



Sino-French Joint Workshop on Atmospheric Environment

第8届中法大气环境国际研讨会



November 7th-8th, 2024

BORDEAUX - FRANCE

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Foreword

Clean air is fundamental for maintaining both human health and ecosystems on which our societies rely. However, since the industrial revolution, the quality of the air that people breathe has deteriorated considerably - mainly as a result of human activities such as increased industrial and energy production and traffic, all of which were enabled by the burning of fossil fuels.

The need to reduce outdoor and indoor air pollution has been recognized for several decades and measures have been taken at national and international levels. Despite significant improvements, serious air pollution problems still persist worldwide and are becoming increasingly complex due to local and regional specificities as well as more frequent extreme events linked to climate change (droughts, heatwaves, megafires...).

Consequently, a scientifically sound understanding of the physical and chemical processes affecting air quality and impact on health and ecosystems is more essential than ever to disclose the key reasons for regional complex air pollution problems and for the effective implementation of control measures.

The aim of the Sino-French Joint Workshops on Atmospheric Environment series is to bring together scientists from different fields (chemistry, physics, meteorology, epidemiology,...), industry and representatives of local governments (e.g., cities, regions...), to share their recent progress in research into complex, local, regional and global air pollution.

These conferences have been successfully held since 2008, alternatively in China and France and they have provided the opportunity for fruitful cooperation among interdisciplinary scientists. Most of these workshops led to the publication of dedicated issues of Journal of Environmental Sciences.



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Programme

WEDNESDAY 6TH NOVEMBER 2024

14h00 Welcome to Bordeaux

HOTEL Mercure Bordeaux Château Chartrons
81 cours Saint-Louis, Bordeaux

THURSDAY 7TH NOVEMBER 2024

Place: Espace Beaulieu, 145, rue Saint-Genès, Bordeaux

08h00-08h30 Registration and welcome

08h30-09h00 **Opening ceremony of the 8th Sino-French Joint Workshop on Atmospheric Environment**
Chairs: Christian GEORGE, Yujing MU

Prof. Eric VILLENAVE: Université de Bordeaux

Wahid MELLOUKI: Université Mohammed VI Polytechnique

Prof. Sheng CHEN: Vice President of the Chinese Research Academy of Environmental Sciences/MEE of China

Prof. Fahe CHAI: Chief Scientist of the Chinese Research Academy of Environmental Sciences/MEE of China

SESSION 1, CHAIRS : Wahid MELLOUKI, Hong LI

09h00-09h30 **Tong ZHU** Health Effects of Air Pollution and Climate Change

09h30-10h00 **Tao WANG** Atmospheric reactive halogens reshaped by the clean energy policy on the North China Plain

10h00-10h30 **Jianmin CHEN** Nitrogen-Containing Secondary Aerosol Formation by an on-line VACES

10h30-10h50 Coffee break



SESSION 2, CHAIRS: Véronique DAËLE, Yangang REN

10h50-11h20	Zongbo SHI	Advancing Understanding of Atmospheric Sources and Processes through Machine Learning
11h20-11h40	Min HU	Significant Changes in the Sources and Properties of BC-containing Particles with the Air Pollution Control in Beijing
11h40-12h00	Jianzhen YU	An online instrument for assessing oxidative potential of ambient particulate matter via dithiothreitol assay
12h00-12h15	Marc FADEL	How do different sources impact PM _{2.5} oxidative potential? Insights from four Eastern Mediterranean sites

12h15-14h00 Lunch & Group Photo

SESSION 3, CHAIRS: Eric VILLENAVE, Yanli ZHANG

14h00-14h20	Xinming WANG	Atmospheric Organic nitrogen in the Pearl River Delta region: observations and chamber simulations
14h20-14h40	Likun XUE	Marine formaldehyde and its impacts on secondary aerosols in the coastal atmosphere
14h40-14h55	Rujin HUANG	Chemistry and optical properties of nitrogen-containing organic aerosols
14h55-15h10	Jozef LENGYEL	Uptake and Reactions of Molecules on Hydrated Acid Clusters towards Understanding Aerosol Nucleation
15h10-15h25	Shengrui TONG	The sources and impact on OH radicals of HONO in different atmospheric environment in China

15h25-16h00 Coffee break

SESSION 4, CHAIRS: Christian GEORGE, Lina WANG

16h00-16h30	Sophie SOBANSKA	Evaporation and hygroscopicity properties of single-particle models of SOA
16h30-16h50	Lin DU	Marine aerosol, a good model for multiphase chemistry in the troposphere
16h50-17h05	Liwu ZHANG	Significantly accelerated chemical reactions at the air-water interface of microdroplets
17h05-17h20	Shaojie SONG	Atmospheric Acidity and Interaction with Secondary Aerosols
17h35-17h50	Pengcheng WANG	Gas-phase Kinetics of Criegee Intermediates and their Hydroperoxide products: Expanding the Reactivity Database using a Novel Relative Rate Technique

18h00 Travel together (by Tram B) to Bordeaux Metropole City Hall

19h00 Official Ceremony in the frame of the 60TH Anniversary of Sino-French Relations

20h30 Dinner at the « Comptoir Cuisine » restaurant



FRIDAY 8TH NOVEMBER 2024

Place: Espace Beaulieu, 145, rue Saint-Genès, Bordeaux

08h30-09h00 Late registration and posters

SESSION 5, CHAIRS: Eric VILLENAVE, Lin DU

- | | | |
|-------------|--------------------------|---|
| 09h00-09h30 | Thorsten HOFFMANN | Chemistry in Nanometer Particles: Laboratory Studies on Size-Resolved Chemistry of Organic Model Reactions |
| 09h30-09h45 | Lina WANG | Analysis of Particle Number Size Distribution in Diverse European Monitoring Stations |
| 09h45-10h05 | Emilie PERRAUDIN | LANDEX: a site to study BSOA formation and fate |
| 10h05-10h20 | Defeng ZHAO | Insights into the sources and formation of organic aerosol in Shanghai based on online molecular composition |
| 10h20-10h35 | Yang JIAO | Formation mechanism of H ₂ SO ₄ and its role in the NPF events observed in a sub-urban temperate forest |

10h35-11h00 Coffee break and Poster Session

SESSION 6, CHAIRS: Emilie PERRAUDIN, Liwu ZHANG

- | | | |
|-------------|----------------------|---|
| 11h00-11h20 | Meigen ZHANG | Numerical analysis of aerosol direct and indirect effects on an extreme rainfall event over Beijing |
| 11h20-11h35 | Julien KAMMER | Organic aerosol chemical composition and volatility during ACROSS campaign at PRG urban site in Paris using a CHARON PTR-ToF-MS |
| 11h35-11h50 | Yanli ZHANG | Heatwave Induced Biogenic Volatile Organic Compounds and Their Impacts on Ozone and SOA Formation |
| 11h50-12h05 | Junteng WU | Continuous Variation Of VOCs In A Forest Conservation Area: The Pollution In Saint Paulo Influenced By Biogenic And Anthropogenic Emissions |

12h05-13h45 Lunch and Posters Session

SESSION 7, CHAIRS: Sophie SOBANSKA, Likun XUE

- | | | |
|-------------|--------------------|---|
| 13h45-14h05 | Hongjun MAO | Non-exhaust particulate matter emissions from motor vehicles: current status, trends, and health implications |
| 14h05-14h25 | Lin WANG | Formation of Chlorinated Organic Compounds from Cl Atom-Initiated Reactions of Aromatics and Their Detection in Suburban Shanghai |
| 14h25-14h40 | Qi CHEN | Long-term changes of organic aerosol and the influence of aqueous processing in highly polluted urban environments |



- 14h40-14h55 **Yamina ALLOUCHE** A Comprehensive Study of Carbonaceous Species in PM2.5 and their Origins at an urban site in northern France
- 14h55-15h10 **Shuangxi FANG** How about the representative of our atmospheric observations: A comparison at three sites in the megacity of Hangzhou, China
- 15h10-15h25 **Damien BAZIN** Development, optimization and validation of automated volatile organic compound data analysis using an on-line thermal desorption gas chromatograph with dual detection and application to measurements in ambient air

15h25-15h40 Coffee break

SESSION 8, CHAIRS: Wahid MELLOUKI, Jianmin CHEN

- 15h40-16h00 **Yinchang FENG** Development and Prospects of Source Apportionment Techniques for Air Pollution in China
- 16h00-16h20 **Jian GAO** Experience and Implications in Air Pollution Prevention and Control in China
- 16h20-16h35 **Xiaobing PANG** Unmanned aerial vehicles equipped with sensor packages to study spatiotemporal variations of air pollutants in industry parks
- 16h35-16h55 **Shansi WANG** Current and future prediction of inter-provincial transport of ambient PM2.5 in China

16h55-17h15 **1-Minute poster presentation**

17h15-17h35 **Closing ceremony**

Dr Emilie Perraudin: Université de Bordeaux

Prof. Jianmin Chen: Executive Vice President of the Institute of Atmospheric Sciences, Fudan University

16h50- 19h00 Poster Session and Cocktail

20h00 Dinner at the « Café maritime » restaurant

SATURDAY 9TH NOVEMBER 2024

Visit of CNRS and University facilities

SUNDAY 10TH NOVEMBER 2024

Departure



Abstracts – Orals

Long-term changes of organic aerosol and the influence of aqueous processing in highly polluted urban environments

Qi Chen^{1*}, Ruqian Miao¹, Yan Zheng¹, Theodore Koenig¹, Guannan Geng², Manish Shrivastava³, Qi Zhang⁴, Xu Dao⁵, Guigang Tang⁵, Bingye Xu⁶, Rujin Huang⁷, Hao Wang¹, Xi Cheng¹, Yanli Ge¹, Shiyi Chen¹, Liming Zeng¹, Song Guo¹, Min Hu¹, Tong Zhu¹

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High concentrations of organic aerosol (OA) occur in Asian countries, leading to great health burdens. Clean air actions have resulted in significant emission reductions of air pollutants in China. However, long-term changes in OA and their causes remain unknown. Here, we present both observational and model evidence demonstrating widespread decreases with a greater reduction in primary OA than in secondary OA (SOA) in China during the period of 2013 to 2020. Most of the decline is attributed to reduced residential fuel burning. We find the interannual variability in SOA may have been driven by meteorological variations and contrasting effects of reducing NO_x and SO₂ on SOA production which is associated with the changes of atmospheric oxidative capacity and aqueous processing of SOA. By examining collocated aerosol mass spectrometer (AMS) and iodide chemical ionization mass spectrometer (CIMS) observations in winter 2022 and summer 2023 in Beijing, different aqueous pathways of SOA are discovered. These pathways contribute significantly to the SOA mass in highly polluted urban environments. The underlying drivers of aerosol physical properties, chemistry and gaseous precursors for these aqueous pathways are different, highlighting the need of efforts to understand, predict, and mitigate the contributions of aqueous processing to OA.

Atmospheric Reactive Halogens Reshaped by the Clean Energy Policy on the North China Plain

Xiaorui Chen^{1,a}, Yifan Jiang¹, Zheng Zong^{1,b}, Yanan Wang¹, Yang Wang², Men Xia³, Liwei Guan², Pengfei Liu², Chenglong Zhang², Jianmin Chen⁴, Yujing Mu², Tao Wang^{1*}

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Abstract

The widespread presence of reactive halogen species (RHS) in the atmosphere has garnered global attention given their critical roles in air pollution and climate change. Observational evidence shows that elevated RHS levels in the continental boundary layer are largely attributed to anthropogenic activities such as coal and biomass burning, especially on the North China Plain (NCP) during winter. Over the past 10 years, the Chinese government has enacted various mitigation measures to control the emissions of air pollutants, including a clean energy initiative on the NCP. Despite the success of these measures in mitigating nitrogen and sulphur pollutants, their impact on RHS has yet to be investigated. Here, by revisiting a site where unexpectedly high RHS levels were observed, we show that the clean energy policy has effectively eliminated reactive bromines such as BrCl and Br₂, but high levels of reactive chlorine persist, partially owing to the effect of chlorine-based fertilisers commonly used in agriculture. Moreover, recent changes in aerosol acidity and the NO₃ production rate have reshaped the atmospheric chlorine chemistry, leading to a large increase in the production of ClNO₂. The high levels of ClNO₂ (averaging 150 pptv and peaking at 3.8 ppbv) accounted for 43% of the oxidation of alkanes, increased the levels of conventional radicals (OH, HO₂, RO₂) by 8%–23%, and increased net ozone production by 16%. Our findings highlight the continuing importance of chlorine in aggravating secondary pollution on the NCP and emphasize the need to consider crop fertilisation as a potentially important source of chlorine in the context of air pollution control.

Nitrogen-Containing Secondary Aerosol Formation by an on-line VACES

Jianmin Chen¹, Xiaona Shang¹, Munira Abdumutallip¹, Haiping Xiong¹, Christian George², Wahid Mellouki³

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Nitroaromatic compounds (NACs) have significant impacts on air quality, climate, and public health. These aerosols deteriorate aerosol particle characteristics and considerably contribute to secondary organic aerosol (SOA) formation. Here, in application of versatile aerosol concentration enrichment system (VACES) coupled with HPLC-Q-TOF-MS as well as a non-target screening approach of chromatogram-mass spectra were used for a semi-continuous study of the chemical characteristics and potential formation of reduced NOCs was conducted at Shanghai. Our results shows that NOCs account for a large proportion (>60%) of urban atmospheric organic aerosol, of which compounds with O/N<3 compounds being main contributors (>70%). The observed preference in positive ionization mode, indicates that these NOCs mainly consist of reduced NOCs in our study.

Seven types of common reduced NOCs qualitatively identified during autumn and winter aerosols were rich in CH₂ long-chain homologous characteristic compounds. Alkyl, cyclic, and aromatic amide were found in CHON compounds, whilst heterocyclic or cyclic amines, and aniline homolog series were found in CHN compounds, both of which are believed to be related to anthropogenic activities such as combustion, manufacture, and tire-wear-derived organic chemicals. We conclude that both primary emission and ammonium chemistry (e.g., amination) may play the significant role in reduced NOCs compounds pollution.

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References:

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Xiaona Shang, Huihui Kang, Yunqian Chen, Munira Abdumutallip, Ling Li, Xiang Li, Hongbo Fu, Xiaofei Wang, Lin Wang, Xinke Wang, Huiling Ouyang, Xu Tang, Hang Xiao, Christian George, Jianmin Chen. PM1.0-Nitrite Heterogeneous Formation Demonstrated via a Modified Versatile Aerosol Concentration Enrichment System Coupled with Ion Chromatography. Environ. Sci. Technol. 2021, 55, 9794–9804

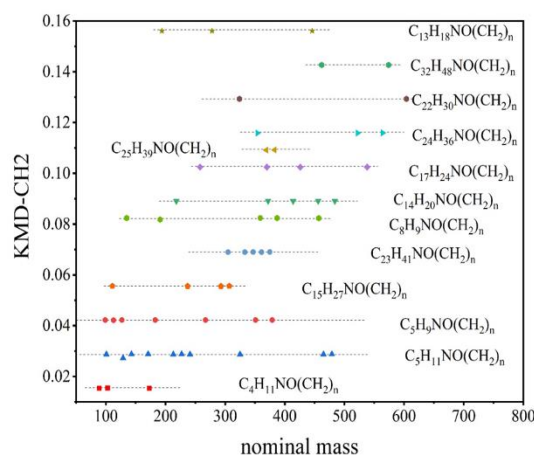


Fig. 1 KMD-CH₂ of PM_{2.5}-

Advancing Understanding of Atmospheric Sources and Processes through Machine Learning

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The availability of long-term, high-resolution atmospheric data has created vast datasets that are challenging to process with traditional statistical methods. These datasets often involve complex, nonlinear relationships, making machine learning (ML) techniques particularly well-suited for their analysis. Therefore, ML approaches are increasingly applied in atmospheric science to better understand sources and processes, offering enhanced capabilities for analyzing and predicting intricate atmospheric phenomena that traditional methods struggle to handle efficiently. This shift improves both the precision and insight into atmospheric data interpretation.

In this presentation, I will give two examples to demonstrate the application of ML techniques

- 1) **Aerosol sources and processes:** By developing machine learning models based on long-term data on aerosol size distributions, chemical compositions, and meteorological conditions, we uncovered the nonlinear relationships between particle numbers from different sources such as sea salt, dust, and anthropogenic particles, and meteorological factors like temperature, solar radiation, and wind speed. These factors regulate the seasonal variations of aerosol sources. This method, particularly when combined with receptor modeling, has proven to be a powerful tool for better understanding and predicting aerosol dynamics (Song et al., 2023).
- 2) **Air quality trend analysis:** Machine learning algorithms can be used to decouple meteorological effects from emissions, enabling a clearer understanding of trends in air pollutant concentrations (Grange et al., 2018). By "weather normalizing" pollutant data, these models provide more accurate assessments of the impact of interventions, such as clean air zones and clean heating policies, on air quality (Shi et al., 2021; Song et al., 2023). Together with synthetic control method, this approach helps in isolating the true effects of human interventions on air pollutant levels by removing the variability introduced by weather patterns and natural trends, leading to more reliable policy evaluations and decision-making (Shi et al., 2021; Song et al., 2022, 2023; Liu et al., 2023).

Finally, using the above examples, I will discuss both the advantages and limitations of applying machine learning (Messeri and Crockett, 2024) in the context of atmospheric research.

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References:

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- 2) Liu, B., 2023. *Environmental and Resource Economics*, 86, 203-231.
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Significant Changes in the Sources and Properties of BC-containing Particles with the Air Pollution Control in Beijing

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During the past ten years the ambient air quality in China has improved significantly under strict emission controls, such as “The Action Plan on Prevention and Control of Air Pollution” (2013~2017) and the “Three-year Action Plan to Fight Air Pollution” (2018~2020). Black carbon (BC), as a short-lived climate forcer, profoundly impacts the air quality and climate. It is necessary to understand the variations of the sources and the properties of BC-containing particles with the air pollution control in Beijing.

In our study, long term trend (2013 - 2022) of BC levels and sources in Beijing are analyzed based on the measurements of a seven-wavelength Aethalometer (AE31, Magee Scientific). It shows that a decrease in BC concentrations from $2.23 \pm 1.94 \mu\text{g m}^{-3}$ in 2013 to $0.84 \pm 0.71 \mu\text{g m}^{-3}$ in 2022 with a large reduction of 62%. Reductions in BC have been observed from both biomass burning and fossil fuel sources, decreasing from $0.50 \pm 0.60 \mu\text{g m}^{-3}$ and $1.73 \pm 1.62 \mu\text{g m}^{-3}$ to $0.11 \pm 0.15 \mu\text{g m}^{-3}$ and $0.74 \pm 0.64 \mu\text{g m}^{-3}$, respectively. The decrease in BC from biomass burning is more substantial, with an 78% decrease. We also characterized the chemical compositions and size distributions of BC-containing particles during the cold season of 2022 in Beijing. The optical properties of BC-containing particles were further calculated based on the Mie theory, compared with the results of previous studies. The diameters of BC cores became larger while the coating thickness of BC-containing particles became thinner, the mass fraction of nitrate increased obviously, and even replaced organic matter as the dominant component. Variations in chemical compositions and size distributions resulted in lower mass absorption cross-sections (MAC) of BC-containing particles. Our results demonstrate the synergistic benefits of air pollution control in improving air quality and mitigating climate change.

An online instrument for assessing oxidative potential of ambient particulate matter via dithiothreitol assay

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The oxidative potential (OP) of airborne particulate matter (PM) is a valuable metric for assessing PM toxicity. Here we present an online system capable of measuring OP using the acellular dithiothreitol (DTT) assay with hourly resolution. The system consists of a particle-into-liquid sampler (PILS) as online sampling component, a solution distribution, mixing and heating module, and a miniature spectrometer. Compared with existing automated systems described in the literature, our design is simpler, less expensive, and easier to maintain. The improved features are realized through using a more durable visible light source and a simpler flow cell. The system provides a limit of detection of 0.027 $\mu\text{M}/\text{min}$ or 0.84 $\text{nmol}/\text{min}/\text{m}^3$, based on measurements of ambient blank samples. During a field deployment with hourly $\text{PM}_{2.5}$ in the range of $\sim 2\text{-}31 \mu\text{g}/\text{m}^3$, it enables determination of 99.9% of hourly samples ($N=704$) above detection limit. Compared to previous systems, our system provides comparable precision ($\text{CV}=2\text{-}8\%$) and better consistency with offline method (slope: 1.06, intercept: -0.02, R^2 : 0.99). Additionally, the system requires less frequent maintenance (weekly), making it more desirable for field deployment. We field-tested the system for one-month at a suburban site in Hong Kong. The average field blank corrected OP was $3.18 \pm 2.20 \text{ nmol}/\text{min}/\text{m}^3$, corresponding to ambient $\text{PM}_{2.5}$ concentrations averaged at $10.5 \pm 6.1 \mu\text{g}/\text{m}^3$. Over the $\text{PM}_{2.5}$ mass range encountered, the relationship between OP and $\text{PM}_{2.5}$ exhibited an increasing trend of OP with $\text{PM}_{2.5}$ up to $\sim 13 \mu\text{g}/\text{m}^3$, after which it reached a plateau. Within a narrow $\text{PM}_{2.5}$ mass bin of $5 \mu\text{g}/\text{m}^3$, considerable sample-to-sample variation in OP was observed. The system effectively captured a rapid rise in OP as the dominant wind direction shifted from southerly, bringing in clean marine air, to northerly, transporting polluted air. We have demonstrated the adequate sensitivity of our system for monitoring OP of ambient $\text{PM}_{2.5}$ at an hourly resolution. By offering real-time measurements, this system has the potential to enhance our understanding of the dynamic nature of PM toxicity and its implications for human health.

How do different sources impact PM_{2.5} oxidative potential? Insights from four Eastern Mediterranean sites

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Exposure to ambient particulate matter (PM) has been linked to diverse respiratory and cardiovascular diseases, with oxidative stress identified as a key biological mechanism through which PM induces adverse health effects¹. Consequently, the assessment of the oxidative potential (OP), defined as the capacity of PM to invoke oxidative stress, has become widely acknowledged as a proxy for aerosol toxicity².

In this study, the OP of PM_{2.5} was evaluated using dithiothreitol (DTT) and ascorbic acid (AA) assays on nearly 300 samples collected from 4 sites in Lebanon, an East-Mediterranean country: Zouk Mikael (ZK), an urban site under the influence of the biggest power plant in the region which runs on heavy fuel oil (HFO); Fiaa (FA), a rural site; USJ, a sub-urban site; and Hersh (HR) a residential urban site, characterized by high traffic density. Moreover, all the samples were characterized for their carbonaceous, inorganic, and organic fractions. Several tracers were gathered into the USEPA-Positive Matrix Factorization model (PMF) in order to identify possible emissions sources and quantify their contribution. A multiple linear regression approach was applied to the contribution of the sources obtained by PMF and the OP values at the different sites in order to estimate the contribution of PM sources to OP values.

The mean volume normalized OP-AA values (in nmol·min⁻¹·m⁻³) were 0.65 ± 0.29 at ZK, 0.41 ± 0.26 at FA, 0.81 ± 0.34 at HR, and 0.73 ± 0.26 at USJ. As for OP-DTT, the mean values (in nmol·min⁻¹·m⁻³) were 0.49 ± 0.26 at ZK, 0.26 ± 0.12 at FA, 0.36 ± 0.16 at HR, and 0.32 ± 0.17 at USJ. Moreover, the highest intrinsic OP values among the 4 sites and for the two assays were observed for traffic non-exhaust, biomass burning, and HFO combustion sources. As for the OP apportionment, crustal dust source, considered as one the major PM_{2.5} sources at the 4 sites (contributing between 12 and 27%), does not highly contribute to OP values (between 0 and 9% for OP-AA_v and between 0.1 and 7% for OP-DTT_v). A remarkable contribution of the ammonium sulfate source to OP (between 2 and 30% for OP-AA_v and between 11 and 32% for OP-DTT_v) was highlighted and possibly due to the presence of carbonaceous species in the profile of this source. On the other hand, local anthropogenic sources (namely biomass burning, exhaust and non-exhaust road traffic, and HFO combustion) contribute the most to the OP-AA_v (30-67%) and OP-DTT_v (36-80%).

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Atmospheric Organic nitrogen in the Pearl River Delta region: observations and chamber simulations

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Organic nitrogen (ON) is a crucial component of atmospheric organic compounds that significantly impacts both air quality and climate. However, it remains one of the least understood in terms of its chemical composition, sources, and atmospheric fate. In this study, we measured bulk ON in PM_{2.5} as well as in dry and wet depositions in the Pearl River Delta (PRD). Our results reveal that water-soluble ON (WSON) constitutes, on average, 26% and 31% of the dry and wet deposition water-soluble nitrogen, respectively, and 12-29% of water-soluble total nitrogen (WSTN) in PM_{2.5}. PMF source apportionment indicates that PM_{2.5}-bound ON originates primarily from vehicle exhaust, biomass burning, and secondary formation. Additionally, we characterized ON in fresh emissions from vehicle exhaust using tunnel and chassis dynamometer tests, as well as in the plume of open burning of crop residues. Ambient PM_{2.5} samples were analyzed using advanced techniques such as FT-ICR-MS. The results highlighted that nitrated aromatic compounds alone pose potential health risks comparable to or even exceeding those of polycyclic aromatic hydrocarbons (PAHs). To further investigate ON evolution, we introduced vehicle exhaust and biomass burning plumes into a smog chamber, simulating photochemical aging. Chamber experiment results were utilized to explain the spatial-temporal variations and sources of ON, particularly the hazardous nitrated aromatic compounds observed in PM_{2.5} in the PRD region.

Algae emissions of formaldehyde and nitrous acid and their significance to marine atmospheric chemistry

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Formaldehyde (HCHO) and nitrous acid (HONO) are essential components of the troposphere, playing a crucial role in determining the atmospheric oxidation capacity. Consequently, they play a pivotal part in determining the fate of various air pollutants and greenhouse gases. Although the sources of these compounds on land have been extensively studied, their marine emissions remain poorly understood. In this study, we aim to quantify the emissions of HCHO and HONO from algae by conducting high-resolution field observations and chamber experiments, with *Enteromorpha* serving as a representative algae species. Our results confirm significant emissions of HCHO, HONO, and volatile organic compounds (VOCs) resulting from the photodecomposition of *Enteromorpha*. Additionally, we identify the source intensities and influencing factors of these emissions. These marine-emitted reactive compounds can significantly contribute to the oxidation capacity of the atmosphere and the formation of ozone and secondary aerosols in coastal regions, as demonstrated by detailed multi-phase chemical box modeling simulations. This study highlights the intense emissions of highly reactive substances from the ocean, which can profoundly impact atmospheric chemical processes.

Chemistry and optical properties of nitrogen-containing organic aerosols

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Nitrogen-containing organic compounds (NOC) are a group of key species in organic aerosols (OA), which affect atmospheric physicochemical properties and climate. The species and formation processes of NOC, however, are still not well understood. In this study, we report the optical properties, chemical composition, and formation processes of NOC (including nitroaromatics, N-heterocyclic compounds, and organic nitrates) in urban fine particles. Nitroaromatics are the main light-absorbing NOC quantified in urban PM_{2.5}, and the seasonal variations of their chemical composition, sources and contribution to light absorption of OA are discussed. Nitrate-mediated photooxidation of nitroaromatics (including 4-nitrocatechol, 3-nitrosalicylic acid and 3,4-dinitrophenol) in aqueous phase under different pH and temperature conditions are also studied. The dynamic changes in light absorption of nitroaromatics during photolysis are measured, and the photolysis rates and products of nitroaromatics are further characterized. The photolysis rate of nitroaromatics generally increases with the increase of temperature. The photooxidation of nitroaromatics starts with the addition of -OH or/and -NO (-NO₂) groups to aromatic ring, followed by further ring-opening of aromatic ring with the formation of smaller, highly oxygenated molecules. Besides, the nighttime formation processes of secondary organic nitrates are investigated based on size-resolved aerosols measured in urban PM_{2.5} with a soot particle long-time-of-flight aerosol mass spectrometer. Aqueous processing plays an important role in the nighttime formation of particulate secondary organic nitrates in large size particles, especially in fog-rain days. N-heterocyclic compounds from aqueous reaction of dicarbonyls with amines and ammonium under different pH are also studied. 155 newly N-heterocyclic compounds are identified and mainly involve four formation pathways.

Uptake and Reactions of Molecules on Hydrated Acid Clusters towards Understanding Aerosol Nucleation

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Aerosol particles represent one of the most important, yet possibly the least understood, components of our atmosphere. They play a significant role in global warming, influence atmospheric chemistry by participating in heterogeneous reactions, and severely impact human health in polluted areas. It is, therefore, essential to understand aerosol formation and growth in great detail, particularly by uncovering the molecular mechanisms by investigating collisions between gas-phase molecules and small particles.

In this context, we have developed a new approach to quantify the uptake process of various molecules by hydrated nitric acid clusters, providing direct information about their sticking efficiency.^[1,2] Our molecular beam experiment combines cluster mass spectrometry with cluster velocity measurements. However, the determination of relative uptake cross sections from the experimental data relies on simplifying assumptions about molecule-cluster collisions. To support these assumptions, we performed detailed molecular dynamics simulations, enabling us to identify the underlying processes in our experiment.^[3]

In the experiment, we investigate the uptake of different volatile organic compounds by hydrated nitric acid clusters. In parallel to the experimental work, we conduct extensive molecular dynamics simulations of the molecule-cluster collisions. These simulations provide detailed insights into various processes such as fly-by, elastic and inelastic scattering, uptake, and the evaporation of water or adsorbed molecules from the cluster. This combined approach allows us to evaluate the scattering and uptake processes during collisions, and subsequently derive uptake cross sections for comparison with experimental values.

In this contribution, we explore the relationship between uptake and carbon chain length, the position of the O—H group, and alkyl chain branching. Particular attention is given to the effect of different functional groups on sticking efficiency. The integration of experimental results with molecular dynamics simulations provides a detailed understanding of the dynamics involved in molecule-cluster collisions.^[3,4] The next step is to translate the molecular-level understanding to macroscopic experiments and field observations.

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The sources and impact on OH radicals of HONO in different atmospheric environment in China

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Gaseous nitrous acid (HONO) is one of the most important sources of atmospheric hydroxyl radicals ($\text{OH}\cdot$), which leads to the formation of secondary pollutants, enhances the ability of atmospheric oxidation and drives the formation of haze. Due to the lack of on-line instruments for accurately detection of related nitrogen-containing species, the main HONO sources are unclear, which results in the inability to accurately estimate the atmospheric oxidation. Comprehensive field observations for HONO and related species were conducted under different environmental conditions by different anthropogenic activities (megacity Beijing, Sanmenxia, suburban Xianghe, and rural Wangdu). Combined with Box model simulation (MCM), the relationships of HONO with haze pollution have been deduced, and their impacts on atmospheric $\text{OH}\cdot$ also were investigated. The significant contribution of coal combustion in rural areas to atmospheric HONO levels were confirmed. It has also been found that HONO can be directly emitted from industrial coal combustion in the Sanmenxia, while vehicle emissions in Beijing urban areas contribute more significantly to HONO levels, and specific calculation methods for different combustion sources of direct HONO emissions have been proposed. It has been found that the efficiency of NO_2 heterogeneous conversion to HONO has an optimal temperature ($\sim 10^\circ\text{C}$), and considering the promoting effect of the optimal temperature significantly improves the simulation results of HONO at night. By analyzing the HONO concentrations during four severe haze events in Beijing winter, it has been discovered that NH_3 concentration, relative humidity, and particulate matter concentration in the actual environment contribute significantly to the heterogeneous formation of HONO. New parameterization scheme has been developed, significantly improving the accuracy of simulating HONO and OH radical concentrations during haze pollution periods.

Evaporation and hygroscopicity properties of single-particle models of SOA

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It is now well known that atmospheric aerosols have a major impact on air quality and climate change. Among them, secondary organic aerosols (SOA) are formed *in situ* into the atmosphere following the gas-phase oxidation of volatile organic compounds (of anthropogenic and biogenic origin) by the main atmospheric oxidants such as ozone, hydroxyl and nitrate radicals. The secondary organic aerosol can then evolve during its transport in the atmosphere according to various physical and/or photochemical aging processes. These aging processes have an impact on the physico-chemical properties of aerosols, such as their hygroscopicity, viscosity and optical properties.

Water is ubiquitous in the atmosphere. By absorbing water, aerosols can act as condensation nuclei (CCN) and induce cloud formation, affecting the Earth's radiation balance. The liquid water content of aerosols, which varies according to the relative humidity of the surrounding gas phase, governs phase transitions, liquid-gas partitioning, absorption of trace gases (reactive or not), multiphase reactions and the microphysical properties of particles. Surface properties of atmospheric particles, such as surface tension, can directly affect a particle's interactions with water vapour and thus its activation into cloud droplets. However, the complexity of aerosol aging processes occurring at the gas/particle interface is not yet well described. Recent developments using single-particle approaches are making it possible to study various aging processes and microphysical properties at the particle scale.

In this context, we have studied the evaporation and hygroscopicity properties of single particles, composed of mixtures of biogenic AOS evolution marker compounds (such as MBTCA - 3-methylbutane-1,2,3-tricarboxylic acid) - and inorganic salts, using an acoustic levitator coupled to an optical camera and a Raman microspectrometer. The experimental results obtained were compared with thermodynamic models (d^2 law, Köhler-based theories) to gain a better understanding of the influence of different environmental parameters on the physico-chemical properties of aerosols and, in particular, SOA.

Acknowledgments

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Marine aerosol, a good model for multiphase chemistry in the troposphere

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Marine aerosols, including sea spray aerosols (SSA) and secondary marine aerosols formed by oxidation of volatile organic compounds (such as dimethyl sulfur and isoprene), are ideal candidates in tropospheric multiphase chemistry. The multiphase reactions of SO₂ on the surface of marine aerosols would lead to chlorine depletion of SSA particles. Our study showed that chlorine depletion increased as the concentration of SO₂ increased. In addition, the addition of dimethyl sulfide will further increase the degree of chlorine depletion. SO₂ and NO₂ also have nonlinear effects on the transformation of marine aerosols. NO₂ affects the gas phase mechanism, and SO₂ affects the particle phase mechanism. Under the condition of high relative humidity, the occurrence of heterogeneous reactions of marine aerosols was promoted. It is showed that high relative humidity will increase the particle formation yield, change the reaction path, and increase the liquid phase oxidation. We also investigated key chemical processes at the air-water interface, such as interaction between surface-active substances and persistent organic pollutants and soluble saccharides, which can interact with the surface-active substances to achieve the enrichment in marine aerosols. This interaction can facilitate its air-sea transport and transfer to inland and polar regions. The introduction of persistent organic pollutants also changes the arrangement of the organic film at the SSA interface, which in turn affects a series of heterogeneous chemical processes that occur at the interface.

Significantly accelerated chemical reactions at the air-water interface of microdroplets

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Aerosol particulate matter pollution poses a serious threat to air quality and human health. Currently, the characteristics of air pollution in China are shifting from primary pollution to secondary pollution, and atmospheric interface processes are an important pathway for the generation of secondary components of aerosols. However, due to technological limitations, the study of microscale interface phenomena faces many challenges.

In recent years, our team has focused on the chemical processes of aerosol gas-liquid interfaces, developed spectroscopic measurement and imaging methods for micro interfaces, and analyzed the formation mechanism of secondary pollutant interfaces at the molecular level. The main innovative achievements include: 1) the creation of a single particle micro interface stimulated Raman spectroscopy imaging method, which achieves high-speed imaging and pH gradient distribution at the interface of micro droplets; 2) It was found that the photochemical reaction rate at the interface of micro droplets far exceeded that of the bulk phase, quantitatively revealing the gas mass transfer, chemical enrichment, and electric field effects at the gas-liquid interface; 3) The spontaneous electric field at the interface is proposed as an important driving force for the rapid formation of secondary pollutants. It was found that the semi solvation effect at the gas-liquid interface significantly accelerates atmospheric photochemical reactions, and the atmospheric chemistry model was revised accordingly.

The above findings reveal the particularity of atmospheric gas-liquid interface processes from a microscopic perspective, providing a new perspective for a deeper understanding of secondary air pollution and having important scientific significance for precise control of particulate matter pollution.

Atmospheric Acidity and Interaction with Secondary Aerosols

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Acidity (typically referred to as aerosol acidity and cloud water acidity) is a central component of atmospheric aqueous chemistry. While conventional techniques have proven effective in quantifying cloud pH, their applicability to aerosol water acidity remains limited. Presently, direct methodologies for assessing aerosol pH, although under continuous refinement, are not yet ubiquitously adopted for field measurements. In addressing this gap, thermodynamic equilibrium box models have emerged as pivotal tools, facilitating the estimation of chemical species partitioning across distinct phases—solid, liquid, and gas—and subsequently enabling precise aerosol pH calculations. However, recent discussions underscore substantial discrepancies in aerosol water pH estimates, particularly evident during winter haze episodes in the North China Plain. This study provides an in-depth examination of the computational methods and applicability of the typical thermodynamic models such as ISORROPIA and E-AIM. Notably, reverse (using only aerosol composition as input) calculations, predicated solely on aerosol composition, have exhibited sensitivity to inaccuracies in ion measurements, necessitating cautious interpretation. And aerosol phase state does not have a significant effect on aerosol water pH. Furthermore, multiphase buffering theory elucidates the dynamic pH variability within aerosols, with the $\text{NH}_4^+/\text{NH}_3$ (ammonium/ammonia) acid-base pair assuming a predominant buffering role within densely populated continental regions. Concurrently, ongoing research endeavors have sought to delineate the consequential effects of acidity on secondary aerosol, including sulfate, nitrate, and organic sulfur compounds, underscoring the intricate interplay between aerosol composition and environmental factors.

Gas-phase Kinetics of Criegee Intermediates and their Hydroperoxide products: Expanding the Reactivity Database using a Novel Relative Rate Technique

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Ozonolysis, wherein alkenes undergo 1,3-cycloaddition by ozone, produces a variety of carbonyl oxides, commonly known as Criegee intermediates (CIs). These CIs are reactive species that can insert into labile hydrogenous bonds, such as those present in organic acids, alcohols, amines, sulphides and even water. Such insertion reactions lead to highly functionalized hydroperoxides could help produce secondary organic aerosol. Despite the importance of this class of reactions, there is still a lot that remains unknown about the kinetics in these systems. This is partly because of the limitations of current absolute kinetic methods, which rely on gem-diiodoalkane CI precursors, which are for the most part commercially unavailable, and possess low vapour pressures. A second consideration is that current absolute kinetic methods require a large excess of organic co-reactant. Both of these factors conspire to limit the size and volatility of reactants that can be studied, which could limit our atmospheric understanding.

For this reason, a relative rate methodology has been developed, in which chamber facilities (in this case, the HELIOS chamber at CNRS-Orléans) can be used to acquire kinetic data for a large variety of CI-co-reactant combinations. CIs are generated in-situ via classic ozonolysis reactions, where the use of symmetric, well-characterized alkene precursors and radical scavengers allows for unambiguous determination of rate coefficients. Peroxidic products can be synthesized in-situ through ozonolysis and characterized using high-resolution time-of-flight proton-transfer reaction mass spectrometry. We demonstrate how variations in structure and substitution affect the reactions between Criegee intermediates and a series of alcohols and organic acids. Additionally, we selected representative hydroperoxides to study their insertion reactions with CIs and their subsequent oxidation by OH radicals. Here, we are able to explore the gas-phase kinetic information of these highly functionalized compounds, which may help explain the special capacity of ozonolysis reactions to produce secondary organic aerosol under atmospheric conditions.

Chemistry in nanometer particles: laboratory studies on size-resolved chemistry of organic model reactions

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The formation of new particles and their subsequent growth in the troposphere are important processes that influence the composition of the atmosphere and global climate change. After the formation of nanoparticles by nucleation, their growth is determined by organic molecules. Currently, the formation of the extremely low volatility compounds required for the growth of nanoparticles is mostly discussed on the basis of gas-phase chemistry. However, the particle embryos themselves provide a unique nanoscale environment that can influence chemical reactions within the newly formed condensed phase. One of these peculiarities is the Laplace pressure in very small particles, which is caused by the surface tension of the interface between the particle and the gas phase. However, not only pressure-dependent reactions can be influenced by the size of the aerosol particles. Differences in surface-to-volume ratio, interface curvature, and length of diffusion paths can also influence dynamic equilibrium reactions (condensation reactions), which also lead to high-molecular-weight compounds. The contribution discusses laboratory results of these and similar reactions using an online CI-Orbitrap MS system.

Analysis of Particle Number Size Distribution in Diverse European Monitoring Stations

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Particle Number Size Distribution (PNSD) is crucial for evaluating air quality and environmental pollution, with various impacts of different particle sizes on human health and climate,. Additionally, PNSD exhibits significant spatiotemporal variability, attributable to the diverse sources and transformations of particulate matter during transport. This study analyzed hourly PNSD data from 30 environmental air monitoring stations across Europe, encompassing rural, urban, mountainous, and suburban areas. The data were parameterized using a multi-log-normal distribution model to examine three size modes: nucleation mode, Aitken mode, and accumulation mode, revealing temporal trends in particle sizes.

Results indicate that the distribution of PNSD is influenced by site type and anthropogenic factors, with variations in particle concentrations observed across different locations. Seasonal and diurnal changes, as well as differences between weekdays and weekends, reflect shifts in emission sources and particle characteristics.

This research underscores the importance of ground-based monitoring for understanding aerosol properties and supports the development of global observational networks. Such networks enhance spatial coverage and provide essential data for effective pollution control policies.

LANDEX: a site to study BSOA formation and fate

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The aim of this presentation is to outline the characteristics required for a measurement site to investigate, in ambient air, the physico-chemical processes involved in the formation and ageing of secondary organic aerosols (SOA) at the molecular scale. Generally speaking, given (i) the extreme complexity of atmospheric reaction mixtures, (ii) the continuous variability of experimental conditions (temperature, relative humidity, concentrations of oxidizing species and air mass turbulence etc.) and (iii) the impossibility of repeating experiments by choosing the parameters to be varied, field studies at the molecular scale represent a real challenge to describe the chemical reactions at work in the atmosphere. Considering more specifically the multiphase processes (gaseous, gas-solid, gas-liquid, condensed phases) involved in the reactivity of SOA, the difficulties are even larger. Nevertheless, it seems essential, in order to ensure understanding these processes, to compare their description when studied in controlled and simplified environments such as reactors (flow or quasi-static) or atmospheric simulation chambers, with the measurements obtained in the real atmosphere.

These considerations will be illustrated by the example of the LANDEX site located in the Landes forest in southwestern France. The Landes forest is a man managed-forest planted almost exclusively with maritime pines, resulting in specific high monoterpene (mostly α - and β -pinene) and very poor isoprene emissions. As it may also benefit from strong solar irradiation, sea spray inputs as well as air masses weakly impacted by anthropogenic emissions, the LANDEX site can be considered as an open-air laboratory to study biosphere-atmosphere interactions and more specifically biogenic SOA formation and fate at the molecular level. The relevance of this site to document scientific questions related to BSOA will be illustrated by some major results obtained over the last 10 years as well as some future outlooks

Insights into the sources and formation of organic aerosol in Shanghai based on online molecular composition

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Organic aerosol (OA) constitutes a major fraction of particulate matter in the atmosphere. Its source apportionment is key to understand the formation and air pollution control for policy makers. However, the detailed sources of OA particularly in megacities remain challenging due to lack of information of chemical composition of OA at molecular level. Particularly, specific precursors and formation processes of secondary organic aerosol (SOA) remain largely unclear. In this study, we measured chemical composition of OA at molecular level using extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) in Shanghai and investigated the sources of OA. More than 1000 organic species were detected. Twelve sources (factors) are determined on mass spectra by Positive Matrix Factorization (PMF), of which seven factors are identified as POA including OA from cooking, cigarette smoking, biomass burning, plastic burning, and special events and five factors as SOA. POA sources are identified its source based characteristic tracers and time series. SOA sources are identified by linking to their precursors and processes based detailed mass spectra, their time series, and concomitant measurement of physiochemical parameters and gas-phase species, particularly VOCs. The results of source apportionment indicate that both POA and SOA contribute significantly to OA in winter at urban Shanghai. Online molecular composition in this study reveals under-appreciated sources and processes of OA in megacities, such as OA from aged biomass burning and nighttime NO₃ oxidation of carbonyl compounds. These information enables better understanding of OA sources, formation and more effective air pollution control strategy.

Formation mechanism of H₂SO₄ and its role in the NPF events observed in a sub-urban temperate forest

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Atmospheric new particle formation (NPF) events contribute significantly to the global aerosol number budget and therefore may effect considerably climate and air quality. On the basis of large number of observations in different environments showing a close connection of gas-phase sulfuric acid (H₂SO₄) concentration and the NPF rates and occurrence, the H₂SO₄ is considered to be a major precursor of newly formed atmospheric nucleation mode particles. At the same time, based on observations at different sites strongly influenced by biogenic organic compounds, like monoterpenes and their oxidation products, low-volatility highly oxygenated molecules (HOMs) have been identified as a major source of new particles playing also significant role in the particles growth. The objective of this study was to clarify formation mechanism of H₂SO₄ and its role in the NPF events observed in a sub-urban temperate forest.

Measurements of OH, H₂SO₄, HOMs and others were performed as a part of ACROSS project (Atmospheric ChemistRy Of the Suburban foreSt) during June-July of 2022 at a forest site of Rambouillet located on the path of pollution plumes from Paris.

Formation of H₂SO₄ was observed for every day during measurements period with diurnal concentration profile reaching maximum at around 10 h (local time). The median maximum H₂SO₄ concentration, 2.5×10⁶ molecule cm⁻³, was similar to that observed at other forested sites. However, on some days H₂SO₄ reached unusually high concentrations, up to 1.5×10⁷ molecule cm⁻³. The calculated and measured daytime H₂SO₄ concentrations were highly correlated with formation of sulfuric acid via SO₂+OH reaction accounting for (90±20)% of the observed H₂SO₄.

The NPF events were identified for 7 days during the measurements campaign. All the NPF events corresponded to the days of highest H₂SO₄ concentrations, > 5×10⁶ molecule cm⁻³, with onset of the NPF occurring about 1 h before the H₂SO₄ maximum. For all days when H₂SO₄ concentrations was lower than 5×10⁶ molecule cm⁻³ no NPF events was observed. Analyzing relation of particles formation rate with concentrations of H₂SO₄ and HOMs (total HOMs or selected HOMs groups) we conclude that the observed NPF were governed by H₂SO₄ with HOMs possibly contributing to the particle growth.

Numerical analysis of aerosol direct and indirect effects on an extreme rainfall event over Beijing

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The impact of aerosol direct (ADE) and indirect effect (AIE) on an extreme rainfall event occurred on 19 to 21 July 2016 over Beijing was studied by conducting four numerical experiments using Weather Research and Forecasting model coupled with Chemistry (WRF-Chem). The results show that the ADE and AIE change the distribution of rainfall centers and concentrate rainfall in urban areas. In the early rainfall period, the ADE-induced hourly rainfall intensity increases, while AIE-induced hourly rainfall intensity decreases in Beijing, region A and region B. In the later period, the ADE has a slight impact on the hourly rainfall intensity, while AIE increases the hourly rainfall intensity in Beijing; the ADE and AIE increase the hourly rainfall intensity in region A, while decrease the hourly rainfall intensity in region B. The ADE destabilized the atmosphere due to the increased in atmospheric diabatic heating, thus increased the rainfall in the early rainfall in Beijing. The AIE-induced more aerosols nucleating to cloud droplets, which decreased the droplets size and inhibited collision, thereby decreasing rainfall at this moment. The impact of ADE on rainfall was weakened due to the wet deposition caused by rainfall decreased the aerosol concentration in the later period. The AIE increased the collision process, and thus increased rainfall at this moment. Besides, the difference in vertical speed is responsible for the difference in local hourly rainfall intensity for regions A and B in later period.

Organic aerosol chemical composition and volatility during ACROSS campaign at PRG urban site in Paris using a CHARON PTR-ToF-MS

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Secondary Organic Aerosols (SOA) are generated from the condensation of low volatility organic compounds, mainly produced by the reaction of Volatile Organic Compounds (VOCs) with ozone (O₃), nitrate (NO₃) and hydroxyl radicals (OH). SOA represent a major fraction of atmospheric fine particles and have an unambiguous impact on air quality, climate, and human health. However, current understanding of SOA formation and related processes is still unclear, leading to large uncertainties in chemistry transport models. Recent studies showed that in urban areas, intermediate and semi-volatile organic compounds (IVOCs/SVOCs), that can easily partition between gas and particle phase, represent an important fraction of SOA. But their modelling showed that current knowledge are still too scarce to accurately reproduce observations. As a result, identification and quantification of the major organic compounds distributed in both gas and particle phases, and their volatility in various conditions are necessary.

In this context the goal of the present study is to characterize the chemical composition of organic gas and aerosols in urban conditions. Then, the aim is to target compounds detected in both phases, to estimate their partitioning between the 2 phases and understand the main drivers.

An intensive field campaign was conducted in June/July 2022 at PRG (Paris Rive Gauche), an urban site in Paris, as part of the *ACROSS - Atmospheric ChemistRy Of the Suburban forest* project. A "CHemical Analysis of aeRosol ON-line (CHARON)" inlet coupled to a Proton Transfer - Time-of-Flight - Mass Spectrometer (PTR-ToF-MS) was used to alternatively measure gas and particle phase composition at molecular level, and completed by a large range of instruments to characterize meteorological conditions and physico-chemical parameters (NO_x, O₃, SO₂, particle number and size distribution, black carbon, etc.)

The aerosol average mass spectrum obtained during the campaign was composed of more than 500 ions. Among the most abundant compounds, long chain oxygenated species were identified, such as C₁₈H₃₄O₂ (m/z 283.26) or C₁₆H₃₂O₂ (m/z 257.25), that were exclusively detected in the condensed phase. The analysis of their diurnal trend suggests that they may originate from cooking activities. Numerous compounds in the C₆₋₉ range were also identified, and are believed to be oxidation products of monoaromatic compounds, highlighting the importance of photochemistry. Among them, several were detected in both gas and particle phases, such as C₆H₆O₂ (m/z 111.05) or C₈H₈O₂ (m/z 137.06), allowing to estimate their partitioning coefficient at a hourly time resolution. The partitioning coefficient of selected compounds and their temporal evolution will be presented and discussed, especially in light of laboratory derived partitioning coefficients using an aerosol flow tube.

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Heatwave Induced Biogenic Volatile Organic Compounds and Their Impacts on Ozone and SOA Formation

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Heatwaves have the potential to substantially affect the isoprene emission from plants, yet their impact on the temperature response of isoprene emission, especially from tropical and subtropical plants, remain poorly understood. In this study, *in situ* and controlled experiments were conducted to investigate the effect of the 2022 September heatwave on isoprene temperature response of subtropical eucalyptus in South China. Our results demonstrated that the heatwave significantly restricted plant physiological processes and forced isoprene temperature response curve peaking (E_{opt}) at a lower optimum temperature (T_{opt}) compared to normal conditions. Current model failed to capture the variation in E_{opt} and T_{opt} of isoprene emission and predicted significantly larger values during heatwaves, leading to a positive prediction bias under high temperatures. Our research further underscores that the estimation bias would be amplified under future warmer climates with more intense extreme thermal events.

Continuous Variation Of VOCs In A Forest Conservation Area: The Pollution In São Paulo Influenced By Biogenic And Anthropogenic Emissions

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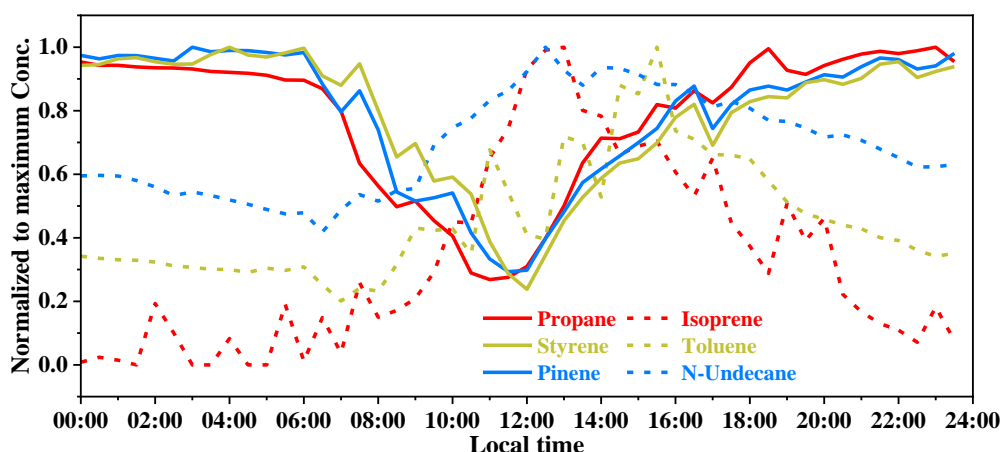
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Metropolitan Area of São Paulo (MASP), the biggest urban area of Brazil, is still experiencing air quality problems due to both ozone and particulate matter. In the past 10 years, biogenic volatile organic compounds (VOCs) were speculated as one of the precursors of the pollution, since MASP has a forest cover of 30% and is characterized by a subtropical climate favoring biogenic emissions and photochemical processes. Therefore, a field test was conducted to monitor variation of VOCs, ozone, particulate matter and other species in the atmosphere from April to June 2023. The “Reserva do Morro Grande” (RMG) was chosen as the sampling site, which is an important forest conservation area located outside the densely urbanized area, containing more than 90% remnant Atlantic Forest. A 30m observational tower was deployed in the site, which was connected to two GC-FIDs (for organic compounds with 2 to 6 carbons and 6 to 12 carbons), an ozone analyser, a Picarro (for CO, CO₂ and CH₄), a NO_x analyser and the gas line of MOCCA (a modified PTR-MS for organic gases and particulate matter). According to the current GC results, several VOCs dropped regularly and sharply near noon. Meanwhile, some compounds of anthropogenic origin (3-Methylheptane, Ethylbenzene group, Propylbenzene group and Styrene) showed high concentration and good correlation, and their distribution is similar to that in MASP city site^[1], suggesting the potential influences of anthropogenic emission on the RMG site. However, why the VOCs dropped and how biogenic and anthropogenic emissions interact remain unexplained.



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Formation of Chlorinated Organic Compounds from Cl Atom-Initiated Reactions of Aromatics and Their Detection in Suburban Shanghai

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Chlorine (Cl) atoms generated from the photolysis of atmospheric reactive chlorine species can rapidly react with various volatile organic compounds (VOCs), forming chlorine- and non-chlorine-containing low-volatile oxygenated organic molecules. Yet, the formation mechanisms of chlorine-containing oxygenated organic molecules (Cl-OOMs) from reactions of Cl atoms with aromatics in the presence and absence of NO_x are not fully understood. Here, we investigated Cl-OOMs formation from Cl-initiated reactions of three typical aromatics (i.e., toluene, m-xylene, and 1,2,4-trimethylbenzene (1,2,4-TMB)) in the laboratory and searched for ambient gaseous Cl-OOMs in suburban Shanghai. From our laboratory experiments, 19 Cl-containing peroxy radicals and a series of Cl-OOMs originating from the Cl-addition-initiated reaction were detected, which provides direct evidence that the Cl-addition-initiated reaction is a non-negligible pathway. In addition, a total of 51 gaseous Cl-OOMs were identified during the winter in suburban Shanghai, 38 of which were also observed in laboratory experiments, hinting that Cl-initiated oxidation of aromatics could serve as a source of Cl-OOMs in an anthropogenically influenced atmosphere. Toxicity evaluation of these Cl-OOMs shows potential adverse health effects. These findings demonstrate that Cl-OOMs can be efficiently formed via the Cl-addition pathway in the reactions between aromatics and Cl atoms and some of these Cl-OOMs could be toxic.

Long-term changes of organic aerosol and the influence of aqueous processing in highly polluted urban environments

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High concentrations of organic aerosol (OA) occur in Asian countries, leading to great health burdens. Clean air actions have resulted in significant emission reductions of air pollutants in China. However, long-term changes in OA and their causes remain unknown. Here, we present both observational and model evidence demonstrating widespread decreases with a greater reduction in primary OA than in secondary OA (SOA) in China during the period of 2013 to 2020. Most of the decline is attributed to reduced residential fuel burning. We find the interannual variability in SOA may have been driven by meteorological variations and contrasting effects of reducing NO_x and SO₂ on SOA production which is associated with the changes of atmospheric oxidative capacity and aqueous processing of SOA. By examining collocated aerosol mass spectrometer (AMS) and iodide chemical ionization mass spectrometer (CIMS) observations in winter 2022 and summer 2023 in Beijing, different aqueous pathways of SOA are discovered. These pathways contribute significantly to the SOA mass in highly polluted urban environments. The underlying drivers of aerosol physical properties, chemistry and gaseous precursors for these aqueous pathways are different, highlighting the need of efforts to understand, predict, and mitigate the contributions of aqueous processing to OA.

A Comprehensive Study of Carbonaceous Species in PM_{2.5} and their Origins at an urban site in northern France

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Fine particulate matter (PM_{2.5}) has received considerable attention from the scientific community and public authorities due to its adverse effects on climate and health (Wan Mahiyuddin *et al.*, 2023). Carbonaceous species are a major fraction of PM_{2.5} (Xiang *et al.*, 2017), leading many studies to focus on them. This study aims at characterizing PM_{2.5} composition in Dunkerque, a medium-sized city in northern France, focusing on carbonaceous components such as organic carbon (OC), elemental carbon (EC), secondary organic carbon (SOC), and some organic compounds. The main objectives are to better understand their sources and to study their temporal variability.

PM_{2.5} were collected at an urban site in Dunkerque from March to July 2022, using a high-volume sampler Digitel® DA80. Samples were analyzed for their content in EC, OC, water-soluble organic carbon (WSOC), humic-like substances (HULIS-C), and organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and n-alkanes. Secondary organic carbon (SOC) concentration was also estimated. The sources and variations in the concentrations of chemical components were analyzed using various tools, including concentration roses, diagnostic ratios, and considering air-mass backward trajectories.

The mean concentration of PM_{2.5} was 12.6 µg.m⁻³, with mean OC and EC concentrations of 1.6 µg.m⁻³ and 0.3 µg.m⁻³, respectively. A strong correlation was observed between OC and EC ($r=0.91$, $p<0.01$), with an OC/EC concentration ratio value ranging from 0.1 to 9.5, indicating that PM_{2.5} concentrations were influenced by biomass burning, fossil fuel combustion, and vehicular emissions (Khan *et al.*, 2021). The average concentration of WSOC was 0.7 µg.m⁻³, accounting for 42% of OC. Additionally, the strong correlation between WSOC and OC ($r=0.92$, $p<0.01$) suggested similar sources, both primary and secondary (Kawichai *et al.*, 2024). SOC concentrations represented 52% of OC and 7% of PM_{2.5}. A strong correlation was observed between SOC and WSOC ($r=0.86$, $p<0.01$), highlighting the significant contribution of secondary formation to WSOC concentrations in the study area. HULIS-C accounted for nearly 50% of WSOC, with an average concentration of 0.4 µg.m⁻³. The study also examined PAHs and n-alkanes, which had average concentrations of 0.8 µg.m⁻³ and 1.2 µg.m⁻³, respectively. The analysis of diagnostic ratios for PAHs revealed the impact of local anthropogenic emission sources, including industrial activities and vehicular emissions. The 72-hours air-mass backward trajectory analysis identified five dominant air mass origins, with higher concentrations of PM_{2.5}, OC (including SOC, WSOC, and HULIS-C), and EC associated with air masses originating from northeastern Europe and the French continental sector.

This study provided a comprehensive characterization of PM_{2.5} pollution and its emission sources in Dunkerque, highlighting the important role of carbonaceous species in air quality.

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How about the representative of our atmospheric observations: A comparison at three sites in the megacity of Hangzhou, China

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Cities are emission hotspots of greenhouse gases, as well as atmospheric compositions like ozone. Numerous observations have been deployed in cities to constrain the source/sinks and mitigation strategy for them. However, the observations in cities were frequently influenced by very local contaminations, which may bias the understanding of their characteristics. Here, in this study, we presented continuous CO₂ observations at three urban sites (i.e., Hangzhou Atmospheric Composition Monitoring Center Station (HZ), Lin'an Regional Atmospheric Background Station (LAN) and the high-altitude Daming Mountain Atmospheric Observation Station (DMS). Although the three sites were all identified as 'city' background stations and the results observed at the sites could represent the 'well-mixed' conditions in the Hangzhou city, we found a distinct difference of CO₂ among these three sites, indicating that the observations at some sites could NOT represent the background conditions in Hangzhou. For example, we found the average CO₂ mole fraction at city central site (HZ) was higher than LAN and DMS. We also observed that the seasonal variations of CO₂ at LAN and DMS were strongly influenced by vegetation canopy and the CO₂ at the lower altitude sites were strongly regulated by the boundary layer heights. As the LAN station is one of the four regional background stations in the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) program, we found the conventional understanding of regional CO₂ level in the Yangtze River Delta might overestimate by approximately 10.92 ppm. That means that we need to be cautious when adopts the observations in the city sites as the 'background' condition.

Development, optimization and validation of automated volatile organic compound data analysis using an on-line thermal desorption gas chromatograph with dual detection and application to measurements in ambient air

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Volatile Organic Compounds (VOCs) are a particularly wide range of chemicals emitted both from anthropogenic and biogenic sources¹. VOCs play a major role in outdoor and indoor air pollution and are responsible for both environmental and health issues. To accurately determine the impact of these compounds, it is essential to identify and quantify them. Usually, their concentration varies from pptv levels in outdoor air to ppbv levels in indoor environment. Among the different monitoring techniques available, on-line thermal desorption with gas chromatography coupled to a flame ionization detector and a mass spectrometer (TD-GC-FID/MS) has shown its capacity to accurately quantify VOCs in ambient air^{2,3}. FID and MS detectors are often coupled together because of their complementarity: compounds identification on the FID is achieved solely based on the retention time of the compounds. This often leads to misidentification in ambient air because of the risk of coelution. On the contrary, the MS is very useful to identify coeluted compounds but shows less linearity and stability than the FID. However, the presence of two different detectors generates twice as many results that need to be thoroughly analyzed, especially when dealing with such low concentrations. The goal of this study is to present an improved version of an on-line TD-GC-FID/MS dedicated to automatic monitoring of a wide range of VOCs (between 2 and 16 carbon atoms). The improvement is based on the development and optimization of a comparison algorithm to fasten data reprocessing and analysis. This algorithm is designed to automatically select, for each identified compound, the most accurate result between the FID and MS result. This algorithm was applied to calibration data and indoor and outdoor field campaign data.

An automatic dual thermal-desorption gas chromatograph equipped with flame ionization detector and mass spectrometer was used to monitor VOCs in ambient air during indoor and outdoor measurement. This system is composed of two independent modules: one is designed for the analysis of light VOCs from 2 to 6 carbon atoms and the other for the analysis of heavier VOCs from 6 to 16 carbon atoms. The global solution was equipped with air and hydrogen generators, a calibration system and a mass spectrometer detector. The system was calibrated using two certified gas cylinders: PAMS 58 containing 58 hydrocarbons and TO-15 containing a mixture of 68 oxygenated and halogenated compounds. Six points calibration curves were performed in the range 0.5-10 ppbv using 6 replicates for each dilution points (10 replicates for the first calibration point at 0.5 ppbv). Two software programs were used to acquire and process the data coming from the detectors: Vistachrom for FID data and VistaMS for MS data. The comparison algorithm is implemented in the VistaMS software. VistaMS imports the FID data from Vistachrom to subject both FID and MS data to the algorithm. The algorithm is based on the comparison of FID and MS results based on several criteria. These criteria consider the performances of each detector such as the method detection limit and the accuracy of each compound. The algorithm can be divided into 3 sections: S1, S2 and S3. S1 compares the MDLs of the 2 detectors, S2 compares the compounds that are calibrated with a certified gas cylinder and S3 compares the compounds that are not calibrated with a certified gas cylinder. At the

end, the algorithm gives a “validated result” which can correspond to the FID result, or the MS result, or “Not detected”. To test the algorithm efficiency, the data obtained from two measurement campaigns were used. Data collected in a suburban Parisian forest were used for outdoor measurements and data collected from a workplace composed of various offices and a quality control laboratory were used. Thanks to these two different datasets, the algorithm was challenged on different types of concentrations and VOCs.

The performance of the on-line TD-GC-FID/MS was evaluated for 60 compounds. The calibration curves obtained show determination coefficient (R^2) to be between 0.9825 and 0.9999 for FID and between 0.9850 and 0.9998 for MS. The poorer R^2 obtained in FID are compensated by better R^2 obtained in MS, thus demonstrating the complementarity of the two detectors. The detection limits have also been evaluated. The values vary between 0.006 and 0.618 ppbv with 58 % of them under 0.1 ppbv for the FID and between 0.032 and 0.760 ppbv with 41 % of them under 0.1 ppbv for MS. Accuracy was studied at 4 ppbv and the percentage recovery was considered acceptable when above 90 %. The algorithm was tested on calibration data and on the field measurement data. The algorithm has shown its ability to give accurate results and to sometime correct some issues happening on a detector. For example, during the outdoor measurement campaign, a baseline default occurred resulting in a misidentification of the toluene on the FID. This problem occurred on 93 out of 900 chromatograms in total (due to the variations of ambient conditions). For each chromatogram showing this default, the algorithm successfully picked the MS result whereas it usually chooses the FID result for toluene. Finally, to evaluate the robustness of the algorithm, the average automatic result of 24 h indoor and outdoor measurements were compared with manual treatment. Manual treatment requires experience and training and may introduce significant human error. It is also a time-consuming process. The comparison between the manual treatment and the treatment obtained with the algorithm showed a good correlation coefficient: 0.9915 for outdoor measurement and 0.9934 for indoor measurement.

This work evaluated the performances of an on-line auto TD-GC with dual detection FID and MS for the monitoring of VOCs. The performance studies of both detectors for the quantification of 60 VOCs showed linear regressions, with 55 % of method detection limits below 0.1 ppbv and acceptable accuracies between 77 % and 100 %. The results further proved the complementarity of the dual FID and MS detection. To decrease the data analysis time, which can be quite long in the case of ambient air monitoring given the potentially large number of compounds and the low concentrations expected, an algorithm was implemented and tested on real datasets. This algorithm proved its capacity to automatically correct potential misidentification on data obtained during a field campaign. When compared to manually processed data, the correlation coefficient obtained was also quite good. The implementation of this type of algorithm could be an important tool for the monitoring of large number of compounds, for long period of time and when multiple instruments are used.

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Development and Prospects of Source Apportionment Techniques for Air Pollution in China

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China's air quality has significantly improved over the past few decades. Substantial source apportionment (SA) studies have been conducted to support policymakers in implementing effective and efficient air quality management strategies. SA research in China has gradually shifted from being predominantly academic to becoming a routine component of regulatory work. This talk will provide an overview of recent advancements in the framework of SA techniques in China from five perspectives: updated knowledge on source emissions, enhanced ambient air pollution monitoring, methodological improvements, development of technical standards, and various applications in air quality management. Recent efforts in using SA techniques to evaluate the effectiveness of air pollution control policies will also be highlighted. Finally, the prospects for the future development of precision SA techniques in the context of big data will be discussed.

Experience and Implications in Air Pollution Prevention and Control in China

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This report is based on the process of air pollution prevention and control in China and the experience in recent ten years in the prevention and control of PM_{2.5} pollution. We will introduce the content and implementation effects of China's Air Pollution Prevention and Control Action Plan. And we also provide a detailed introduction to the supporting role of scientific research in policy formulation, including regional atmospheric environment observation and research, research on the causes of heavy pollution, source apportionment of PM_{2.5} in regions and cities, and the one-city-one-policy approach to urban air pollution prevention and control. Then we summarize the experience in air pollution prevention and control in China and looks forward to the future challenges.

Unmanned aerial vehicles equipped with sensor packages to study spatiotemporal variations of air pollutants in industry parks

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Unmanned aerial vehicles (UAVs) equipped with a miniaturized sensor package were developed for aerial observations, which realizes aerial observations affordable to scientists in atmospheric science and achieves aerial measurements in high spatial resolution. UAVs are deployed to a variety of aerial detecting tasks in different scientific scenarios including chemical industry parks (CIPs) with hazardous gases emissions, and some places difficult for humans to reach. In this study, UAV sensing technology was deployed to detect air pollutants in a suburb, a CIP and a natural gas plant, respectively. The effects of atmospheric conditions such as the atmospheric boundary layer height, long-distance transport and atmospheric stability on the spatiotemporal variations of the air pollutants vertical profiles were investigated by the UAV. The UAV with the sensor package was deployed to capture the methane (CH₄) leakages in a natural gas plant. The spatiotemporal variations of CH₄ in both vertical and horizontal directions studied by UAV were employed to calculate accurate CH₄ emissions, which is crucial to reducing the emissions of greenhouse gases.

Current and future prediction of inter-provincial transport of ambient PM_{2.5} in China

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Abstract: Regional transport is as much important as local sources that contributing to PM_{2.5} pollution and causing associated environmental inequality. In the context of future climate change, the effect of the responses of regional transport to the warming climate and controlling emissions has not been thoroughly investigated. Here we establish cross-province PM_{2.5} source-receptor matrix in China in 2015 and two climate pathways in 2050s (SSP585 and SSP126), using Community Multi-scale Air Quality model embedded with the Integrated Source Apportionment Method. Results suggest that across-regional transport contributes 36.1 % - 62.3 % of PM_{2.5} in five severely polluted regions, which is even more important compared to inner transport within the target region (3.8 % - 19.4 %), especially in Chuanyu and Fenwei regions which are polluted by large PM_{2.5} transport (over 50 %) from outside regions. Such results imply that joint-control policy should not only focus on neighboring provinces. Controlling pollutant emission is undoubtedly reduced the concentration of PM_{2.5} regional transport (by -5.25 µg/m³ on average), largely exceeding the influence from the meteorological fluctuations (by -0.82 µg/m³ on average) driven by the climate change in 2050s. On the other hand, future controlled pollutant emissions proved that strengthen across-regional transport with an enlarged relative contribution to total PM_{2.5} concentration (8.46%) in 2050, along with a decreased contribution from local sources (8.54%). Therefore, environmental inequality issue should be pay more attention in the context of the reduction of pollution and carbon emissions.



Abstracts – Posters



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China air pollutants and CO₂ integrated emission inventory and influence of development

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To achieve the goals of building a beautiful China and reaching carbon peak and carbon neutrality, it is crucial to strengthen the management of atmospheric emission sources, enhance the integration of atmospheric pollutants and greenhouse gas emission inventories, improve the foundational capacity for pollution reduction and carbon mitigation, and provide technical support for the coordinated advancement of carbon reduction, pollution control, afforestation, and economic growth. Our team is conducting research on “China air pollutants and CO₂ integrated emission inventory”.

Initially, the framework of air pollution source classification was utilized for the integrative inventory, followed by the precise arrangement of CO₂ emissions for each sector/subsector/source in the greenhouse gas (GHG) inventory within the Air Pollutants (APs) framework. Subsequently, efforts were made to infer the activity data of diverse industrial processes by appropriately interpreting the information contained in Pollutant Permits.

Based on the results of the inventory, further analysis can reveal that the calculated emissions of air pollutants (APs) and CO₂ were found to be comparable with findings from other studies. Additionally, the average per capita CO₂ and pollution equivalents (PEs) were 10.29 ± 6.75 tons and 11.72 ± 7.35 tons, respectively, over the provincial regions with per capita gross domestic product (GDP) lower than ¥ 70000 (about \$10000). Whereas the average per capita CO₂ and PEs dropped to 6.10 ± 1.83 tons and 6.70 ± 2.09 tons, respectively, over the provincial regions with per capita GDP higher than ¥ 70000. This somewhat supports the philosophy of the Environmental Kuznets Curve (EKC) regarding the close connection between emission and development. Moreover, the two emission intensities (for APs and CO₂) were found to vary synchronously among the provinces, reflecting the inter-linked fates of the two emissions under the control measures oriented toward either APs or GHGs.

Fine Plastic Particles in Atmospheres: Quantification, Sources, and Implications

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Objective

There is growing concern about the presence of Fine plastic particles (FPPs) in the atmosphere, which not only have different sources with PM_{2.5}, but also have complex connections with organic carbon (OC) and black carbon (BC). Not only does it have potential impacts on radiative forcing, but it also poses a challenge to global carbon neutrality goals.

Method

This study used a versatile aerosol concentration enrichment system (VACES) to conduct continuous high temporal resolution measurements. A Thermal desorption/pyrolysis-gas chromatography–mass spectrometry system (TD/Py-GC–MS) was used to quantify the FPPs. Surface-enhanced Raman spectroscopy (SERS), high-resolution scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), and Agilent 65 laser infrared imaging spectrometer (LDIR) were used to characterize FPPs.

Result

By continuously identifying and measuring FPPs in ambient PM_{2.5}, it was found that the average concentration of FPPs in 98 samples of urban Shanghai was 5.6 μg/m³. These FPPs are mainly derived from human activities, and have different sources compared with PM_{2.5}.

By analyzing the correlation between OC&BC and FPPs, we found that FPPs was a significant component of atmospheric OC, with contrasting radiative effects to BC. Although FPPs belong to OC, it was found that their correlation with modeled POC was weak. In addition, the concentration of microplastics in snowfall in Shanghai and four different urbanized areas in Northeast China was compared. 34 different types of plastics were found, with the proportion of plastic in the snow in Shanghai exceeding 40% and that in Northeast China being less than 20% (Fig. 2 a-e). The higher the per capita GDP in areas, the higher the proportion of plastic particles in snowfall (R²=0.99, p-value <0.0005, Fig. 2f). This is new evidence of the strong link between human activities and plastics.

Discussion

The existence of micro- and nano- plastic particles in the atmosphere is not only an atmospheric problem, but also has an impact on global urbanization development and climate effects. Researchers need to monitor and quantify the temporal and spatial distribution of FPPs. Besides, the correlation between the per capita GDP and the proportion of plastic particles in snowfall underscores the substantial contribution of urban areas to plastic pollution. Considering that world plastic production will double by 2050, both the goal of carbon neutrality in 2050 and the requirements for the control of atmospheric pollutants require us to take measures to explore FPPs' temporal and spatial distribution characteristics, as well as its connection and Implications with human beings.

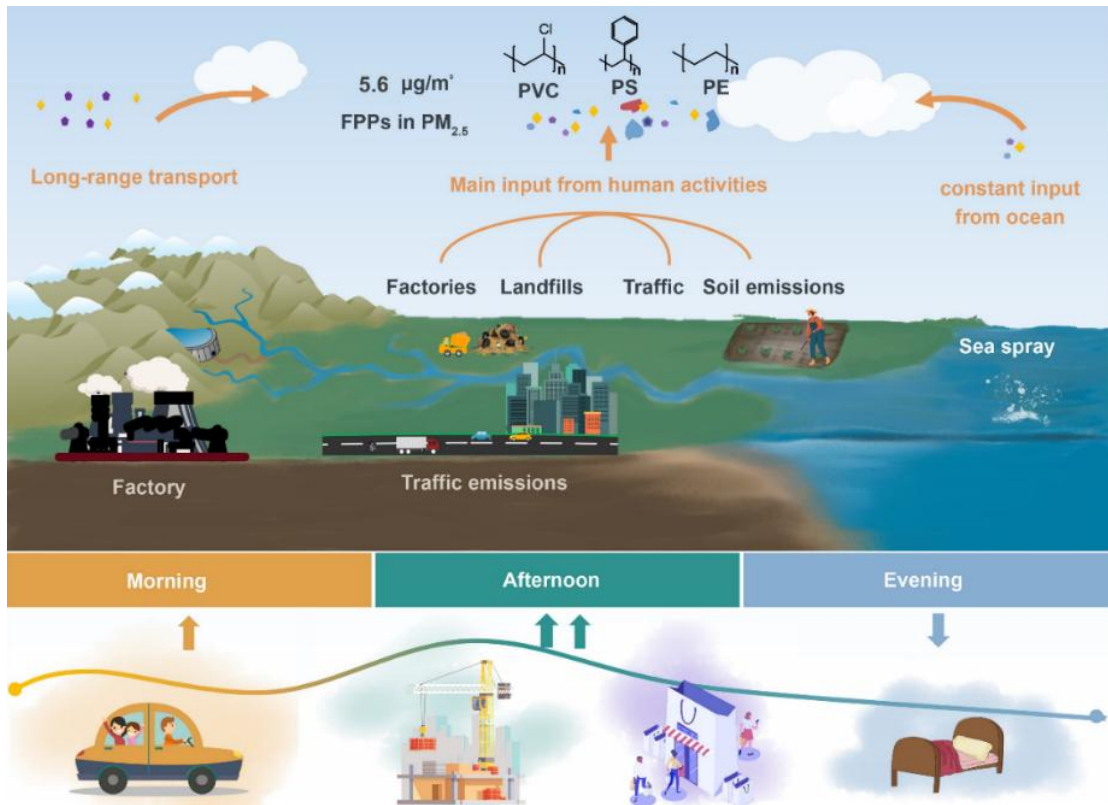


Fig. 1 | Representation of the major sources of FPPs in the atmosphere.

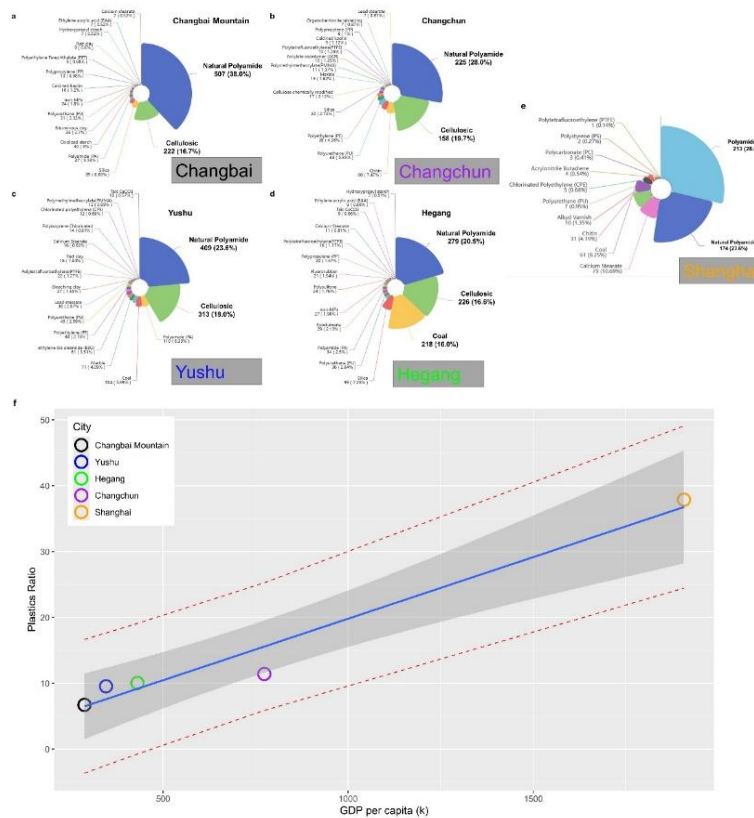


Fig. 2 | Relationships between the plastic ratio of snowfall and GDP per capita (k) in five cities.

Summertime response of ozone and fine particulate matter to mixing layer meteorology over the North China Plain

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Measurements of surface ozone (O_3), $PM_{2.5}$ and its major secondary components (SO_4^{2-} , NO_3^- , NH_4^+ , and OC), mixing layer height (MLH) and other meteorological parameters were made in the North China Plain (NCP) during the warm season (June–July) in 2021. The observation results showed that the summertime regional MDA8 O_3 initially increased and reached the maximum value ($195.88 \mu\text{g m}^{-3}$) when the MLH ranged from approximately 900 to 1800 m, after which the concentration of O_3 decreased with further increase in MLH. Interestingly, synchronous increases in $PM_{2.5}$ concentration along with the development of the mixing layer (MLH < 1200 m) were observed, and the positive response of $PM_{2.5}$ to MLH was significantly associated with the increase in SO_4^{2-} and OC. It was found that this increasing trend of $PM_{2.5}$ with elevated MLH was driven not only by the wet deposition process but also by the enhanced secondary chemical formation, which was related to appropriate meteorological conditions ($50\% < RH < 70\%$) and increased availability of atmospheric oxidants. Air temperature played a minor role in the change characteristics of $PM_{2.5}$ concentration, but greatly controlled the different change characteristics of SO_4^{2-} and NO_3^- . The concentrations of $PM_{2.5}$, its major secondary components, and SOR and NOR increased synchronously with elevated MDA8 O_3 concentrations, and the initial increase in $PM_{2.5}$ along with increased MLH corresponded well with that of MDA8 O_3 . We highlight that the correlation between MLH and secondary air pollutants should be treated with care in hot weather, and the superposition-composite effects of $PM_{2.5}$ and O_3 along with the evolution of mixing layer should be considered when developing $PM_{2.5}$ - O_3 coordinated control strategies.

Application of versatile aerosol concentration enrichment system and online ion chromatography technology in PM_{2.5}

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Water soluble ion concentration in PM_{2.5}, related to the haze formation mechanism plays a crucial role in exploring the evolution aerosols chemical components such as winter haze, biomass combustion, and fireworks emissions. However, the limitation of commercialized instruments detection limit makes it difficult to characterize the hourly resolution of water-soluble inorganic ions in PM_{2.5} due to the recent great improvement of air quality in China. The developed versatile aerosol concentration enrichment system combined with ion chromatography (VACES-IC) can concentrate aerosols 8-10 times, thus addressing this urgent need. Through continuous hourly resolution online testing in the Shanghai area from January 1 to March 29, 2023, the hourly average mass concentrations of water-soluble inorganic ions (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻), organic small molecule acids (HCOO⁻, CH₃COO⁻, C₂O₄²⁻) in atmospheric fine particulate matter were well observed. The stability and accuracy of the hourly average mass concentration of water-soluble inorganic ions and organic small molecule acids in a versatile aerosol concentration enrichment system combined with ion chromatography (VACES-IC) can be characterized by the ratio before and after enrichment, and the calculation of ion equivalent equilibrium. The calculation of the equivalent balance of ions plays a crucial role in monitoring, detecting water-soluble ions and organic small molecule acids^[2]. The authenticity and accuracy of the experimental data can only be characterized when the equivalent concentration and ratio of anions and cations were between 0.9-1.1. In this online detection, the equivalent concentration ratio of anions and cations between 0.9-1.1.

Keywords: PM_{2.5}; VACES-IC; Ion equivalent equilibrium

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Vertical Ozone Formation Mechanisms Resulting from Increased Oxidation on the Mountainside of Mt. Tai, China

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The vertical distribution of ozone (O_3) within the boundary layer (BL) and its ground-level effects have been extensively studied. However, observational limitations in obtaining high-resolution, real-time data on O_3 and its precursors, especially volatile organic compounds (VOCs), have led to a scarcity of research on O_3 formation sensitivity and mechanisms. Online measurements for O_3 , nitrogen oxides (NO_x), and VOCs were made on the mountainside of Mt. Tai (~550 m above sea level) in China during the summer of 2022 and were compared with data from a ground-level site. The Master Chemical Mechanism (V3.3.1) was used to uncover a positive correlation between NO_x and photochemical reaction rates on the mountainside, marking it as a NO_x -limited regime in contrast to the VOC-limited regime identified at surface. On the mountainside, lower NO levels limited hydroxyl radicals (OH) recycling reactions, resulting in earlier O_3 peaks and higher concentrations of hydroperoxy radicals (HO_2) and organic peroxy radicals (RO_2). The arrival of fresh air masses rich in NO accelerated OH-radical cycling, enhanced atmospheric oxidization, and significantly impacted surface O_3 concentrations through vertical transport. Moreover, NO_x reduction scenario simulations show that when considering vertical transport, the peak O_3 production rate at the surface is lower due to differences in O_3 formation sensitivity vertically. This study highlights the significant sensitivity of O_3 formation to NO within the BL, underscoring the potential impact of vertical in-situ O_3 formation above the ground on surface-level O_3 concentrations through vertical exchange, particularly in cities with mountainous terrain.

Reference:

(1) **Wanqi Wu**, Yanzhen Ge, Yan Wang, Jixin Su, Xinfeng Wang, Bin Zhou, and Jianmin Chen*. Vertical Ozone Formation Mechanisms Resulting from Increased Oxidation on the Mountainside of Mt. Tai, China. PNAS Nexus, August 22, 2024, pgae347.

Water clusters-catalyzed formation of nitroaromatic compounds in atmospheric particulate matter

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Nitrogenous organic compounds (NOCs) typically contribute between 10 and 40% of the organic matter content found in environmental aerosol particles. Nitroaromatic compounds (NACs) are among the most abundant species of NOCs and have significant impacts on air quality, climate, and public health. They deteriorate aerosol particle characteristics and considerably contribute to the secondary organic aerosol (SOA) formation. While most research emphasized the role of aerosol water in enhancing aqueous phase formation of NACs-SOA, the contribution mechanism of gaseous water to NACs-SOA formation has not been fully elucidated.

Here, supported by field observations, theoretical calculations, and smog chamber simulations, we propose a new mechanism involving water clusters (WCs) to catalyze NACs and NACs-SOA formation. Using our newly developed VACES-OE-LC-MS system, an online observation of particulate NACs ([NACs]_p) with a 3-hour resolution was conducted. We found that the [NACs]_p concentrations were closely related to the relative humidity (RH), especially on sunny days. Combined with quantum chemical calculations, it was further revealed that WCs notably lower energy barriers, with a reduction of 91.3% by (H₂O)₃ clusters, resulting in the spontaneous formation of NACs and NACs-SOA, and different weathers could influence this formation pathway. Furthermore, a series of smog chamber experiments was conducted to validate the effect of RH on NACs formation and the crucial role of WCs for NACs formation. This study provides new insight into SOA formation, highlighting the crucial role of WCs in NACs-SOA formation.

Persistent residential burning-related primary organic particles during wintertime hazes in North China: insights into their aging and optical changes

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Primary organic aerosol (POA) is a major component of PM_{2.5} in winter polluted air in the North China Plain (NCP), but our understanding on the atmospheric aging processes of POA particles and the resulting influences on their optical properties is limited. As part of the Atmospheric Pollution and Human Health in a Chinese Megacity (APHH-Beijing) programme, we collected airborne particles at an urban site (Beijing) and an upwind rural site (Gucheng, Hebei province) in the NCP during 13–27 November 2016 for microscopic analyses. We confirmed that large amounts of light-absorbing spherical POA (i.e., tarball) and irregular POA particles with high viscosity were emitted from the domestic coal and biomass burning at the rural site and were further transported to the urban site during regional wintertime hazes. During the heavily polluted period (PM_{2.5} > 200 µg m⁻³), more than 60% of these burning-related POA particles were thickly coated with secondary inorganic aerosols (named as core–shell POA–SIA particle) through the aging process, suggesting that POA particles can provide surfaces for the heterogeneous reactions of SO₂ and NO_x. As a result, during the heavily polluted period, their average particle-to-core diameter ratios at the rural and urban sites increased to 1.60 and 1.67, respectively. Interestingly, we found that the aging process did not change the morphology and sizes of POA cores, indicating that the burning-related POA particles are quite inert in the atmosphere and can be transported over long distances. Using Mie theory we estimated that the absorption capacity of these POA particles was enhanced by ~1.39 times in the heavily polluted period at the rural and urban sites due to the “lensing effect” of secondary inorganic coatings. We highlight that the “lensing effect” on burning-related POA particles should be considered in radiative forcing models and the governments should continue to promote clean energy in rural areas to effectively reduce primary emissions..

Identifying of carbonyl compounds in the atmosphere and environmental effects

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Carbonyls have an important effect on atmospheric chemistry and human health because of their high electrophilicity. Maillard-like reactions between carbonyl and amino compounds have been identified as an important pathway forming secondary brown carbon. Carbonyl precursors play a more important role in determining the molecular diversity of brown carbon. However, due to the lack of effective analytical methods, our understanding on the molecular composition of these carbonyl compounds is still limited. Here, we developed a high-throughput screening method to detect carbonyl molecules in complex samples by combining chemical derivatization with electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR-MS). Results showed that water-soluble organic matter (WSOM) in PM_{2.5} contains a large variety of carbonyls (5147 in total), accounting for 17.6 % of all identified organic molecules. Compared with non-carbonyl molecules, carbonyl molecules are more abundant in winter than in summer and have unique molecular composition and chemical parameters. For the first time, a significant positive correlation was found between the abundance of carbonyl molecules and the dithiothreitol (DTT) activities of WSOM, and the elimination of the carbonyl group remarkably reduced the DTT activities, highlighting the pivotal role of carbonyls in determining the oxidative potential (OP) of organic aerosol. Among various molecules, oxidized aromatic compounds containing the carbonyl group produced in winter contributed more to the enhancement of DTT activity, which could be used as potential markers of atmospheric oxidative stress. This study improves our understanding of the chemical diversity and environmental health effects of atmospheric carbonyls, emphasizing the need for targeted strategies to mitigate the health risks associated with carbonyl-rich aerosols.

Primary sources of HONO vary during the daytime: Insights based on a field campaign and machine learning

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Nitrous acid (HONO) is an established precursor of hydroxyl (OH) radical and has significant impacts on the formation of PM_{2.5} and O₃. Despite extensive research on HONO observation in recent years, knowledge regarding its sources and sinks in urban areas remains inadequate. In this study, we monitored the atmospheric concentrations of HONO and related pollutants, including gaseous nitric acid and particulate nitrate, simultaneously at a supersite in downtown Chengdu, a megacity in southwestern China during spring, when was chosen due to its tolerance for both PM_{2.5} and O₃ pollution. Furthermore, we employed the random forest model to fill the missing data of HONO, which exhibited good predictive performance ($R^2=0.96$, RMSE=0.36 ppbv). During this campaign, the average mixing ratio of HONO was measured to be 1.0 ± 0.7 ppbv. Notably, during periods of high O₃ and PM_{2.5} concentrations, the mixing ratio of HONO was more than 50% higher compared to the clean period. We developed a comprehensive parameterization scheme for the HONO budget, and it performed well in simulating diurnal variations of HONO. Based on the HONO budget analysis, we identified different mechanisms that dominate HONO formation at different times of the day. Vehicle emissions and NO₂ heterogeneous conversions were found to be the primary sources of HONO during nighttime (21.6%, 28.8%, respectively, from 18:00 to 7:00 the next day). In the morning (7:00-12:00), NO₂ heterogeneous conversions and the reaction of NO with OH became the main sources (31.5%, 34.0%, respectively). However, in the afternoon (12:00-18:00), the heterogeneous photolysis of HNO₃ on PM_{2.5} was identified as the most substantial source of HONO (contributing 52.8%). This study highlights the significant variations in primary HONO sources throughout the day.

Apportioning Pollution Sources in Real-Time Particle Size Distributions: A New Perspective in Air Quality Monitoring

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Abstract:

Particle size is a fundamental characteristic of particulate matter, and it can be precisely measured using electrical mobility and optical methods. Recent advancements in monitoring technology and computational algorithms now allow for the utilization of real-time particle size distributions (PSD) to investigate the sources of ultrafine particles (UFPs, $<0.1 \mu\text{m}$), $\text{PM}_{2.5}$, and PM_{10} . This approach offers a new perspective on environmental air quality monitoring and source apportionment.

We conducted simultaneous observations at two suburban sites in Shanghai, China—Dianshan Lake (inland) and Dongtan (coastal). Particle number size distributions (PNSD) were measured, and the non-negative matrix factorization (NMF) algorithm was applied to identify the main sources of UFPs. The findings revealed significant differences between the two sites: traffic emissions and nucleation processes dominated UFPs' sources at the Dianshan Lake site, while photochemical nucleation and marine ship emissions were primary contributors to UFPs at the Dongtan site. Further analysis showed that industrial emissions and regional background factors were more associated with particle volume concentrations (PVC) than particle number concentrations (PNC), indicating a stronger link to $\text{PM}_{2.5}$ than UFPs.

We applied the NMF algorithm on particle mass size distribution (PMSD) determined by optical particle counter (OPC) to achieve a novel, cost-effective method for simultaneous apportioning $\text{PM}_{2.5}$ and PM_{10} . Applied in Baoding and Shijiazhuang, Hebei Province, this method effectively apportioned pollution sources including combustion, secondary, industrial and dust aerosols.

Related publications:

1. Q. Wang‡, J. Huo‡, H. Chen*, etc., Traffic, marine ships and nucleation as the main sources of ultrafine particles in suburban Shanghai, China, *Environmental Science: Atmospheres*, 2023, 3, 1805-1819.
2. P. Wang, Q. Wang, Y. Jia, , etc., A Novel Apportionment Method Utilizing Particle Mass Size Distribution across Multiple Particle Size Ranges, *Atmosphere*, 2024, 8, 1508-0955.
3. Q. Wang‡, P. Wang‡, H. Chen*, etc., Unraveling Contributions from Combustion, Secondary, Traffic, and Dust Sources through Particle Mass Size Distribution Measurement, *Aerosol Air Qual. Res*, 2024, 8, 240135.

Understanding the formation mechanism of particulate sulfate under controlled real ambient air conditions

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Sulfate is one of the major composition of particulate matter (PM), and plays a leading role in PM formation. However, its formation mechanism still needs to be clarified due to uncertainty in the multiphase chemistry of SO₂ in particles. In particular, The heterogeneous oxidation of SO₂ by NO₂ on aerosol particles has recently been a major debatable issue as one of the major formation pathways of PM sulfate in the polluted troposphere. In this work, a large outdoor (100 m³) atmospheric simulation chamber facility at the Research Center for Eco-Environmental Sciences, Chinese Research Academy was applied to simulate the PM sulfate formation process by in taking real ambient air. A series of experiments were conducted by exposing different concentrations of SO₂ and NO₂ in different concentrations of real ambient PM, which were adjusted by in taking real ambient air at different air quality days in Beijing, China including excellent (PM_{2.5} <25 µg/m³), Good (PM_{2.5}<50 µg/m³) and light polluted (PM_{2.5}<113 µg/m³) and heavy (?). The role of relative humidity and light was evaluated. Finally, whether reactive nitrogen species oxidation pathways are dominant in addressing the missing sources of PM sulfate was discussed by comparing the experimental result and model simulation result.

A New Analytical Paradigm to Determine Concentration of Brown Carbon and Its Sample-by-sample Mass Absorption Efficiency

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Brown carbon (BrC) has a substantial direct radiative effect, but current estimates of its impact on radiative balance are highly uncertain due to a lack of measurements of its light-absorbing properties, such as mass absorption efficiency (MAE). Here we present a new analytical paradigm based on a Bayesian inference (BI) model that takes multi-wavelength aethalometer measurements and total carbon data to resolve the concentrations of black carbon (BC) and BrC, and MAEs of BrC on a sample-by-sample basis. Hourly MAEs, unattainable in previous studies, can now be calculated, enabling the first-time observation of darkening-bleaching dynamics of BrC in response to photochemical transformation. We demonstrate the application of this BI-model to analyze measurements collected over one year (2021-2022) in Hong Kong. Diel variations in $MAE_{370\text{ nm}}$ of BrC reveal a darkening-to-bleaching transition occurring between 8 and 10 o'clock when the solar irradiance ranges from 30 to 400 $W\ m^{-2}$. Furthermore, we consistently observe an increase in $MAE_{370\text{ nm}}$ of BrC with nitrogen oxide concentrations, suggesting enhanced formation of nitrogenous organics. This BI model-based data analysis would bring forth a breakthrough in amassing observation data of BrC and its MAEs in diverse ambient environments and with high time-resolution.

Identification of instrumental artefacts in terpene detection: field studies and follow-up chamber campaign ACROSS-HECTIC

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Keywords: BVOCs, field measurements, instrumental comparisons.

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Terpenes, a subset of biogenic volatile organic compounds (BVOCs), are major emissions that strongly affect the air chemistry of forested environments. Despite this, their quantification and speciation remain challenging. As a recent example, we take an extensive suite of field measurements that took place in the Rambouillet forest, the ACROSS (Atmospheric ChemistRy Of the Suburban foreSt) campaign (Cantrell *et al* (2023)).

Among the instruments deployed, 8 were used to measure VOCs. They form two groups: Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-ToF-MS) and Thermal Desorption Gas Chromatographs with Flame Ionization Detector / Mass Spectrometer (TD-GC-FID/MS). As shown in figure 1, the comparison of these instruments from different teams revealed a strong disagreement in monoterpene measurements: from tens of ppt to low ppbs measured by GCs and PTR-MS respectively.

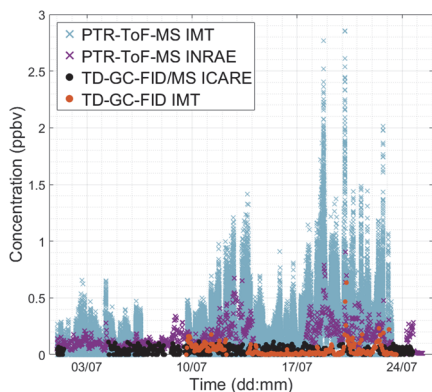


Figure 1: Time series of monoterpenes obtained by PTR-ToF-MS and TD-GCs above the canopy during the ACROSS 2022 campaign

There are several possible causes for these differences, including: calibration problems, sample decomposition, effects of ambient conditions, sampling line problems and interferences.

To help to resolve these discrepancies, we invited the participants of ACROSS to the HELIOS platform, situated at CNRS-Orléans, in a measurement campaign called HECTIC (HElios Chamber Terpenes Instrumental Comparison). This consisted of a series of experiments which were designed for investigating analytical responses to terpenes and the possible systematic differences between measurement methods. Of the two

groupings, it is expected that the GC instruments tend to underestimate terpene concentrations for the following reasons: calibration, inefficiency of trapping, sample decomposition, sample isomerization, ozone reaction, and sample line conditions. Conversely, PTR-MS measurements may be susceptible to overestimation of terpene concentrations, due to: calibration factors, sample fragmentation and interfering masses on m/z 69, 81 and 137. For this purpose, we designed a hybrid setup (presented in figure 2) whereby stable concentrations in the chamber could be perturbed with various different conditions (humidity, ozone, interferences, calibrations).

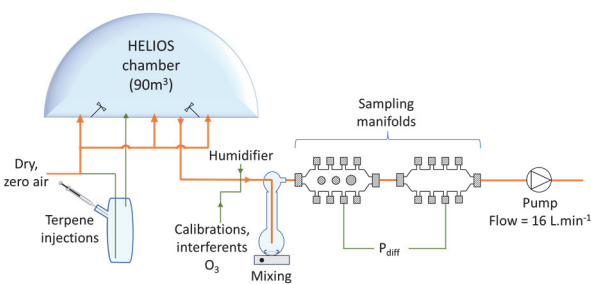


Figure 2 : Experimental set-up of HECTIC campaign

Some calibration problems were encountered, as sampling line effects. In some cases, strong humidity effects were observed in the GC techniques, leading to sample degradation and/ or isomerization. Similarly, a sensitivity to ozone concentrations was encountered. Investigating a variety of terpenes indicated systematic problems with isomerization. Also, positive interferences were observed for PTR-ToF-MS and GC.

These results highlight a potential problem of ambient measurements of an important class of compounds, whereby, depending on the analytical technique and manner in which it's used, significant differences in concentrations and speciation could be observed. We note that cold-trapping with GC systems remains an important source of information regarding ambient terpene composition, however, this sensitive class of compounds is susceptible to a variety of ambient and instrument factors, leading to a misinterpretation of air composition, and highlights a need for optimized analytical protocols for future studies.

Impact of the chirality on the formation of highly oxidized organic molecules from the ozonolysis of monoterpenes

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The largest mass fraction of atmospheric fine particulate matter (PM_{2.5}) is generally organic and dominated by secondary organic aerosol (SOA). SOA is generated from the gas-phase oxidation of volatile organic compounds (VOCs) followed by gas-particle conversion of oxidized products. Biogenic VOCs (BVOCs), such as isoprene and monoterpenes, are typically the most abundant SOA precursors, especially in regions of dense terrestrial vegetation. For example, in the boreal forest, α -pinene contributes significantly to SOA formation, mainly through the generation of highly oxygenated molecules (HOMs). Such compounds are expected to have low vapor pressures and to significantly contribute to the formation of new particles in the atmosphere. Although most monoterpenes have been studied without considering the impact of their structure, anthropogenic emissions (e.g., limonene) or severe drought (e.g., α -pinene) are released into the atmosphere a specific isomer (i.e., enantiomer). As a result, SOA formation from the oxidation of these (+) and (-) enantiomers has been largely overlooked in most experiment studies and model simulations. Here, we investigated the O₃/OH initiated oxidation of two common chiral monoterpenes (limonene (+), (-); α -pinene (+), (-)) in a flow tube reactor under atmospheric relevant conditions (i.e., reacted VOC ranged from 0.25 to 5 ppb). Oxidation products were characterized using online chemical ionization mass spectrometry. Our results demonstrate that the chirality of the precursors (i.e., (+) vs (-)) highly impacts HOM formation. Experimental results were further supported by quantum chemical calculation. Overall, this work reveals the differing potentials of particle formation from the oxidation of chiral monoterpenes, providing new insights into the formation of biogenic SOA.

WECARE Project: Wastewater treatment plants: an active source of Emerging Contaminants into Atmosphere?

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1. Introduction and context

Emerging contaminants (ECs) are predominantly unregulated anthropogenic chemicals that are ubiquitous, i.e., present in air, soil, water, human/animal tissues in trace concentration, with impact on the environment and human health still poorly understood.¹ Environmental studies are mostly focused on the occurrence and fate of ECs in aqueous environments. In contrast, less attention is paid to the atmospheric compartment, which plays a significant role in the global cycling of pollutants.

In wastewater treatment plants (WWTPs), ECs are frequently detected at concentrations ranging from ng/L to $\mu\text{g/L}$. In the common activated sludge processes, ambient air is used into deep aeration basins to allow diffusion of oxygen into water to enhance biological degradation. The diffused aeration process results in bursting bubbles at the liquid surface through the same mechanisms that generate sea salt particles.^{2,3} Recent studies pointed out that ECs may be adsorbed or trapped on atmospheric particles and transferred into the atmosphere through bubble bursting (Figure 1a).⁴⁻⁷ Shoieb et al., (2016) have investigated the WWTPs as potential sources of ECs into atmosphere and estimated annual emissions to air of siloxanes and UV-filters to be around 5000 - 112,000 and 16 - 2000 g/tank, respectively.⁷ In addition, pharmaceutical compounds,^{4,6} and perfluorated compounds⁷ have also been detected in gaseous or particulate phases in WWTP areas.

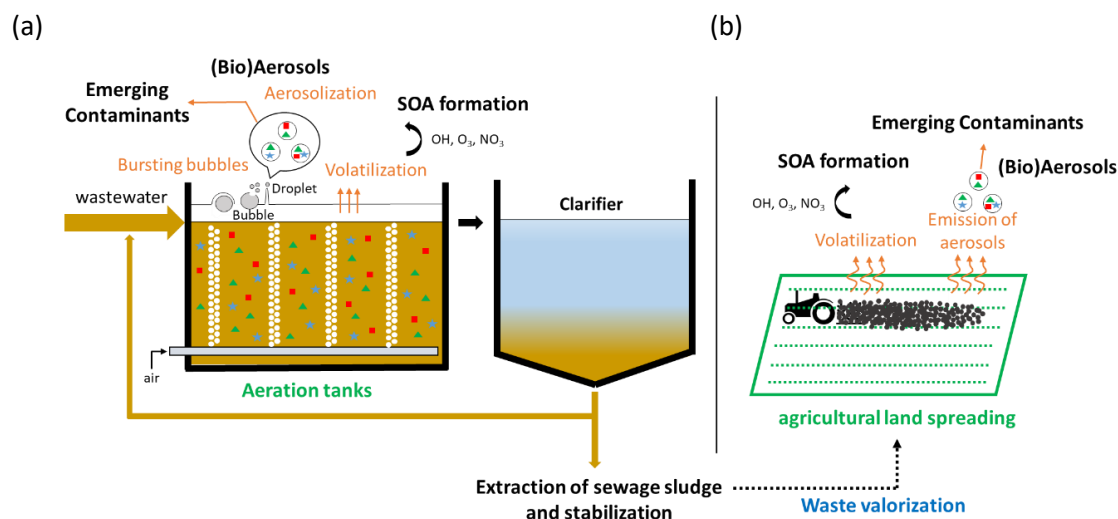


Figure 1. Key processes studied in WECARE project. Aerosolization/Emission of aerosols and volatilization processes from (a) aeration tank and (b) agricultural land spreading

Biosolids produced by WWTPs, can be used for waste valorization as a sustainable alternative to chemical fertilizers (ammonium nitrate) used in agriculture. However, they emit aerosols in the atmosphere during loading or land spreading activities (Figure 1b).⁸ The presence of high concentration of ECs in treated sewage sludge ($\mu\text{g/kg}$ or mg/kg) raises concerns that land applications of biosolids may result in a transfer of ECs in the atmosphere. Finally, new particle formation may also be observed from organic precursors emitted from WWTP activities. Recently, Ciuraru et al. (2021) demonstrated that sewage sludge, applied to cropland as fertilizers, is an uncounted source of nucleation precursors, such as skatole (C₉H₉N).⁹ Emission

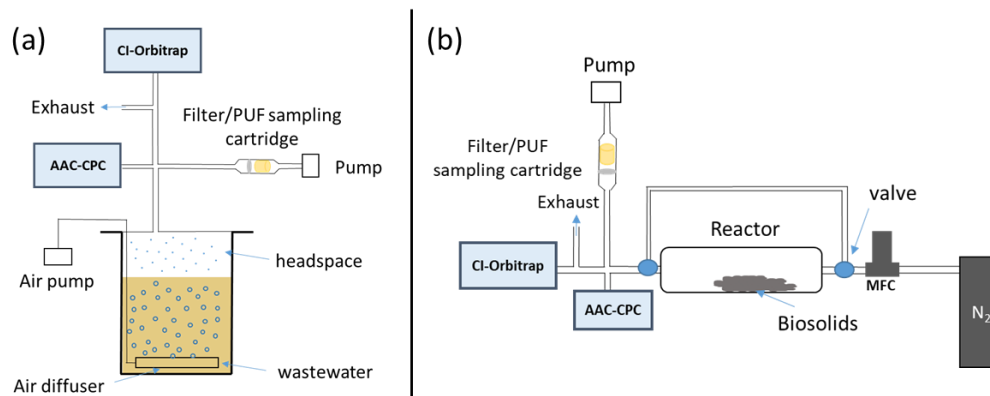


Figure 2. Experimental design of (a) laboratory-scale activated sludge reactor set-up and (b) Emission chamber

For both laboratory experiments, an aerodynamic aerosol classifier combined with condensation particle counter (AAC-CPC) will continuously be measuring aerosol size distribution. Real-time measurements of gas-phase compounds will be performed with CI-Orbitrap. ECs will be also identified by off-line GC-MSMS or LC-HRMS analysis (filter + PUF sampling).

WP3: EC emissions in the real environment

The previous WP2 is limited to laboratory conditions at small scale. To overtake this limit, translate to larger scale and confirm our finding from laboratory experiments, the WP 3 will be devoted to field campaigns in 3 sampling sites: i) near WWTP aeration tank (site 1), ii) at a background site (site 2), and iii) at an agricultural land during biosolid spreading event (site 3). The aim of WP3 is to provide valuable data to describe the atmospheric impact of WWTP and biosolid land spreading on the emissions of aerosols and ECs in the atmosphere and demonstrate the complementarity of sampling and analytical methodologies deployed/developed in the WECARE project. The figure 3 presents the sampling and analytical strategies during the field campaigns.

WP 3.1 – ECs from aeration basin in WWTP (Site 1)		WP 3.2 – Passive sampling in the 3 sites	
<i>Headspace of the aeration basin</i>		<i>Site 1 and 2: simultaneously in both winter and summer seasons</i>	
<i>Sampling in summer and in winter (1 week)</i>		<i>PAS-PUF in triplicate (3-month period) (cumulative monthly air concentrations)</i>	
<i>Atmospheric on-line measurements:</i>	<i>Atmospheric active sampling:</i>	<i>Site 1: headspace of basin volume</i>	
CI-MS: gas phase	HVS (30 m ³ /h) – 24 hours	<i>Site 2: few hundred meters downwind and upwind of the basin</i>	
AAC-CPC: aerosol particle size distribution	Particle phase (filter) / Gas phase (PUF)	<i>Site 3: Agricultural field during biosolid spreading period</i>	
	<i>Wastewater sampling:</i>	<i>PAS-PUF in triplicate (3-month period)</i>	
	24-hours composite wastewater samples	<i>Dewatered biosolid samples</i>	
	<i>Meteorological parameters:</i>	<i>+ on-line AAC-CPC during spreading periods</i>	
	Temperature, RH, wind speed and direction, ...		

Figure 3: Details of sampling and analytical procedures of the field campaigns during WECARE project

WP4: Atmospheric implications

The WP4 aims to combine all the results gathered during the whole project to propose an overall picture and estimate the emission of ECs from WWTPs in the atmosphere, at different scales. The objectives are to propose the atmospheric implications (gas-particle partitioning, aerosol size distribution), estimate the fluxes from the different sources investigated (biosolid land application, aeration basin of WWTPs), providing an evaluation of the significance of this new source of ECs to the atmosphere.

of ammonia (NH₃) have also been reported from WWTPs¹⁰ and have the potential to form ultrafine secondary aerosol that may contribute to the aerosol budget.¹¹

Given the diversity of chemicals in WWTPs, complementary analytical methodologies are needed to extend the chemical space of compounds that can be identified in the atmosphere. Indeed, their detection remains an important analytical challenge due to the complexity of sampling process and their low concentrations into atmosphere

2. Objectives

The WECARE project (2024-2028), funded by the French National Research Agency (ANR JCJC 2023) aims to address two main objectives that will be presented and discussed. First, it seeks to pave the initial fundamental knowledge on the impact of the ECs in the atmosphere for climate and health concerns. Second, it will assess the contribution of WWTPs to EC emissions with description of transfer processes and atmospheric implications. In other words, the research objectives (RO) of the project are the following:

RO1 – To define and develop analytical techniques to identify and quantify ECs in the atmospheric compartment.

RO2 – To characterize the emissions of gaseous and particulate ECs in the atmosphere from WWTP activities (aeration tank and biosolid land spreading) and describe transfer processes.

RO3 – To evaluate atmospheric implication of ECs through gas-partitioning measurement, particulate size partitioning and estimation of emission fluxes.

3. Materials and Methods

The WECARE project is structured around four interlinked scientific work packages (WPs) that promote a multidisciplinary approach.

WP1: Define and develop analytical techniques to identify and quantify ECs in the atmosphere

The objective of the WP1 is to develop complementary analytical techniques to identify and quantify ECs in the atmosphere. ECs represent a large variety of substances including different families and their various physico-chemical properties. WECARE will cover a selection of representative ECs including a broad structural and chemical diversity (chemical function, octanol/water partition coefficient log K_{ow}, vapor pressure (VP), solubility in water, ...). Analytical development will be performed for quantification in two atmospheric sample matrices, i.e. filter for aerosols sampling and polyurethane foam (PUF) for semi-volatile organic compounds (SVOCs) sampling. Off-line mass spectrometry techniques using gas mass chromatography and liquid chromatography will be developed. For the monitoring of a larger range of substances (mainly in field samples), non-target methodologies will be carried out using reverse phase C-18 liquid chromatography (LC) coupled with High Resolution Mass Spectrometer (HRMS-Orbitrap, Resolution 240 000, ThermoFischer) instrumentation, allowing particularly to highlight differences in chemical fingerprints of samples from field campaigns. Real-time measurements are also crucial for a better understanding of atmospheric processes. Thus, the ionization and detection of selected ECs will also be optimized with an on-line chemical ionization interface coupled to an ultrahigh-resolution Orbitrap (CI-Orbitrap).

WP2: EC emissions at pilot scale level – Laboratory experiments

The aim of WP2 is to evaluate the emission of ECs from wastewater treatment activities in controlled experimental conditions (Figure 2), to generate the first hypotheses about atmospheric processes driving ECs transfer to the atmosphere (aerosolization, volatilization of ECs). It will be dedicated to laboratory experiments as proof of concept to understand ECs transfer processes from the two main expected sources: aeration tanks and biosolid spreading on agricultural land. The effect of key environmental parameters on both gas and particle emission will be investigated leading to a comprehensive study.

4. Conclusion

The WECARE project will significantly enhance our understanding of the atmospheric implications of emerging contaminants from wastewater treatment activities. By integrating advanced analytical techniques, laboratory experiments, and field campaign, this project will offer new insights into the role of WWTPs as sources of ECs and their potential effects on air quality and human health.

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Spontaneous Production of H₂O₂ at the Liquid-ice Interface: A Potential Source of Atmospheric Oxidants in Ice and Snow

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Abstract:

In this study, we present experimental evidence for spontaneous production of hydrogen peroxide (H₂O₂) at the liquid-ice interface during the freezing of dilute salt solutions. Specifically, sample solutions containing either NaCl, NaBr, NH₄Cl and NaI at concentrations between 10⁻⁶–10⁻¹ M were subjected to freezing-melting cycles and then analyzed for H₂O₂ content. The relationship between the production rate of H₂O₂ and the salt concentration follows that of the Workman-Reynolds freezing potential (WRFP) values as a function of salt concentration. Our results suggest that H₂O₂ is formed at the liquid-ice interface from the self-recombination of OH radicals, produced from the oxidation of hydroxide anions due to the high electric field generated at the aqueous-ice interface under the WRFP effect. Furthermore, the involvement of O₂ likely acting as an electron capturer could promote to produce more OH radicals and HO₂ radicals, thus enhancing the production of H₂O₂ at the liquid-ice interface. Overall, this study suggests a novel mechanism of H₂O₂ formation in ice and snow via its spontaneous production at the liquid-ice interface induced by the Workman-Reynolds effect.

Unveiling the molecular characteristics, origins, and formation mechanism of reduced nitrogen organic compounds in the Urban atmosphere of Shanghai using a versatile aerosol concentration enrichment system (VACES)

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Reduced nitrogen-containing organic compounds (NOCs) in aerosols play a crucial role in altering their light-absorption properties, thereby impacting regional haze and climate. Due to the low concentration levels of individual NOCs in the air, the utilization of accurate detection and quantification technologies becomes essential. For the first time, this study investigated the diurnal variation, chemical characteristics, and potential formation pathways of NOCs in urban ambient aerosols in Shanghai using a versatile aerosol concentration enrichment system (VACES) coupled with HPLC-Q-TOF-MS. The results showed that NOCs accounted over 60% of identified components of urban organic aerosols, with O/N<3 compounds being the major contributors (>70%). The predominance of the positive ionization mode suggested the prevalence of reduced NOCs. Higher relative intensities and number fractions of NOCs were observed during nighttime, while CHO compounds showed an opposite trend. Notably, a positive correlation between the intensity of NOCs and ammonium during the nighttime was observed, suggesting that the reaction of ammonium to form imines may be a potential pathway for the formation of reduced NOCs during the nighttime. Seven prevalent types of reduced NOCs in autumn and winter were identified and characterized by an enrichment of CH₂ long-chain homologs. These NOCs included alkyl, cyclic, and aromatic amides in CHON compounds, as well as heterocyclic or cyclic amines and aniline homolog series in CHN compounds, which were associated with anthropogenic activities and may be capable of forming light-absorbing chromophores or posing harm to human health. The findings highlight the significant contributions of both primary emissions and ammonium chemistry, particularly amination processes, to the pollution of reduced NOCs in Shanghai's atmosphere.

Measurement Campaign RACLET - Exploring the Composition and Reactivity of Organic Matter in Cloud Conditions

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The composition of atmospheric organic matter is extremely complex and influenced by emissions, which can be natural (such as plant emissions) or anthropogenic (linked to human activity), but also by atmospheric transformations. Organic compounds react with the main atmospheric oxidants (ozone, hydroxyl radicals and nitrate) and undergo chemical aging in this environment in different forms: in gas, condensed on particles or even dissolved in cloud droplets. The equilibrium of organic matter is managed mainly by its physicochemical properties (i.e., volatility, polarity) and environmental conditions. The atmosphere also shelters the atmospheric microbiota (a diversity of microorganisms such as bacteria, yeasts or even molds), which degrades organic matter for their metabolism and produces new compounds. These biological processes in the atmosphere potentially rise to organic transformations that are still unknown.

To characterize the composition and reactivity of atmospheric organic matters in these three phases, a measurement campaign RACLET (Reactive gases, Aerosols and CLOUDS: Exploring organic matter Transformations) was organized by LaMP (Laboratoire de Météorologie Physique) and OPGC (Observatoire de la Physique du Globe de Clermont Ferrand) in April 2024 at the Puy de Dôme atmospheric observatory^[1]. In addition to the on-going routine measurements at the observatory, the collaboration of several national and international laboratories, made it possible to deploy a wide range of state-of-the-art instruments to complete the measurement of chemical composition and meteorological conditions. These instruments included; two proton transfer mass spectrometers (PTR-Q-MS and PTR-Tof-MS), a CHEMICAL ANALYSIS OF aeROSOL ON-line module (CHARON), an Aerosol Composition and Speciation Monitor (ACSM), a fog monitor (DMT), a snow particle counter (ST Niigata), a direct optical measurement of bioaerosols (WIBS), TEM collector, a recent in-situ aerosol instrument (SMPS), and two Formaldehyde instruments (Aerolaser and PICARRO). Lidar measurements and multi-frequency radar measurements were performed at Cézeaux and Opme to characterize the vertical and horizontal extensions of the clouds sampled at puy de Dôme and of the dust event. Dynamical context was also characterized by retro trajectory calculations throughout the entire period duration of the campaign with CAT - ECMWF ERA5.

During the campaign, different atmospheric events were observed, providing the opportunity to explore organic transformations within the gaseous, particulate and aqueous phases under diverse conditions.

Acknowledgements

This initiative is jointly financed by the ATMO-ACCESS, encouraging international collaborations within the European ACTRIS network. The campaign is encouraged by the National Institute of Sciences of the Universe (CNRS-INSU) via the support of the CO-PDD instrumented site, and aerosol measurement activities within the CLAP national observation service, the MOCC@PUY LEFE-CHAT project and the ANR OPTIC project. Many thanks to the participants: ICCF, LSCE, TROPOS (Germany), MRI (Japan). Great thank to ATMO-ACCESS for subsidizing engineers and installing instruments from private sections: TSI (U.S.A), DMT (U.S.A) and PICARRO (U.S.A).

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Far Field and Tip-Enhanced Raman Spectroscopy for characterizing atmospheric Secondary Organic Aerosols

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Atmospheric aerosols are well known to impact both air quality and climate change. The importance of characterizing the composition and the microstructure of atmospheric particles is now well-established for inferring key properties of aerosols such as hygroscopicity, the activity of cloud condensation, the reactivity, the optical properties, etc.. [1] Secondary organic aerosols (SOAs) are formed through the oxidation of biogenic or anthropogenic volatile or semi-volatile organic compounds by atmospheric oxidants. SOAs consist of thousands of organic compounds but only less than 20 % are quantified [2]. Once SOAs are formed in the atmosphere, they may further react with atmospheric reactants leading to the formation of evolutive complex particles. Understanding the formation and aging of SOAs in the atmosphere is of prime importance to evaluate their impact on atmospheric processes. The characterization of atmospheric particles can be conducted at different levels of details including the single particle scale by Raman microspectrometry (RMS). Indeed, the composition and heterogeneity of a particle can be resolved with a high degree of spatial resolution by tip-enhanced Raman spectroscopy (TERS) [3]. The characterization of SOAs collected in the atmosphere by TERS is a challenging task since spectral fingerprints of SOA have not been investigated so far.

In this study, we used RMS and TERS to characterize particles collected in Landes Forest for a better understanding SOA formation and transformation. The sampling site was located in the Landes forest (France) at Bilos. The particles were collected on suitable substrates using a Dekati cascade impactor allowing for collection of size-segregated fractions.

The conventional Raman imaging performed on the submicronic fraction of particles lead to the identification of inorganic species such as nitrate and sulphate-rich particles. TERS measurements were achieved using a bottom-illumination TERS instrument. Additionally, the dark-field Rayleigh scattering imaging [4] of the particles provides indications on their size and help to the particle localization. TERS features highlighted the mixed organic/inorganic composition of submicronic particles and TERS images clearly shown the heterogeneous distribution of organic compounds on the particle surface.

Acknowledgments

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Physico-chemical properties of biogenic organic aerosol at the single particle scale

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Keywords: Atmospheric particles, Raman spectroscopy, PTR-MS, acoustic levitation, secondary organic aerosols

Summary: Biogenic volatile organic compounds (BVOCs) are mostly emitted by vegetation (e.g. isoprene or monoterpenes such as α - and β -pinenes) and lead to the formation of biogenic secondary organic aerosols (BSOAs), which have been estimated to constitute 30% to 50% of the global organic aerosol budget^[1]. Once generated, BSOAs may further react during air mass transport through ageing multiphasic processes in the atmosphere. These reactions may affect both the chemical composition and the physical properties of aerosols, such as hygroscopicity, viscosity and gas-particle partitioning. Studies of the formation and fate of BSOAs, investigated by performing both field observations and laboratory experiments, point out the complexity of the related physico-chemical processes. The relevance of using acoustic levitation in the context of single aerosol particle chemistry has been demonstrated this last decade^[2-4].

In this work, we propose to study the physico-chemical properties of model aerosol particles of atmospheric interest, using an acoustic levitation device inserted in an environmental chamber, for relative humidities varying between 10 % and 95 %, to better simulate atmospheric conditions without any interaction with a substrate. The first studies were carried out using an acoustic levitation device coupled with a Raman microspectrometer (RMS). Particularly, the ability of BSOA-rich aerosols to take up or loose water that governs the solid-to-liquid or liquid-to-solid transitions, was investigated.

In a first step, MBTCA (3 methyl-1,2,3-butanetricarboxylic acid) was selected to model BSOA particles, as a relevant molecular tracer for monoterpene BSOA formation and ageing processes^[5-6]. The hygroscopic properties of MBTCA, alone or in mixture with inorganic salts, investigated in this work were in good agreement with a preliminary work^[7] and with those calculated from the E-AIM thermodynamic model. In a second step, preliminary studies of the gas phase of aerosols have been initiated. The validation was made by following the gas phase composition during the evaporation process of a particle composed of a mixture of inorganic salt and linalool (3,7-dimethyl-1,6-octadien-3-ol). Finally, to enlarge our knowledge of exchanges at the particle surface during ageing processes, experiments were performed on the photolysis of a particle of nopinone in the presence of gaseous acetaldehyde. Preliminary results will be presented.

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Chemical characteristics and Source Apportionment of PM_{2.5} in Summer and Winter in Tai'an, China

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Although the ambient air quality has improved significantly in recent years in China, PM_{2.5} concentrations have not reached the National Ambient Air Quality Standard (NAAQS) in most Chinese cities. In this study, PM_{2.5} samples were collected in Tai'an (famous for Mount Tai, a UNESCO World Heritage Site) from June to August in 2021 and from December 2021 to February 2022. The water-soluble ions (WSIs), metal elements (MEs), organic carbon (OC), elemental carbon (EC), polycyclic aromatic hydrocarbons (PAHs), nitro-aromatic compounds (NACs) and saccharides were analyzed to study the concentration characteristics, assess the human health risk, and analyze the changes of the organic components of PM_{2.5} under high pollution conditions of O₃ in summer and of PM_{2.5} in winter. Further, this study investigated the source differences of PM_{2.5} in summer and winter by applying the positive matrix factorization (PMF) model.

This study showed that the total concentrations of all chemical components of PM_{2.5} in Tai'an were higher in winter than that in summer. Water-soluble ions (WSIs) were identified as the most prevalent chemical components among the studied chemical components of PM_{2.5}. PAHs emerged as the most significant organic components within the studied chemical components of PM_{2.5}. The OC/EC ratio analysis showed that the carbonaceous components were mainly from traffic emissions and coal combustion in summer, while they were mainly from biomass burning and coal combustion in winter. The health risk assessment of the harmful chemical components (MEs and PAHs) in PM_{2.5} was further conducted, and the results showed that the effects of the toxic chemical components in PM_{2.5} in winter were greater than those in summer. Cr(VI), Benzo[a]pyrene (BaP), and Dibenz[a,h]anthracene (DBA) were the dominant species affecting human health. The analyses of the correlation between PM_{2.5} chemical components and atmospheric pollutants, along with the observed variations in organic components under different pollution conditions, revealed that ozone (O₃) facilitated the formation of organic chemical components within PM_{2.5} during summer. Under severe PM_{2.5} pollution in winter, the significant correlation between PM_{2.5} chemical components and both OC and EC showed that secondary pollution is a major driver of organic compound formation in PM_{2.5}. The PMF model was applied to identify the sources of PM_{2.5} in summer and winter, respectively, and six sources were identified, including traffic emissions, fossil fuel combustion, secondary formation, dust particles, plant emissions, and biomass burning. The top three source contributions of PM_{2.5} in summer were secondary formation (32.39%), fossil fuel combustion (31.32%) and dust (17.83%), respectively, while the top three source contributions of PM_{2.5} in winter were secondary formation (41.99%), biomass burning (15.07%) and fossil fuel combustion (14.71%), respectively.



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