial presence of amino compounds in both Fresno and NYC aerosols, whereas concurrently collected fog water contained a broader range of NOON species, including N-containing aromatic heterocycle (e.g., imidazoles) and amides. These findings highlight the significant potential of employing the widespread HR-AMS measurements of ambient aerosols and droplets to enhance our understanding of the sources, transformation processes, and environmental impacts associated with NOON compounds in the atmosphere.

New insights into scavenging effect of aerosol species during summer rainfall process in Beijing

Yele Sun[1,2], Yan Li[1,2], Jiaxing Sun[1,2], Yongheng Bi[3], Qingqing Wang[2], Xiujuan Zhao[4], Lu Lei[1,2], Aodong Du[1,2], Zhijie Li[1,2], Zifa Wang[1,2], Xiaole Pan[1], Congzheng Han[3]

[1]*State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China*
[2]*College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China*
[3]*Key Laboratory for Middle Atmosphere and Global Environment Observation (LAGEO), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China*
[4]*Institute of Urban Meteorology, China Meteorological Administration, Beijing 100089, China*

Precipitation is a critical factor in changing aerosol life cycle, yet its impact on aerosol species with different properties in megacities remains unclear. Here we characterized the changes of $PM_{2.5}$ aerosol species during rainfall processes in five summers (2018–2022) in Beijing using highly time-resolved measurements of aerosol chemical speciation monitor along with precipitation. Average pattern of 233 rainfall processes showed that over 30% decreases in aerosol species before rain start were due to the increased wind speed, and the subsequent decreases were caused by the combined effects of precipitation and winds with an average scavenging of 62–100% in 1 h. We also observed very different responses of aerosol species to precipitation depending on intensities, duration and formation mechanisms. During the rainfall processes, aerosol composition showed decreased contributions of organics and sulfate, particularly from late night to morning, while increased contributions of nitrate and chloride due to enhanced gas-particle partitioning associated with the increase of relative humidity and the decrease of temperature. The scavenging rates of aerosol species significantly increased as the increase of rainfall intensity (> 5 mm h^{-1}) and duration (> 4 h). However, the scavenging effect of light rainfall was negligible although the cumulative contribution was ~50% due to high frequency, and even caused increases in nitrate and chloride. The case analysis of aerosol evolution during weak and heavy rainfall events further illustrated the dual impacts of precipitation on aerosol species through wet scavenging and secondary formation.

Differences in chemical composition depending on air mass changes during winter haze episodes in Seoul

Su-Yeon Choi[1], Suk Hyun Lee[1], Won Jae Lee[1], Hyeji Lee[1], Jin-young Kim[1,2], Hwajin Kim[3], Yele Sun[4], Kyung Hwan Kim[1]

[1]*Center for Sustainable Environment Research, Korea Institute of Science and Technology (KIST), Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea*

[2]*Clean Air Center, Korea Institute of Science and Technology (KIST), Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea*

[3]*Department of Environmental Health Sciences, Graduate School of Public Health, Seoul National University, Seoul 08826, South Korea*

[4]*State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China*

We conducted a study on haze episodes occurring in the Seoul Metropolitan Area (SMA) during the winter season to understand the mechanisms behind severe haze events and to differentiate between various episodes resulting from long-range transportation and domestic atmospheric stagnation. Throughout the campaign, aerosols were monitored using a Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM $PM_{2.5}$) positioned atop Mt. Gwanak (629 m), enabling measurements of the upper atmosphere of the SMA. Additionally, high-resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and ToF-ACSM measurements were conducted at the KIST site in Seoul, Korea, and the Beijing site in China through the AMS international network. Air mass monitoring using the ACSM at the Mt. Gwanak site proved effective in capturing and distinguishing haze episodes associated with transported air masses as well as those resulting from predominant domestic atmospheric stagnation, particularly evident in their diurnal patterns during the campaign. Among the observed haze episodes, two out of three were classified as periods dominated by long-range transport, while one was classified as a period dominated by domestic emissions. Episodes dominated by long-range transport exhibited an increased contribution of nitrate, sulfate, and more oxidized Organic Aerosol (MO-OOA), while those dominated by domestic emissions showed a relatively decreased contribution of nitrate and sulfate, and an increased contribution of organic aerosol, particularly primary organic aerosol (POA) such as cooking OA (COA), biomass burning OA (BBOA), and hydrocarbon-like OA (HOA). Notably, the significant contribution of COA during nighttime between 8:00 PM to 12:00 AM accounted for 35 to 60% of the observed Organic Aerosol (OA), underscoring the necessity of efforts to reduce COA emissions in the measurement area.

Session 2: Smog chamber study (15:10-15:35)

Aerosol formation and aging in the ambient air by a quasi-atmospheric aerosol evolution study (QUALITY) chamber

Min Hu[1*], Jianfei Peng[1], Song Guo[1], Zhuofei Du[1], Dongjie Shang[1], Jing Zheng[1], Yusheng Wu[1], Limin Zeng[1], Sihua Lu[1], Shijin Shuai[2], Renyi Zhang[1,3]

[1]*State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China*

[2]*State Key Laboratory of Automotive Safety and Energy, Department of Automotive Engineering, Tsinghua University, Beijing 100084, China*

[3]*Department of Atmospheric Sciences, Texas A&M University, College Station, Texas, USA*

Email: minhu@pku.edu.cn

The QUALITY chamber is quite unique to simulate secondary formation in real ambient air. The performance of the QUALITY is high UV transmission efficiency (50–60%) and negligible wall loss of primary gaseous pollutants. The chamber captures the evolution of ambient conditions, validated by few differences in gaseous pollutants, T and RH between the chamber and the atmosphere.

The applications of the QUALITY chamber are as below:

- Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments (***PNAS***, 2016, 4266–4271).

- Secondary aerosols formation from gasoline vehicles and engine exhausts with different engines (gasoline direct injection and port fuel injection) and fuels. Gasoline aromatic is a critical determinant of urban secondary organic aerosol formation (*Atmos. Chem. Phys.,* 2017, 17, 10743-10752; *Atmos. Chem. Phys.,* 2017, 17, 10333-10348; *Atmos. Chem. Phys.,* 2018, 18, 9011–9023; *J. Environ. Sci.*, 2018, 66, 348-357).

  Remarkable nucleation and growth of ultrafine particles from vehicular exhaust. Photooxidation of vehicular exhaust yields abundant precursors and organics dominate formation of UFPs, it is implicated that the reduction of both primary particles & VOCs from automobile is effective for urban pollution control (PNAS, 2020, 117, 3427-3432).

Session 2: Smog chamber study (15:35-16:00)

A smog chamber study of effects of copper(II) containing aerosol on ozone formation

Kei Sato[1], Yu Morino[1], Yosuke Sakamoto[1,2], Jiaru Li[1,2], Yoshizumi Kajii[1,2,3]
[1]NIES, [2]Kyoto Univ., [3]Qindao Univ.
Email: kei@nies.go.jp

The increase in the ground-level ozone observed in recent East Asia has been suggested to likely result from the decrease in hydroperoxy radical uptake due to the suppression of anthropogenic aerosol emissions. However, to the best of our knowledge, no chamber experiments have validated the model predictions on the reduction of ozone concentration due to the uptake of hydroperoxy radicals. In order to study the effects of aerosol particles on the potential ozone (PO = O_3 + NO_2) concentration, we performed a series of FEP film bag chamber experiments of the VOC-NOx-air-irradiation system in the presence of ammonium sulfate aerosol particles doped with copper(II) sulfate. A solar simulator consisting of xenon lamps and Pyrex filters was used for irradiation. Aerosol particles were generated using an atomizer from aqueous solution; and chamber experiments were conducted at around 50% relative humidity. The potential ozone concentration after six-hour irradiation was reduced with increasing the initial surface concentration of copper-doped aerosol particles under NOx-limited and transition regions. No reduction of potential ozone concentration was observed when copper was not doped with ammonium sulfate aerosol particles. We confirmed that the experimentally measured reduction of the potential ozone concentration by aerosol particles was quantitatively explained by a Master Chemical Mechanism model in which the uptake process of hydroperoxy radical was introduced.

Session 2: Smog chamber study (16:00-16:25)

Physicochemical properties of secondary organic aerosol: phase state and volatility

Ahsan Ali[1], Seonghyun Kim[1], Hyun-Ah Lee[1], Jooyong Lim[1], Muhammad Hamza Zaman[1], Jaewon Lee[1], Ho-Jin Lim[1,*]

[1]*Department of Environmental Engineering, Kyungpook National University, Daegu 41566, Republic of Korea*

[*]*Email: hjlim@knu.ac.kr*

Physicochemical properties, environmental impacts, and formation yield of secondary organic aerosol (SOA) are intricately interconnected. In this study, aromatic SOA was generated and aged both in a smog chamber and a flow reactor under various mixing conditions of volatile organic compounds, NOx, SO$_2$, and NH$_3$ at ~60% RH and 25°C. The phase states and viscosities of SOA, along with SOA containing secondary aerosol were assessed online using a particle rebound measuring system. Additionally, phase transitions during hydration and dehydration were also observed offline using an optical microscopic system for SOA samples collected on a hydrophobic quartz disk employing an impactor. The evaporation profiles of SOA were characterized using a thermodenuder and time-of-flight Aerosol Chemical Speciation Monitor. The vaporization enthalpy of SOA was estimated through the application of the measured profiles to an integrated volume method. The phase states of the measured secondary aerosol were predominantly influenced by its chemical composition, with NH$_4$NO$_3$ notably impacting particle deliquescence. Moreover, the vaporization enthalpy of SOA exhibited upward trend with extended aging time. Predictions suggest that SOA yield tends to increase with a temperature decrease until reaching a plateau around 0°C. Further elaboration on the findings of this study will be provided during the presentation.

Session 2: Smog chamber study (16:25-16:50)

Modeling the influence of chain length and structure on alkane SOA formation

Azad Madhu, Dr. Myoseon Jang
University of Florida

In urban environments, alkanes represent significant proportions of hydrocarbon emissions and have sufficiently low volatility to form secondary organic aerosol (SOA). Existing semi-explicit gas oxidation mechanisms of linear alkanes C9 to C12 were used to parameterize alkane SOA formation via volatility and reactivity based product distributions. The UNIPAR model, equipped with the product distributions, simulated alkane SOA formation via multiphase partitioning and particle phase reactions. To simulate SOA formation of larger linear alkanes (> C12) without gas oxidation mechanisms available, existing product distributions were unified and extended according to an incremental volatility factor. Similarly, unified linear alkane product distributions were also extended to branched alkanes by accounting for a drop in volatility caused by methyl branches. Furthermore, autoxidation was demonstrated to be a key part of atmospheric alkane oxidation which significantly improved linear alkane SOA predictions in comparison to chamber data. Linear and branched alkane SOA yields are demonstrated to increase in lower NO_x conditions but are insensitive to inorganic seed. SOA formation from linear and branched alkanes found in diesel fuel was simulated and shows the significant capability for SOA formation from long-chain linear and branched alkanes.