Air quality in megacities Faraday Discussion

Concluding Remarks Lecture
Nov 20, 2020

Chak K. Chan (City University of Hong Kong, China)
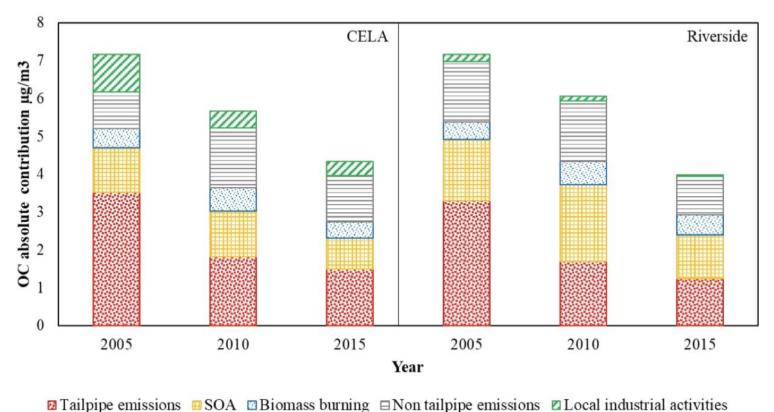Masao Gen (Kanazawa University, Japan)

Theme 1

Current status and trends in air quality in megacities

PM2.5 (Guangzhong Basin, SJV, Beijing, LA Basin, Shanghai)

- Importance of BC, OC, ammonium (Watson et al., GZB vs. SJV)

- OC measurements and comparison of source apportionment techniques of PM in Beijing – CMB, EG (C14), ACSM/AMS PMF, filter based PMF (Xu et al.)

- Real time tracer-based OC speciation by TAG (Zhu et al., Shanghai)

- Importance of vehicular emission controls, tailpipe and non-tailpipe (Altuwayjiri et al., LA Basin)

Absolute contribution of both tailpipe emissions and non-tailpipe emissions to OC decreased in LA Basin

- Tailpipe emissions reduced drastically.

- Non-tailpipe emissions was replacing tailpipe emissions to be the primary source.

- Regulations reduced the emissions of primary organic precursors ——>SOA↓

Altuwayjiri et al., Long-term trends in the contribution of PM2.5 sources to organic carbon (OC) in the Los Angeles basin and the effect of PM emission regulations
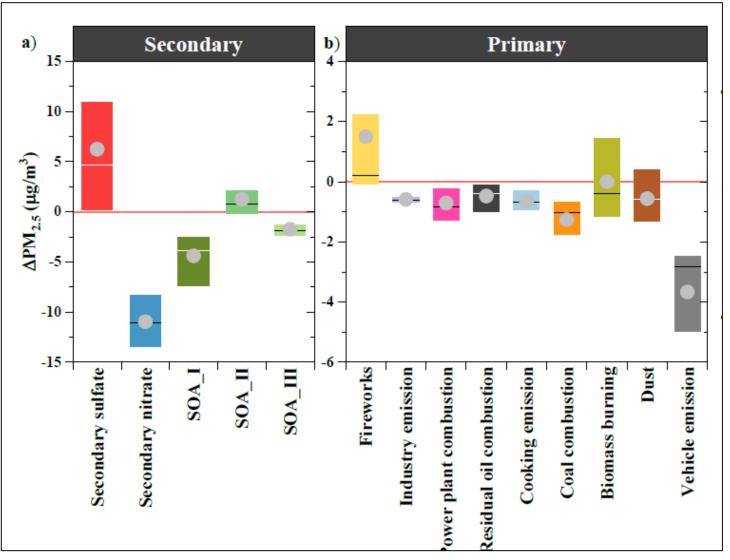
VOC, Ozone and Ox (London, Bangkok, Delhi, Asia)

- Decreasing trend of NOx in both London and Bangkok roadside stations in 2005-2015, but less obvious reductions in O_3 (Khan et al.)

- Despite widespread open biomass burning in India, traffic related petrol and diesel emissions remain the key drivers of gas-phase urban air pollution in Delhi (Stewart et al.)

- VOC limited Ozone formation in Delhi (Chen et al.)

  - 50% reduction in AOD increases maximum hourly ozone concentrations by 5% in June, but increases it by 25% in November.

- Asia road emission trends - Emissions of NOx, CO, and PM2.5 peaked in 2000-2015 but GHG will only peak in 2040 (He et al.)

COVID 19 – lockdown

- Reduction of NOx, SOx, CO in Beijing; weekly and diurnal patterns become less obvious. (Brimblecombe and Lai)

- Tracer based work suggests increase in secondary PM, especially sulfate and SOA. (Zhu et al.)

- Other literature has also reported the increase of ozone and secondary PM2.5 in mega cities in China during COVID 19

Difference of PM$_{2.5}$ contribution between BR and DR by (a) individual secondary factors and (b) individual primary factors.

- Contribution of primary source factors to PM$_{2.5}$ and OC dropped (highest contributors: vehicular emissions, biomass burning, coal combustion)

- Contribution of secondary sources factors (except nitrate) to PM$_{2.5}$ and OC increased; mainly due to sulfate formation and SOA related to later generation organic oxidation products
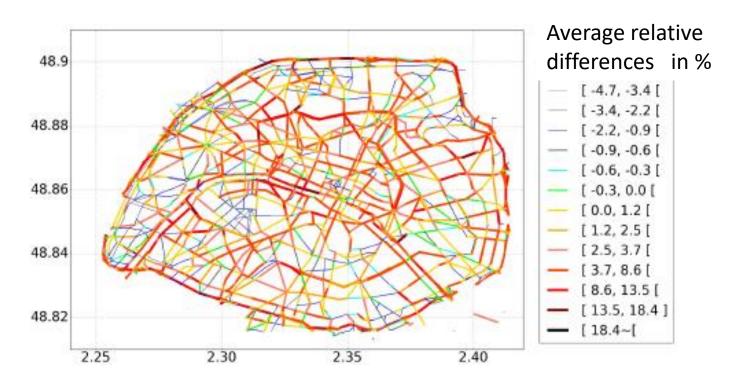
Zhu et al. Tracer-based Characterization of Source Variations of PM2.5 and Organic Carbon in Shanghai Influenced by the COVID-19 Lockdown

Theme 2

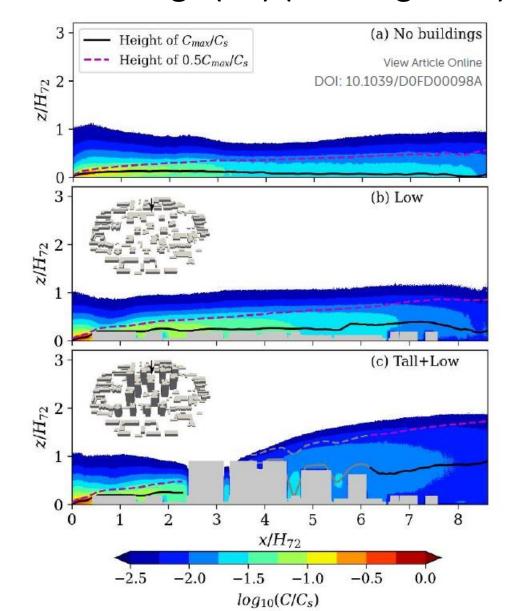Physico-chemical processes in the urban atmosphere (neighbourhood scale)

Impact of secondary aerosol formation on PM$_{2.5}$ concentrations over street network in Paris (Lugon et al.)

PM$_{2.5}$ simulated with and without processes leading to secondary aerosol formation (gas chemistry and aerosol dynamics)

Average relative differences in %

- [-4.7, -3.4 [
- [-3.4, -2.2 [
- [-2.2, -0.9 [
- [-0.9, -0.6 [
- [-0.6, -0.3 [
- [-0.3, 0.0 [
- [0.0, 1.2 [
- [1.2, 2.5 [
- [2.5, 3.7 [
- [3.7, 8.6 [
- [8.6, 13.5 [
- [13.5, 18.4]
- [18.4~[

- Necessity to consider secondary aerosol formation in streets

- Higher impacts (>18%) of secondary aerosol formation on PM$_{2.5}$ concentrations were observed in streets with high traffic strength

Plume characteristics in a cluster of tall buildings (TB) (Hertwig et al.)

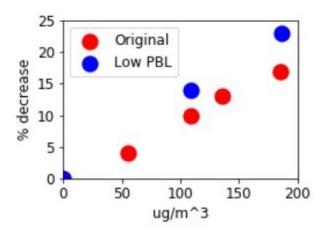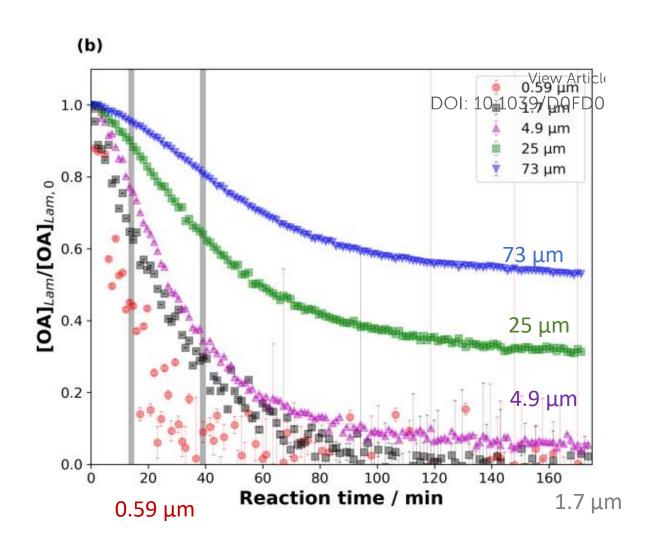## Aerosol-boundary layer feedback via coupled LES aerosol-radiation model (Slater et al.)

Fig. 6 : Aerosol concentration vs PBL % decrease for low initial PBL simulations and original PBL simulations, due to different aerosol loadings

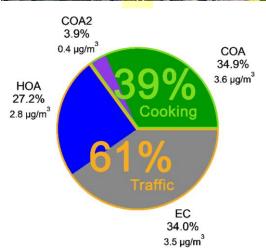Policy implication : Control of BC
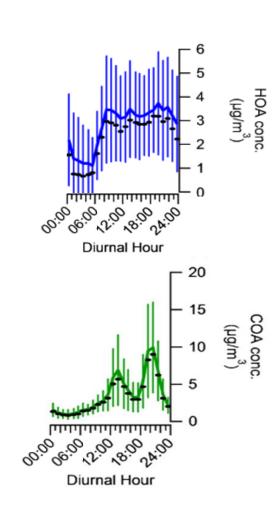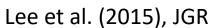
Ozonolysis of cooking emissions (Milsome et al.)

- Kitchen emissions in Hong Kong
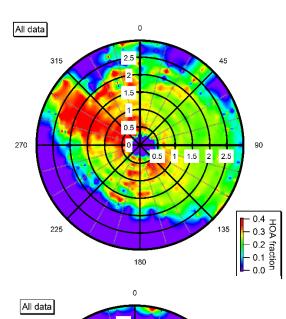- Traffic emissions in Gothenburg
- Primary and Secondary Aerosols

Roadside campaign in Mong Kok (URBAN)
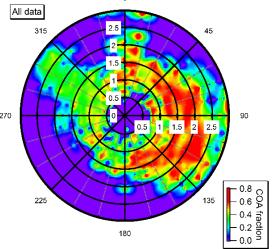## March – July, 2013; AMS + others

Lee et al. (2015), JGR

American Geophysical Union (AGU)
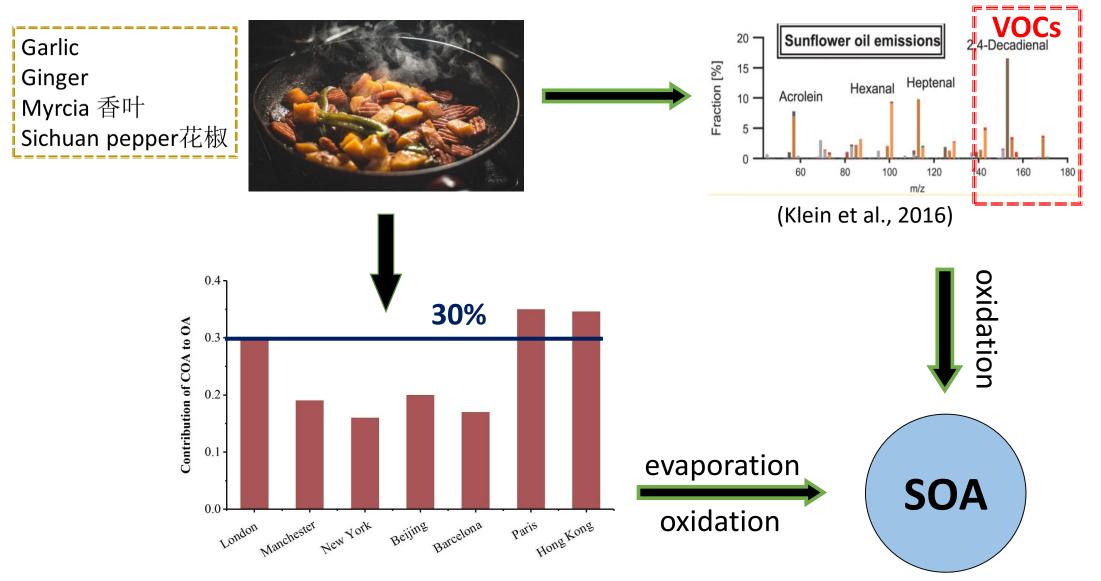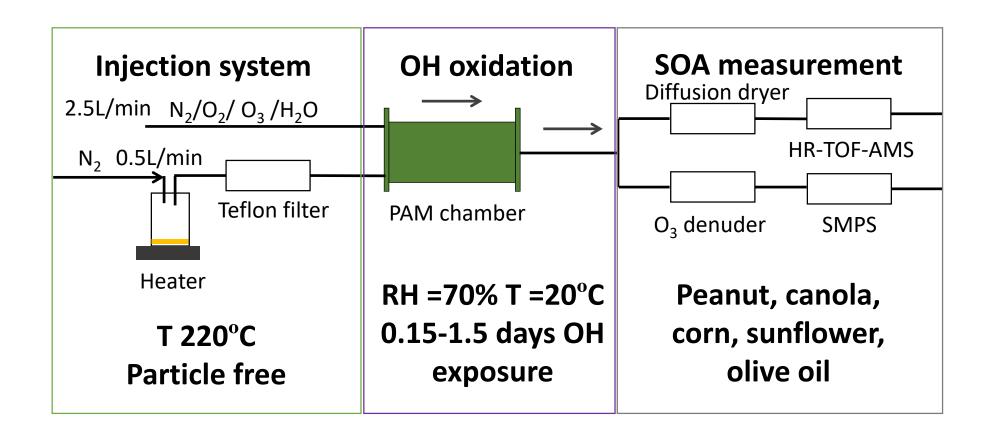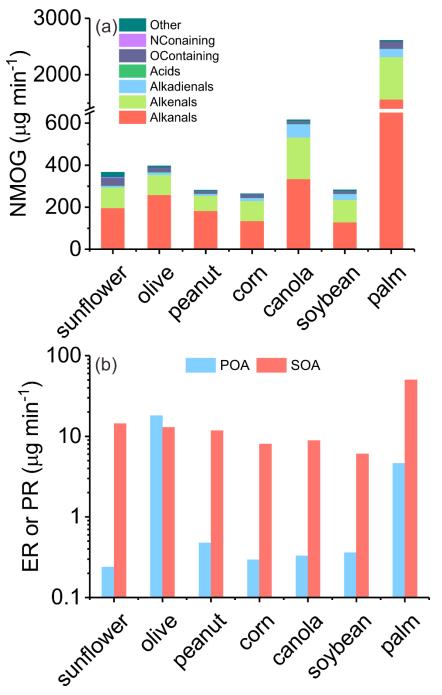
Cooking: important source of OA

Garlic
Ginger
Myrcia 香叶
Sichuan pepper花椒

VOCs

Sunflower oil emissions 2,4-Decadienal

Acrolein Hexanal Heptenal

(Klein et al., 2016)

30%

oxidation

evaporation

oxidation

SOA

(Allan et al., 2010; Sun et al., 2011; 2013; Mohr et al., 2012; Crippa et al., 2013; Lee et al., 2015)

15

SOA formation from gas-phase emissions of heated cooking oils

Injection system

2.5L/min $N_2/O_2/O_3/H_2O$

N_2 0.5L/min

Teflon filter

Heater

**T 220°C
Particle free**

OH oxidation

PAM chamber

**RH =70% T =20°C
0.15-1.5 days OH
exposure**

SOA measurement

Diffusion dryer

HR-TOF-AMS

O_3 denuder   SMPS

**Peanut, canola,
corn, sunflower,
olive oil**
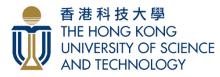
Alkanals and alkenals, dominated the non-methane organic gas (NMOG) emissions

SOA: one order of magnitude higher than POA

PR=[SOA]×Dilution ratio×Flow rate
ER=[POA]×Dilution ratio×Flow rate

(Liu et al., 2018b)
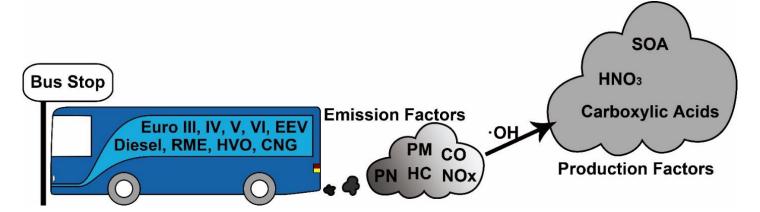
Roadside Assessment of a <mark>Modern City Bus Fleet:</mark> Primary and Secondary Emissions

Qianyun Liu[1], Åsa M. Hallquist[2], Henrik Fallgren[2], Martin Jerksjö[2], Sara Jutterström[2], Håkan Salberg[2], Mattias Hallquist[3], Michael Le Breton[3], Xiangyu Pei[3], Ravi Kant Pathak[3], Tengyu Liu[4], Berto Lee[4], and Chak K. Chan[4]
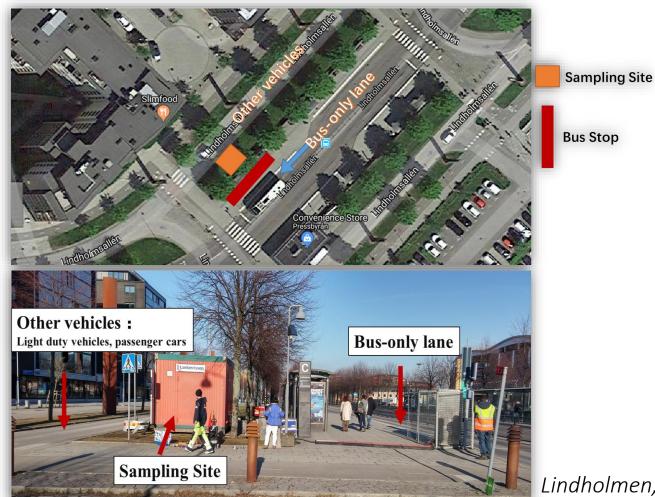
[1]Division of Environment and Sustainability, Hong Kong University of Science and Technology, China
[2]IVL Swedish Environmental Research Institute, Gothenburg, Sweden
[3]Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden
[4]School of Energy and Environment, City University of Hong Kong, Hong Kong, China

Bus emissions - Sweden

Sampling Site

Bus Stop

Lindholmen, Gothenburg, Sweden

Map data: Google, DigitalGlobe
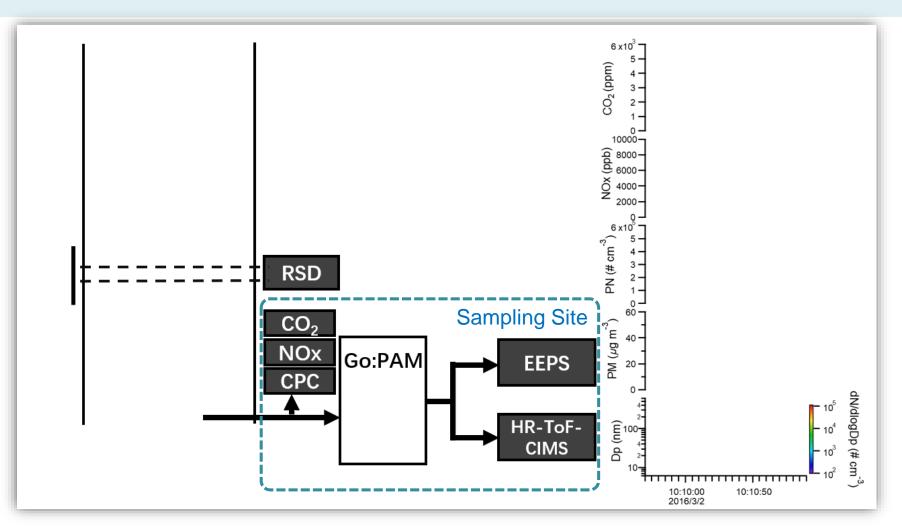
- ⸬ Measurement of primary emissions

- ⸬ Secondary aerosol production using same oxidation flow reactor (OFR)

- ⸬ **Relevance to HK**: majority of franchised buses use similar engine and exhaust treatment technologies

19

Bus emissions – Sweden

- ⁙ Acceleration-phase

- ⁙ Exhaust-plume probing measurements

Instrument	
CO_2 NO NOx	Gas Analyzers
PN	Condensation Particle Counter (CPC)
PNSD	Engine Exhaust Particle Sizer Spectrometer (EEPS)
CO, NO, HC	AccuScan RSD 3000,
VOC, POA, SOA	High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer (CIMS)

20

Bus emissions - Sweden

Fleet characteristics

EU standard	Engine technology	Fuel	Exhaust after-treatment system	Number of buses	Number of passages	Percentage of plumes with detectable CO_2[a]
Euro III[b]	Diesel	DSL[c]	SCR+DPF	2	64	88%
Euro IV	Diesel	RME[d]	SCR	10	58	94%
Euro V	Diesel	DSL[c]	SCR	15	526	87%
Euro V	Diesel	RME[d]	SCR	56	423	95%
Euro V	Diesel	HVO[e]	SCR	59	432	97%
Euro V	Diesel	HVO[e]	EGR+DPF	5	26	91%
Euro V	Diesel[HEV]	HVO[e]-electric	SCR	26	261	75%
EEV	CNG	CNG[f]	-	50	533	67%
Euro VI	Diesel[HEV]	RME[d]-electric	SCR+EGR+DPF	4	22	63%
Euro VI	Diesel[HEV]	HVO[e]-electric	SCR+EGR+DPF	7	350	47%
TOTAL	-	-	-	234	2695	-

[a]Minimum threshold

[b]Retrofitted with SCR (Selective Catalytic Reduction), DPF (Diesel Particulate Filter), EGR = Exhaust Gas Recirculation

[c] DSL = diesel fuel ; [d] RME = Rapeseed Methyl Ester ; [e] HVO = Hydrotreated Vegetable Oil

[f] CNG = Compressed Natural Gas: methane, natural and biogas mixture
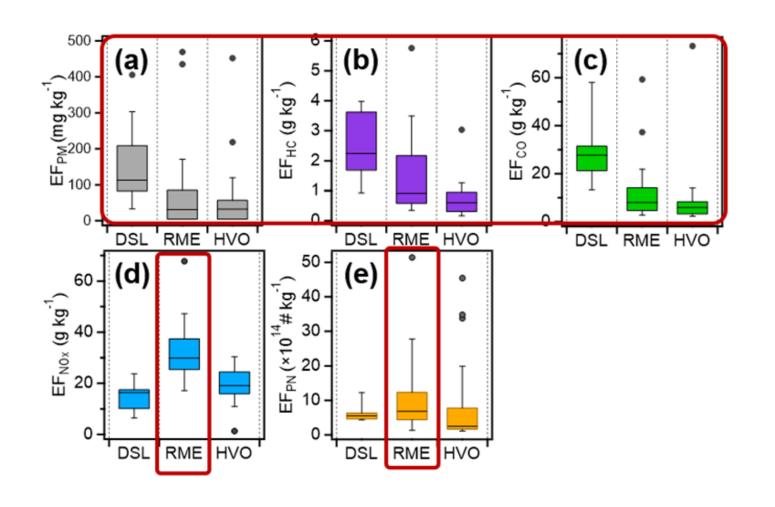
HEV =Hybrid Electric Vehicle

21

> ➢ Significant reductions in PM, HC and CO emissions with biofuels compared to diesel

> ➢ Significant increase in NOx emissions due to higher fuel oxygen content in biofuels

Secondary vs. Primary Aerosol
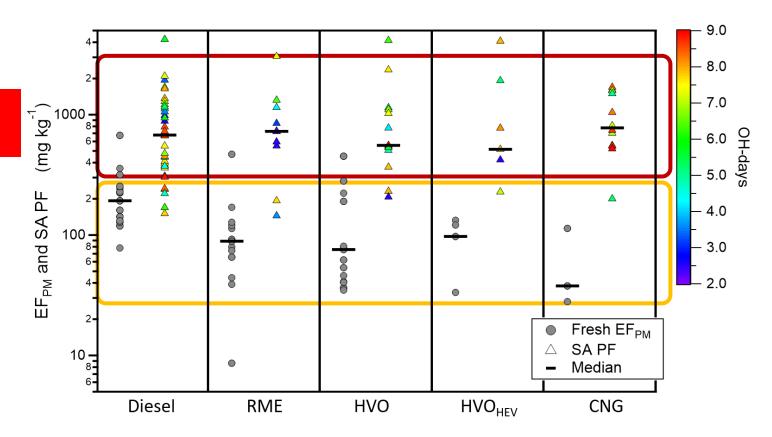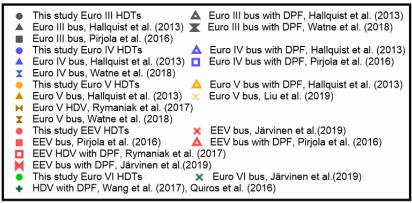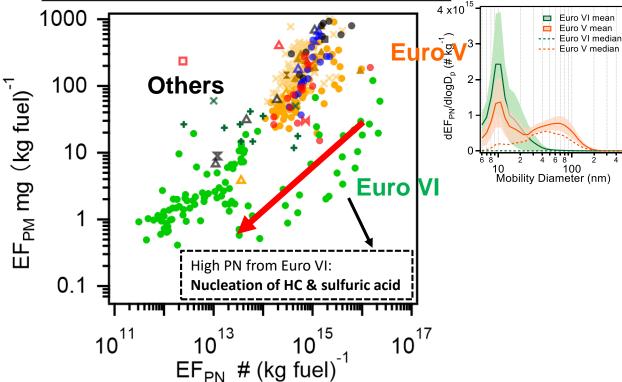
> The variation of median SA PF was less significant compared to that of $^{Md}EF_{PM}$
> The SA PF were high for all fuel types even when the primary emissions were low
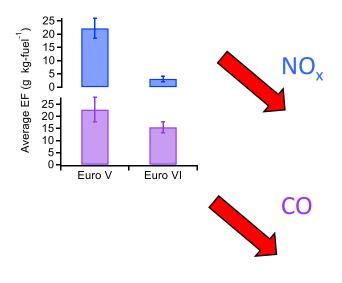
Truck emission measurements on a ramp of a freeway in Gothenburg
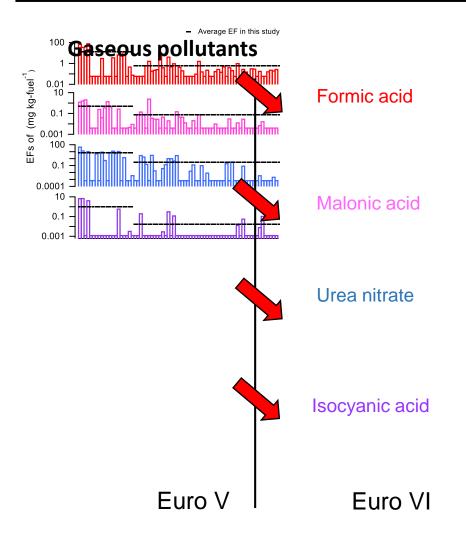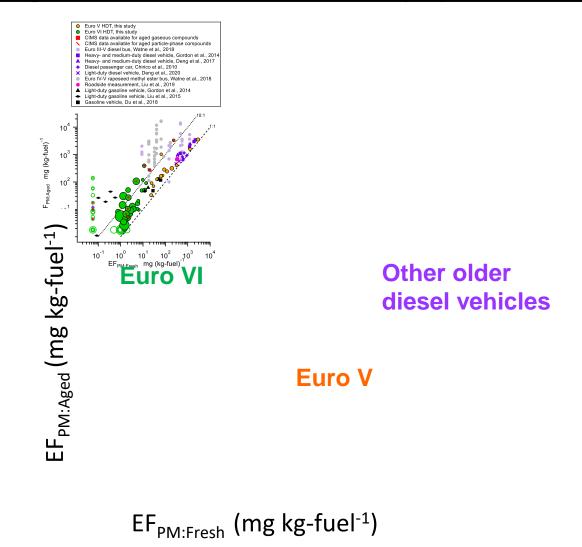
- Decreasing EF_{PM} and EF_{PN} with increasingly stringent Euro standards.

- Drastically lower EF_{PM} for Euro VI HDTs but highly scattered EF_{PN}.

- Average reduction of 13-97% for regulated pollutants from Euro V to Euro VI.

(Zhou et al., 2020 ACP)

Truck emission measurements: non-regulated and secondary pollutants

Gaseous pollutants

— Average EF in this study

EFs of (mg kg-fuel^{-1})

Formic acid

Malonic acid

Urea nitrate

Isocyanic acid

Euro V   Euro VI

$EF_{PM:Aged}$ (mg kg-fuel^{-1})

$F_{PM:Aged}$ mg (kg-fuel)$^{-1}$

$EF_{PM:Fresh}$ mg (kg-fuel)$^{-1}$

- Euro V HDT, this study
- Euro VI HDT, this study
- CIMS data available for aged gaseous compounds
- CIMS data available for aged particle-phase compounds
- Euro III-V diesel bus, Watne et al., 2018
- Heavy- and medium-duty diesel vehicle, Gordon et al., 2014
- Heavy- and medium-duty diesel vehicle, Deng et al., 2017
- Diesel passenger car, Chirico et al., 2010
- Light-duty diesel vehicle, Deng et al., 2020
- Euro IV-V rapeseed methyl ester bus, Watne et al., 2018
- Roadside measurement, Liu et al., 2019
- Light-duty gasoline vehicle, Gordon et al., 2014
- Light-duty gasoline vehicle, Liu et al., 2015
- Gasoline vehicle, Du et al., 2018

Euro VI

Other older diesel vehicles

Euro V

$EF_{PM:Fresh}$ (mg kg-fuel^{-1})

➤ Most of non-regulated gaseous pollutants, e.g. carboxylic acids and byproducts from the urea-SCR exhaust, the average emissions decreased by as high as 90% from Euro V to Euro VI.

➤ Euro VI HDTs generate the lowest secondary particle mass compared with other older diesel vehicles.

(In preparation)

Theme 3

Physico-chemical processes in the urban atmosphere
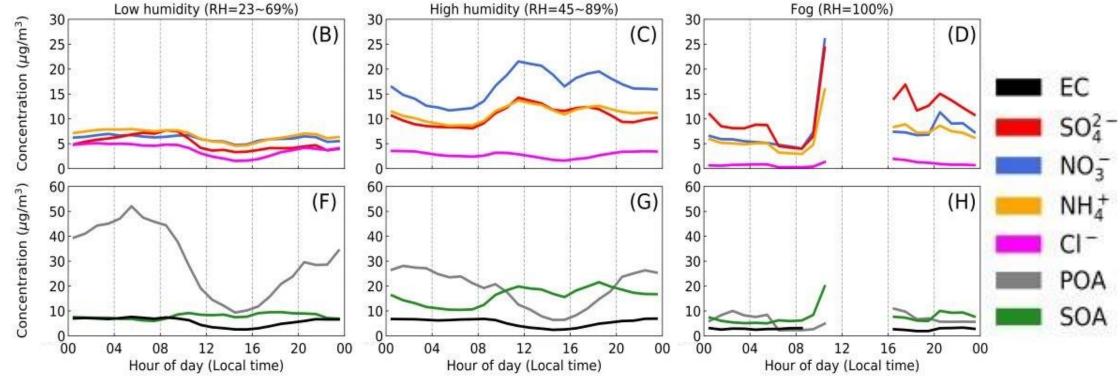(city scale)

Highly polluted environments: haze event in China

- Higher mass fraction of secondary inorganic aerosols and secondary organic aerosols at higher relative humidity: important role of multiphase chemistry during the haze events (Li et al.)

- Missing sulfate production pathways

  - Importance of SO_2 oxidation by NO_2 under high ionic strength conditions (e.g., 60 M) (Bloss et al.)

  - Potential enhancement of sulfate production by multiphase photochemistry (From CKC group)(1-3)

(1) Gen et al., *ES&T Lett.*, 6(2), 86–91, 2019**. (*ES&T Lett* Best Paper Award)**
(2) Gen et al., *ES&T.*, 53(15), 8757-8766, 2019.
(3) Zhang et al., *ES&T.*, 54(7), 3831-3839, 2020.

Diel variations of PM1 mass concentrations of the major components under various RH conditions (Li et al.)
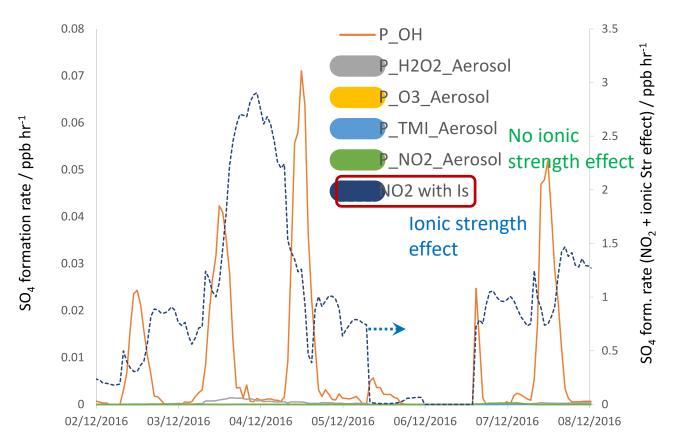
The Gucheng site, 100 km southwest of Beijing (11 Nov – 24 Dec 2018)

- Substantial increase in inorganic mass (SO_4^{2-} and NO_3^-) from low RH, to high RH, and to the fog case (RH = 100%)
- Similar but lesser increasing trend of SOA with RH
- Highlighting enhanced formation of secondary species with increasing RH, due to the multiphase processes

Modeled sulfate formation rates via SO_2 oxidation by OH, dissolved H_2O_2, O_3, TMI, and NO_2: importance of NO_2 under high ionic strength (I) conditions (Bloss et al)
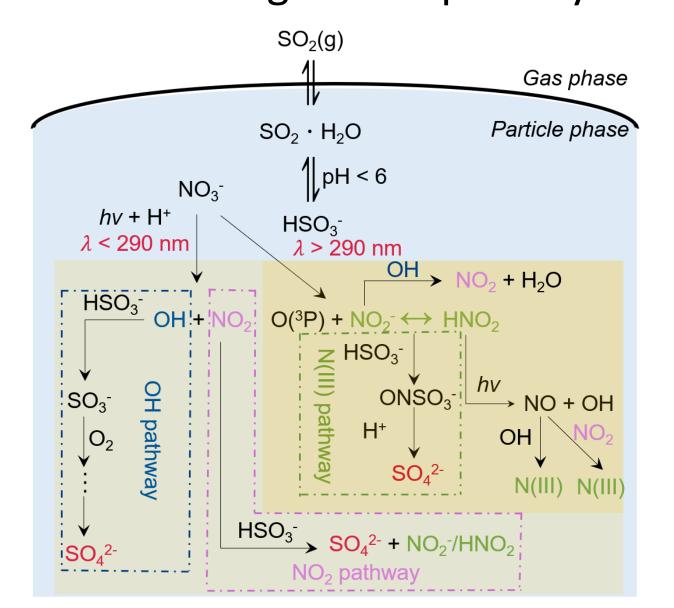
Timeseries modeled sulfate formation rates

SO_4 formation rate / ppb hr^{-1}

SO_4 form. rate (NO_2 + ionic Str effect) / ppb hr^{-1}

P_OH
P_H2O2_Aerosol
P_O3_Aerosol
P_TMI_Aerosol
P_NO2_Aerosol
NO2 with Is

No ionic strength effect

Ionic strength effect

0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0

3.5
3
2.5
2
1.5
1
0.5
0

02/12/2016 03/12/2016 04/12/2016 05/12/2016 06/12/2016 07/12/2016 08/12/2016

- Much low sulfate formation rates via SO_2 oxidation by OH, dissolved H_2O_2, O_3, TMI under high ionic strength conditions

- Significant increase in the predicted overall formation rate of sulfate due to SO_2 oxidation by NO_2 under high ionic strength conditions, comparable to field observations

$$k_{NO2}(I) = k_{NO2}(I=0) \times 10^{bI}$$

Proposed mechanism for heterogeneous oxidation of SO_2 into sulfate during nitrate photolysis
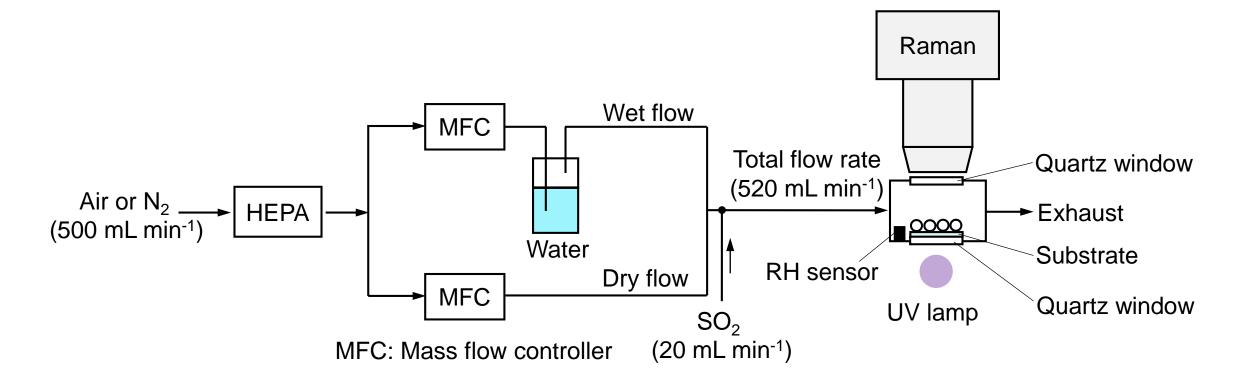

- In-particle oxidants produced from nitrate photolysis at > 290 nm irradiation: OH, NO_2, and NO_2^-/HNO_2

- 4 pathways for oxidation of dissolved SO_2 by: (1) NO_2, (2) OH, (3) NO_2^-/HNO_2 (N(III)), (4) H_2O_2

- Organics react with OH to produce O_2^-/HO_2

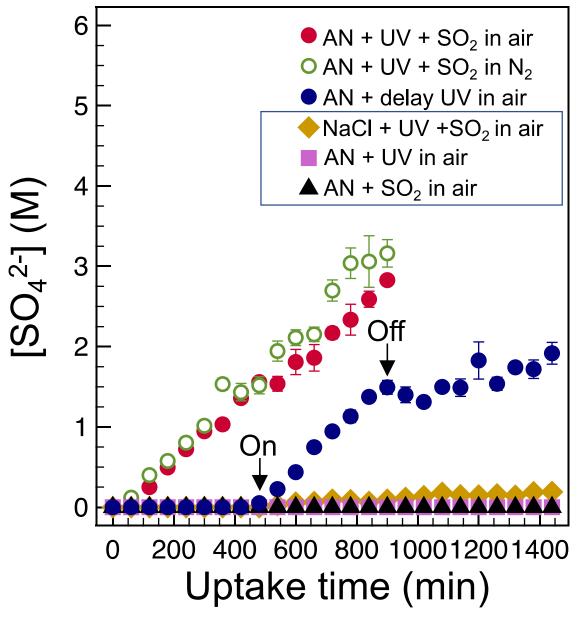- Self reaction of O_2^-/HO_2 for H_2O_2 production

Gen et al. (2019ab)

Methodology: In-situ Raman/Flow cell system to quantify sulfate production

- Sample: NH_4NO_3 (+ halide ions)
- SO_2: 7.7 ppm
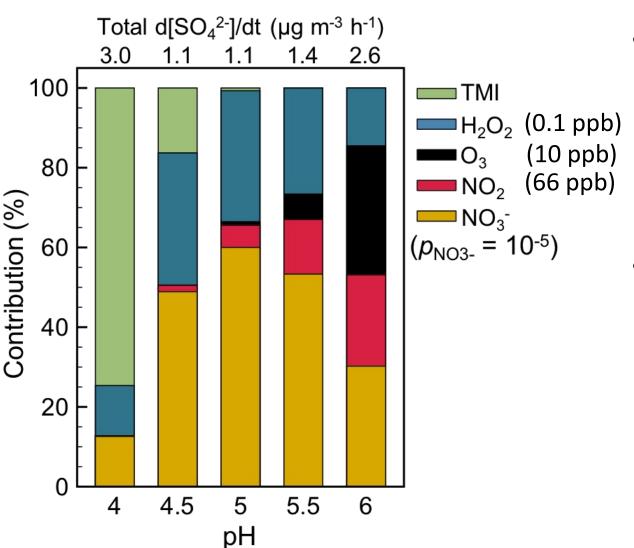- UV lamp: 250-nm (Mercury) or 300-nm (LED)

Sulfate production during nitrate photolysis at 300nm
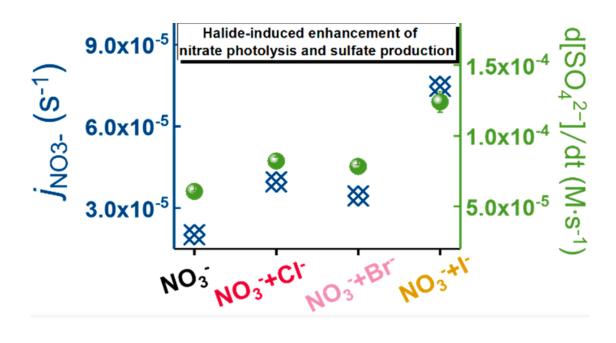
- (i) Dark experiment (AN + SO_2 in air) and (ii) AN photolysis without SO_2 (AN + UV in air): no sulfate production

- NaCl photolysis with SO_2 (NaCl + UV + SO_2 in air): significantly low sulfate production

- AN photolysis with SO_2 in air (AN + UV + SO_2 in air) and N_2 (AN + UV + SO_2 in N_2): sulfate production

- AN photolysis with SO_2 and delay irradiation (AN + delay UV in air): significant sulfate production during irradiation

Nitrate photolysis vs other mechanisms in sulfate production under typical haze conditions in Beijing
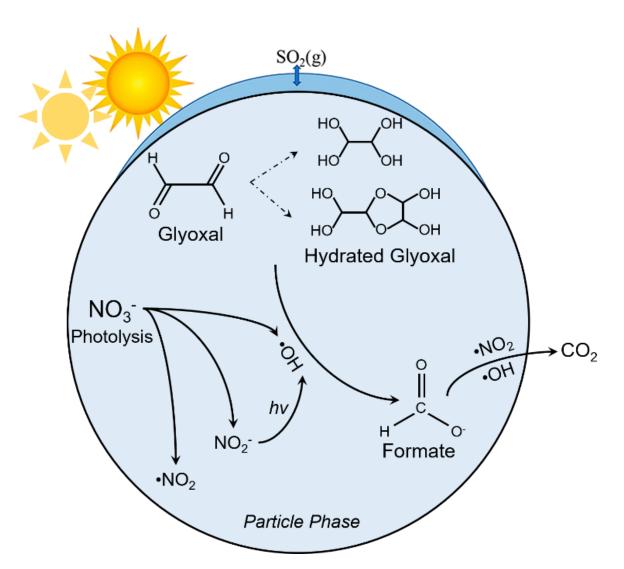
- Nitrate photolysis rate ~ 10^{-5} M s^{-1}:
  - ✓ pH > 4, Total sulfate production rate: ~1 $\mu g\ m^{-3}\ h^{-1}$ → close to missing sulfate production rate ~3 $\mu g\ m^{-3}\ h^{-1}$

- 4.5 < pH < 5.5 (typical pH range under haze event)
  - ✓ Nitrate photolysis process can contribute up to ~60% of sulfate production in aqueous particles.

Halide-induced enhancement of nitrate photolysis leading to increased sulfate production

- High surface propensity of halide ions (Cl^-, Br^- and I^-).

- Halide ions prefer to reside at the surface → increased counterion (i.e., cation) concentration → attract more nitrate ions to the surface.

- Reduced solvent-cage effect at the interface.

Zhang et al., EST, 2020

Implementation of the proposed mechanism in air quality model and on-going work

- $\gamma_{SO2} = 1.64 \times j_{NO3-} \times [NO_3^-]$ according to our experimental data

  Gen et al., *ES&T.*, 53(15), 8757-8766, 2019.

- Nitrate photolysis pathways can contribute to 15% to 65% to sulfate gap when EF* increase from 10 to 100 in haze events in Beijing

  Zheng et al. *ES&T Lett* 7.9 (2020): 632-638.

  *EF: enhancement factor of nitrate photolysis rate constant relative to that of gas phase
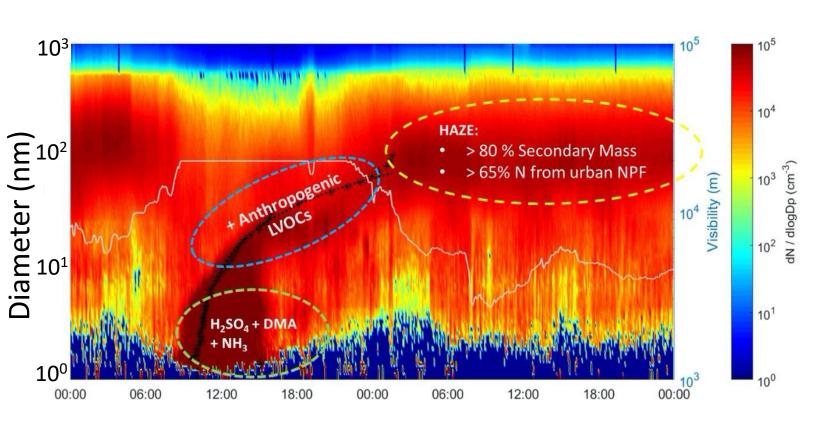
- Oxidation of Glyoxal during nitrate photolysis under 300-nm

  Zhang et al. To be submitted.

Importance of new particle formation (NPF) in air quality in mega cities (Beijing)

- NPF leading to haze episodes (Kulmala et al.)

- Survival of clusters and newly formed particles governed by background aerosols through the coagulation scavenging (Deng et al.)

- Necessity for improved methods for more accurately quantifying the formation and the growth rates of newly formed particles in polluted urban environments (Deng et al.)
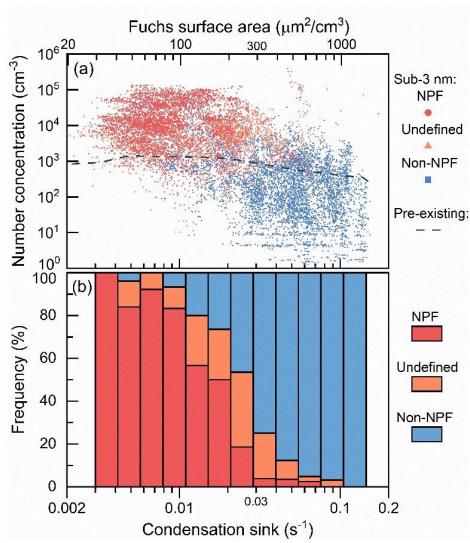
Main mechanisms of NPF and subsequent particle growth leading haze episodes (Kulmala et al.)
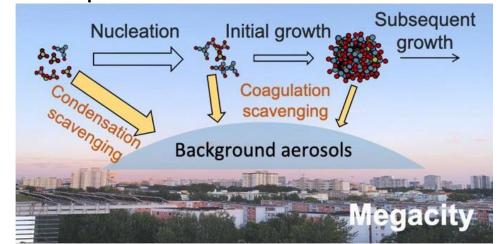

- NPF initiating almost all present-day haze episodes

- Delaying the buildup of haze episodes by 1–3 days by the reduction in the growth rate of freshly formed particles

Number concentrations of sub-3 nm particles and occurrence frequencies of NPF under different condensation sink (CS) (Deng et al.)

- At low CS, frequent NPF events and high concentrations of sub-3 nm particles

- At high CS, rarely observed NPF events and the concentrations of below 10^3 cm^{-3}

- Importance of the coagulation scavenging in governing the survival of clusters and newly formed particles
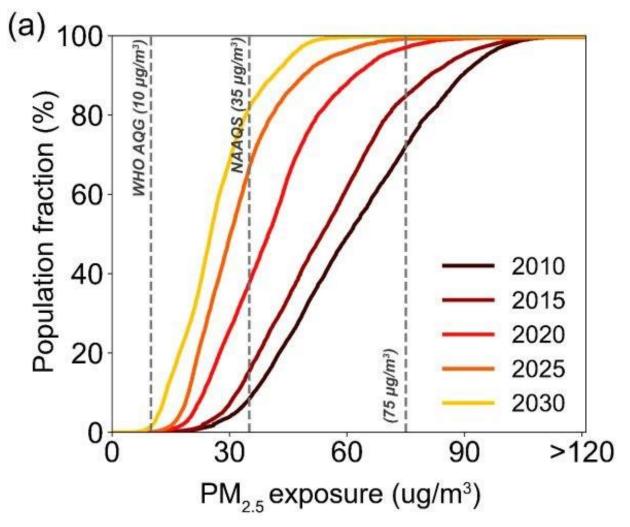
Vertical profiles: effect of surface emissions in boundary layer

- More pronounced vertical gradient for reactive isoprene and monoterpenes in comparison to less reactive CO, benzene, and toluene (Kim et al.)

- More oxidized compounds in submicron particles at 260 m than at ground level (Xie et al.)

- Little obvious difference in aerosol CCN and hygroscopic behavior at different heights, suggesting the usefulness of surface hygroscopicity measurements (Hu et al.)
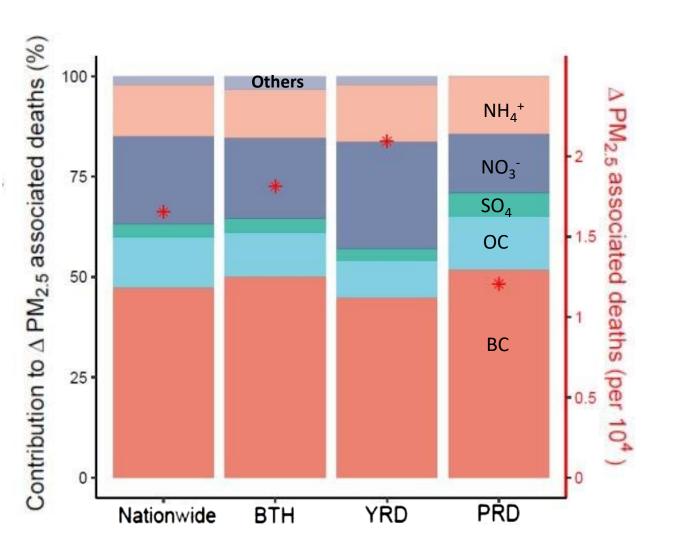
Theme 4

Health Effects

PM$_{2.5}$ air quality improvements over China contributed by clean air policies during 2010-2030 (Cheng et al.)

(a)

- In 2010, more than 91.5% and 30% of the population exposed above 35 μg/m^3, and 75 μg/m^3

- Rapid decrease in PM$_{2.5}$ exposures across China with the clean air policies to 26.4 μg/m^3 by 2030

- By 2030, the majority of China's population (81.7%, 1143.5 million people) exposed below the National Ambient Air Quality Standard (35 μg/m^3)

Contributions of PM$_{2.5}$ component variations from 2000 to 2010 to changes in deaths attributable to PM$_{2.5}$ mixture (Xue et al.)
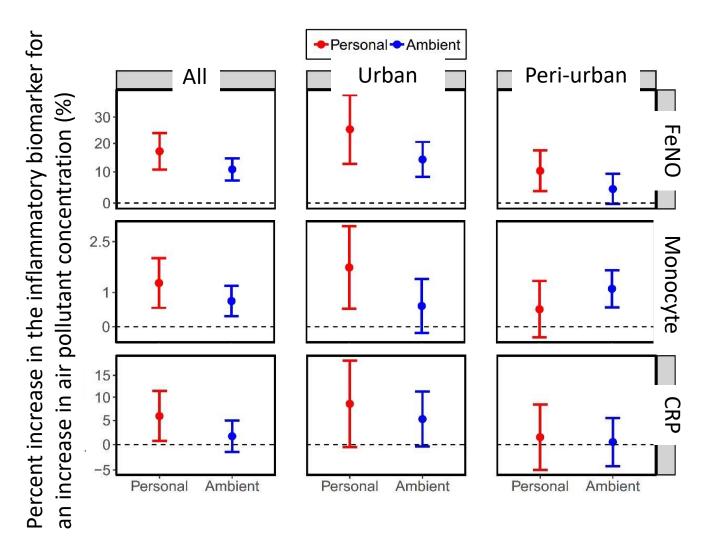

- According to CS-EMM, **BC** was the leading contributor to mortality burden

- At national scale and in BTH, YRD, and PRD, **BC** contributed to 6.4%, 6.2%, 5.8%, and 9.0% of changes in total concentration of PM$_{2.5}$, but to 46.7%, 49.4%, 44.3%, and 51.3% of associated changes in mortality, respectively.

CS-EMM: Components-Specific Exposure-Mortality Model.
BTH: Beijing-Tianjin-Hebei
YRD: Yangtze River Delta
PRD: Pearl River Delta

Association with health effects : personal exposure vs. ambient measurements (Han et al.)

- Three biomarkers for the inflammatory effects of air pollution: exhaled NO, Monocyte, and CRP

- **Among all participants, significant association of personal exposure to PM$_{2.5}$ with an increase in all the three inflammatory biomarkers**

- In general, insignificant association of the ambient exposure with the health effects

CRP: C reactive protein

Going forward

Regional scale air quality :
- Rich literature: emissions, source apportionment, ambient characterization, SOA, BC/OC, SNA, NPF and growth, ammonia, pH, CCN

Health:
- Aging and dense population require better air quality
- Personal exposure assessment vs ambient concentrations
- BC

Indoor and neighborhood scale air quality studies:
- Emission inventories: traffic including non tail pipe emissions, cooking emissions
- Modeling including the above emissions, NPF and growth, and atmospheric chemistry and SOA formation
- Measurements

COVID Lockdown:
- Interesting "new" atmospheric chemistry and physics
- Increased importance of secondary processes
- Projection of the emissions, air quality, and personal exposure under the New Normal and Green Recovery

Air pollution in megacities

- LA, London, Beijing, Shanghai, Mexico City, Delhi, Bangkok, Paris, Seoul etc…

Megacities and Atmospheric Pollution

Mario J. Molina and Luisa T. Molina
Massachusetts Institute of Technology, Cambridge, Massachusetts

Mario J. Molina   Luisa T. Molina

Review

Air pollution in mega cities in China

Chak K. Chan[a],*, Xiaohong Yao[a,b]

[a]Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China
[b]Key Laboratory of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, 238 Songling Road, Qingdao 266100, PR China
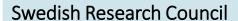
Acknowledgments

Funding Support

Environment & Conservation Fund	
University Grants Committee & Research Grants Council	
Swedish Research Council	
National Science Foundation of China	

CKC research group

Dr. Berto Lee (CE), Dr. Yongjie Li (U. Macao), and Dr. DanDan Huang (SAES) (AMS measurements in MK)
Dr. Teng Yu Liu (U. Toronto) (Cooking SOA)
Dr. Qianyun Liu and Ms Liyuan Zhou (Bus measurements in Sweden)
Dr. Masao Gen (Kanazawa U.) and Ms Ruifeng Zhang (Sulfate)

Collaborators

Prof. Guo Hai – **Hong Kong Polytechnic University**	
Prof. Jianzhen Yu – **Hong Kong University of Science and Technology**	
Prof. Man Nin Chan – **Chinese University of Hong Kong**	
Prof. Mattias Hallquist – **University of Gothenburg**	
Åsa Hallquist - **IVL Swedish Environmental Research Institute**	
Prof. Wang Xinming - **Guangzhou Institute of Geochemistry, CAS**	
Air Science Group – **Environmental Protection Department, HKEPD**	

46