AQUARIUS, Salt Lake city

Fast Photochemistry Discovered in Winter Beijing: Evidences, Reasons and Impacts

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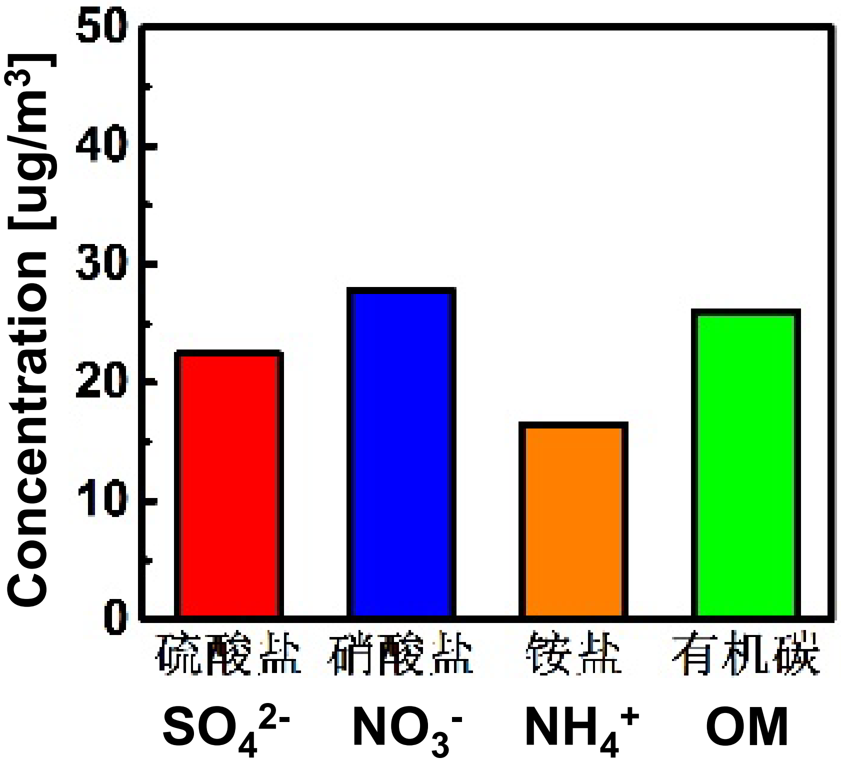
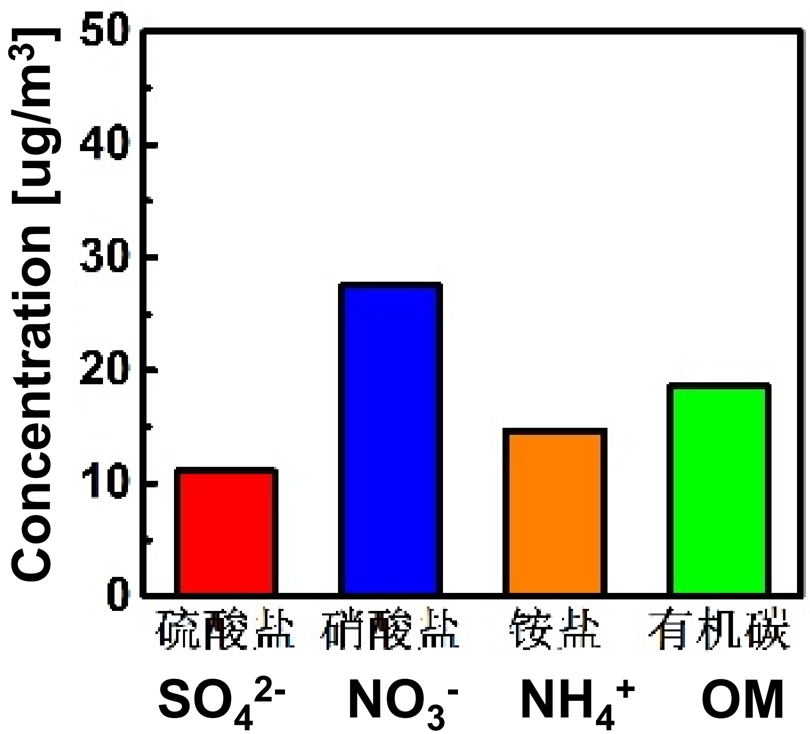
2019-09-25

Winter Air Pollution in NCP

Formation mechanism of the particulate nitrate and POM?

2016 Winter, NCP → 2017 Winter, NCP



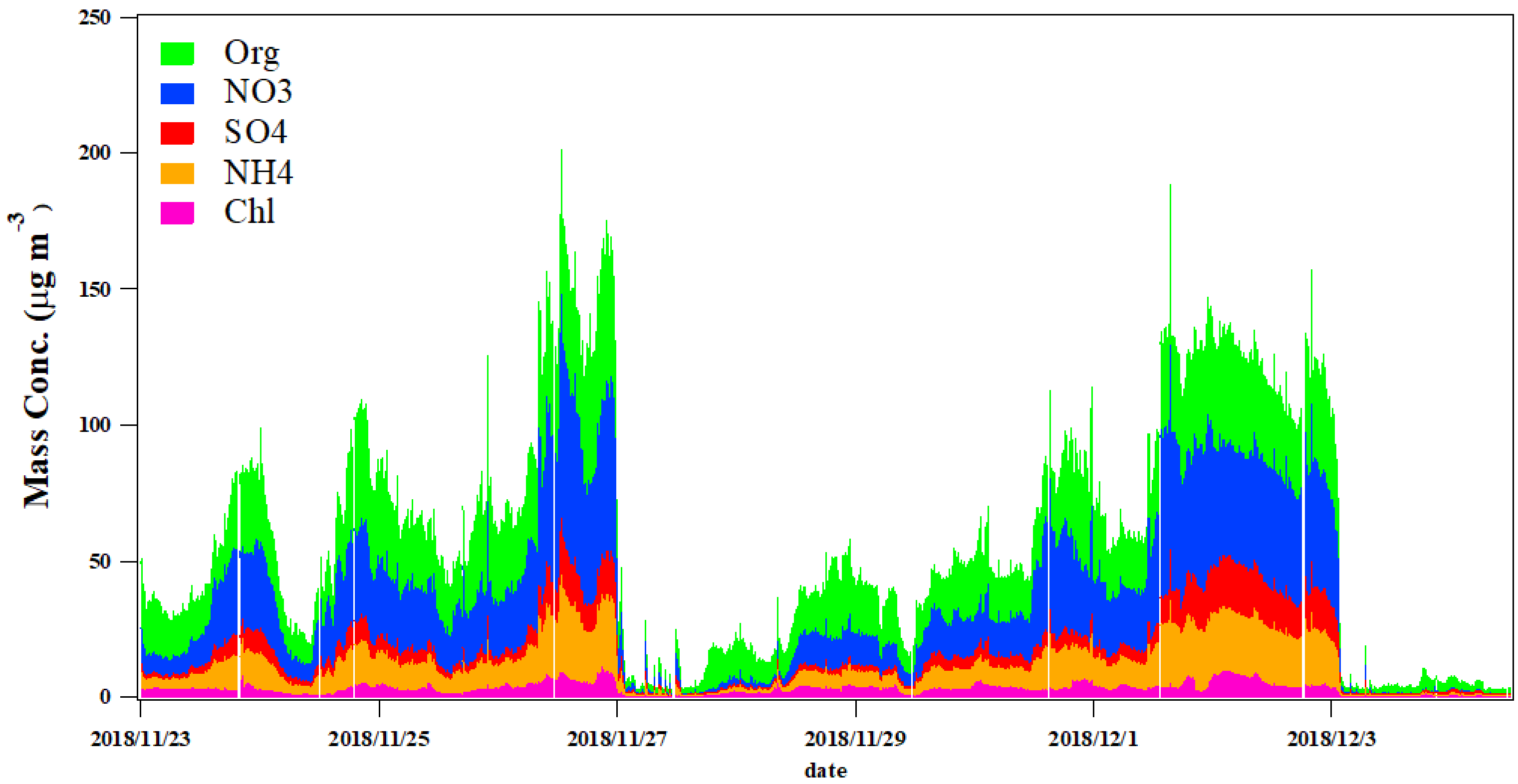


Chinese EPA: NCP particle components monitoring network

Winter Air Pollution in NCP

Formation mechanism of the particulate nitrate and POM?

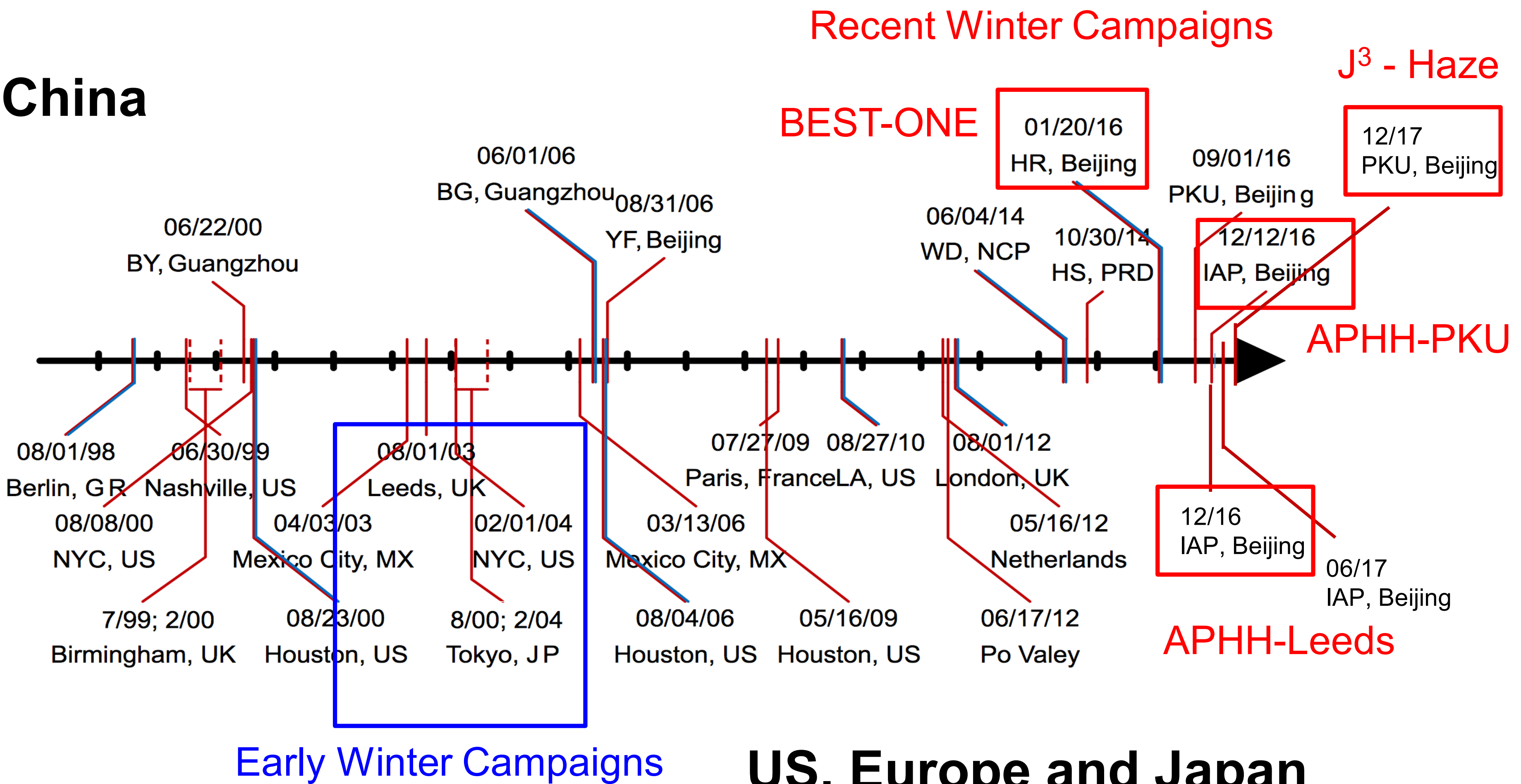
2018 Winter, NCP



Measured by AMS @ Peking University Super site

Winter radical measurements

Field campaigns including HO_X or NO_3 radical measurements



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Winter radical measurements in Beijing

Environmental Science & Technology

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Fast Photochemistry in Wintertime Haze: Consequences for Pollution Mitigation Strategies

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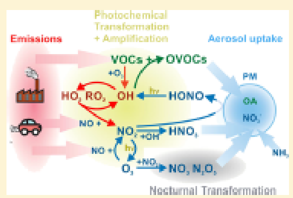
Supporting Information

ABSTRACT: In contrast to summer smog, the contribution of photochemistry to the formation of winter haze in northern mid-to-high latitude is generally assumed to be minor due to reduced solar UV and water vapor concentrations. Our comprehensive observations of atmospheric radicals and relevant parameters during several haze events in winter 2016 Beijing, however, reveal surprisingly high hydroxyl radical oxidation rates up to 15 ppbv/h, which is comparable to the high values reported in summer photochemical smog and is two to three times larger than those determined in previous observations during winter in Birmingham (Heard et al. *Geophys. Res. Lett.* 2004, 31, (18)), Tokyo (Kanaya et al. *J. Geophys. Res.: Atmos.* 2007, 112, (D21)), and New York (Ren et al. *Atmos. Environ.* 2006, 40, 252−263). The active photochemistry facilitates the production of secondary pollutants. It is mainly initiated by the photolysis of nitrous acid and ozonolysis of olefins and maintained by an extremely efficiently radical cycling process driven by nitric oxide. This boosted radical recycling generates fast photochemical ozone production rates that are again comparable to those during summer photochemical smog. The formation of ozone, however, is currently masked by its efficient chemical removal by nitrogen oxides contributing to the high level of wintertime particles. The future emission regulations, such as the reduction of nitrogen oxide emissions, therefore are facing the challenge of reducing haze and avoiding an increase in ozone pollution at the same time. Efficient control strategies to mitigate winter haze in Beijing may require measures similar as implemented to avoid photochemical smog in summer.



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Rural Beijing

Wintertime photochemistry in Beijing: observations of RO_x radical concentrations in the North China Plain during the BEST-ONE campaign

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Winter photochemistry in Beijing: Observation and model simulation of OH and HO_2 radicals at an urban site

Check for updates

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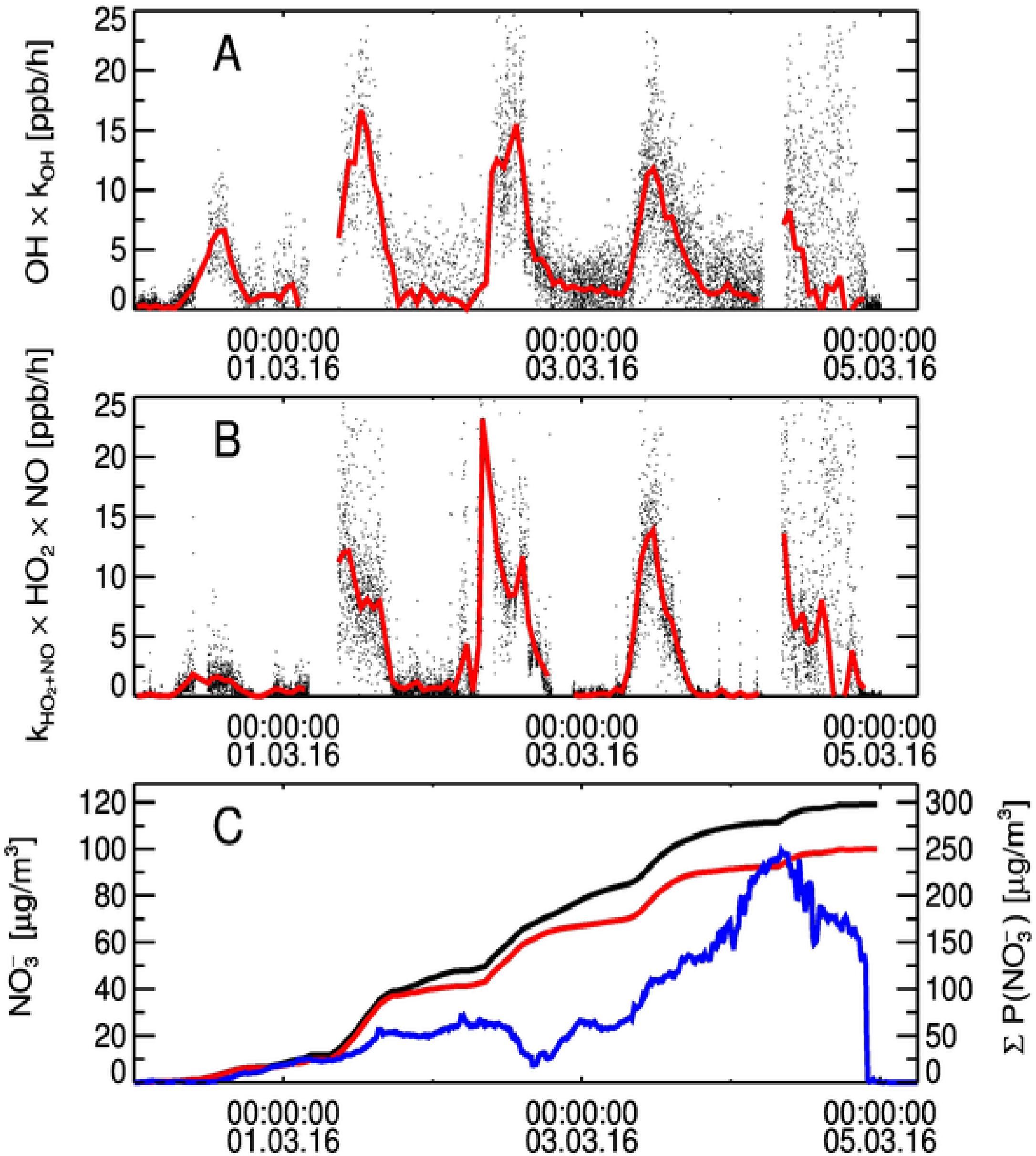
HIGHLIGHTS

- OH and HO_2 radical concentrations are measured in urban Beijing during winter.
- Comparable radical concentrations are observed in clean and polluted episodes.
- Chemical conditions and photochemical reactions show spatially homogeneity throughout Beijing.

GRAPHICAL ABSTRACT

Urban Beijing

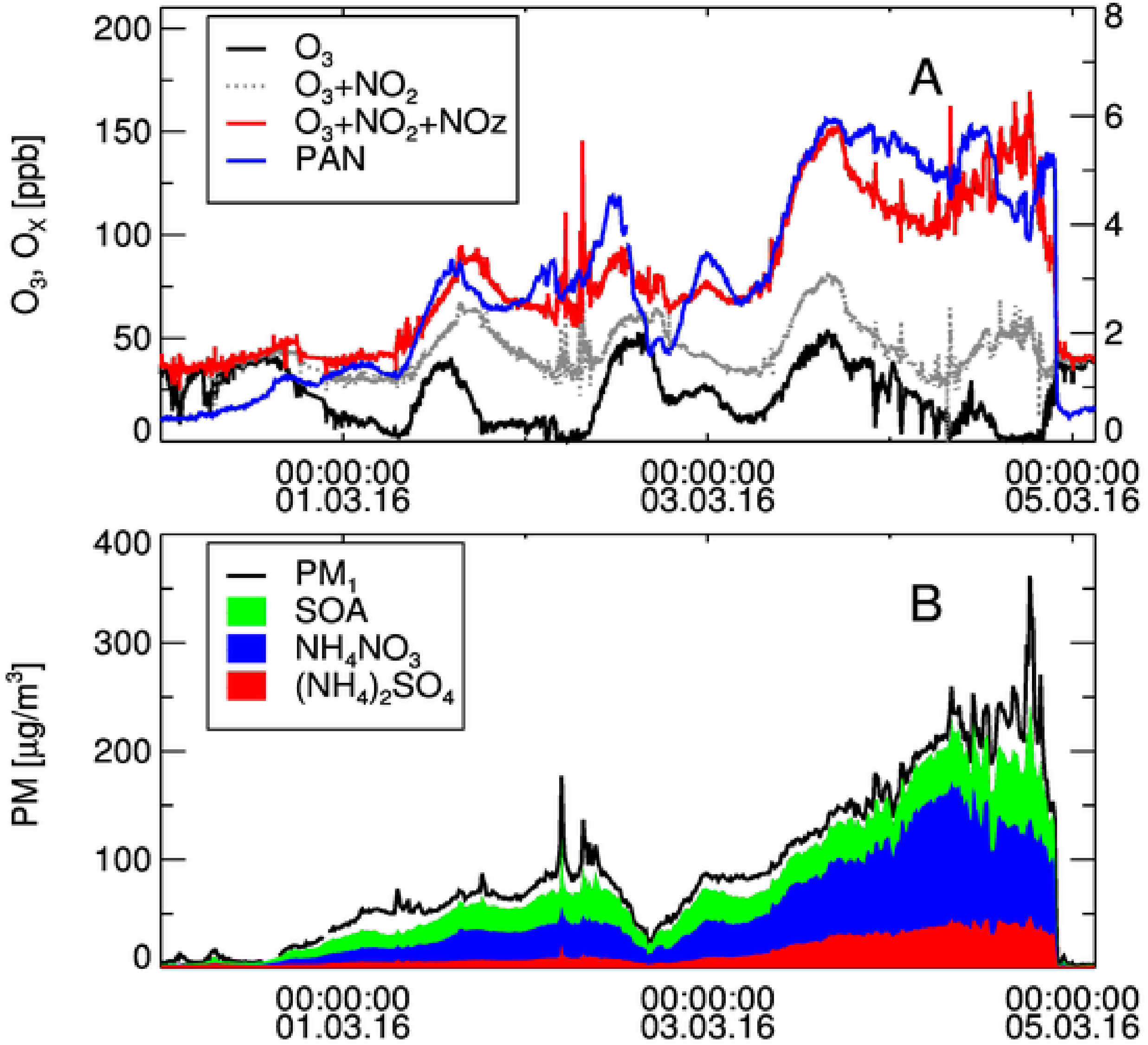
Fast photochemistry: radical turnover rates



Fast OH oxidation and gross **O_3 production** rates were determined, **comparable to summer time !**

The produced **O_3 is quickly titrated to be NO_2** and **further converted to** NOz and particulate nitrate (**NO_3^-**) by OH and NO_3 oxidation.

Fast photochemistry: total oxidants

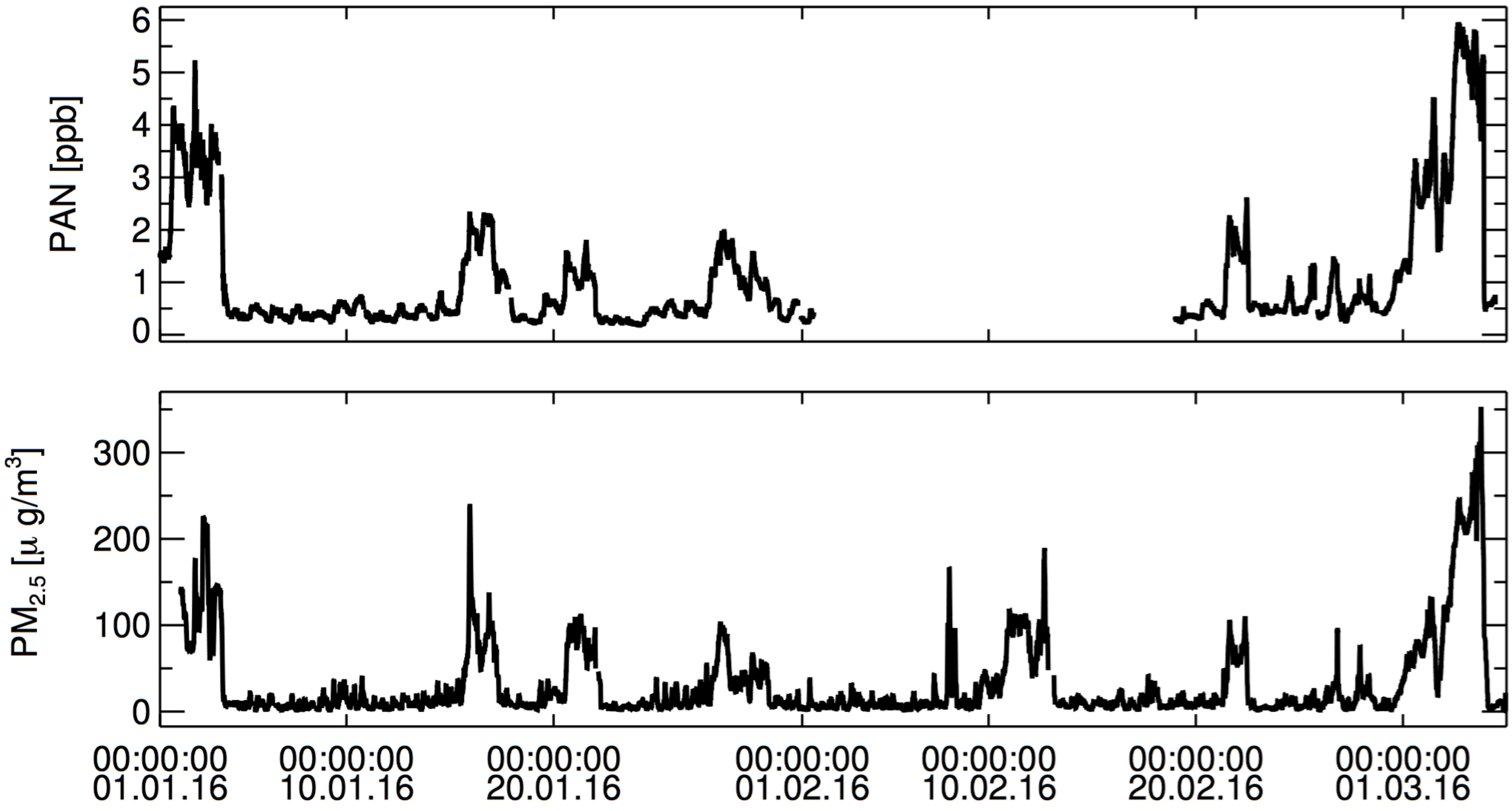


The observed O_3 is small but **the total oxidants** (Ox = O_3 +NO_2 + NOz) and PAN **is quite high, comparable to summer.**

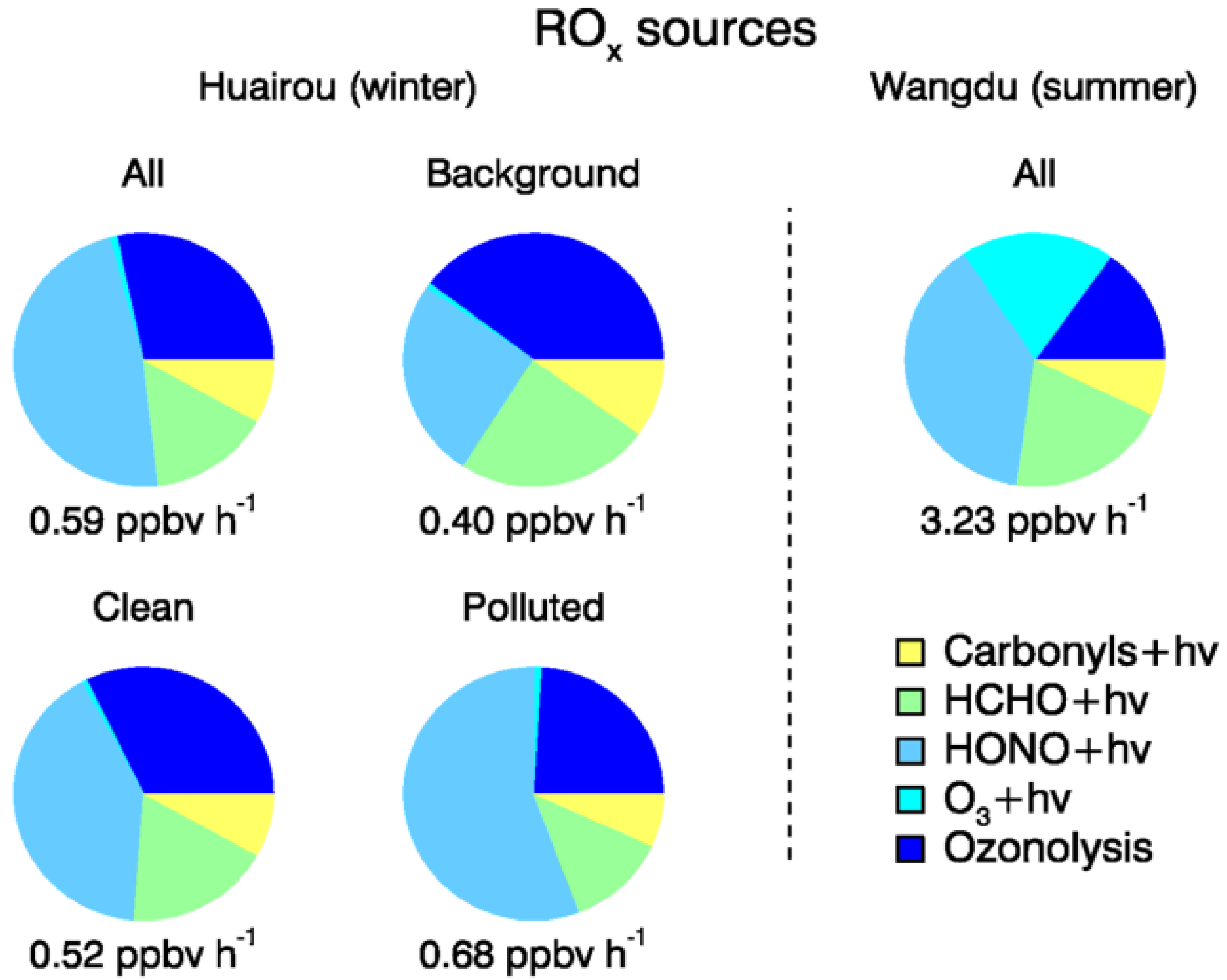
The fine particles are mainly secondary, and ammonium nitrate as the largest components.

Fast photochemistry: PAN

PM pollution always appeared with elevated PAN

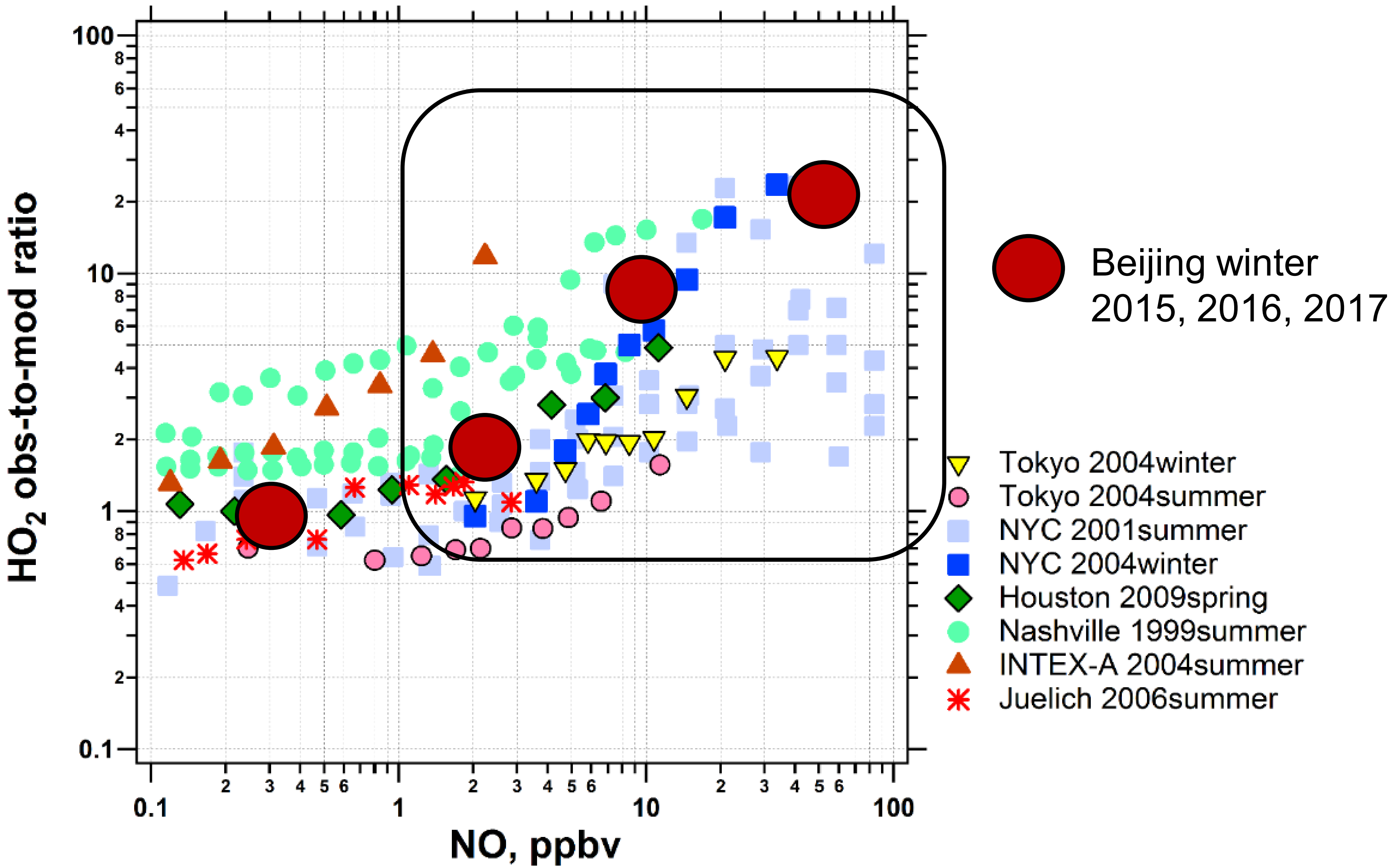


Fast photochemistry: known ROx sources

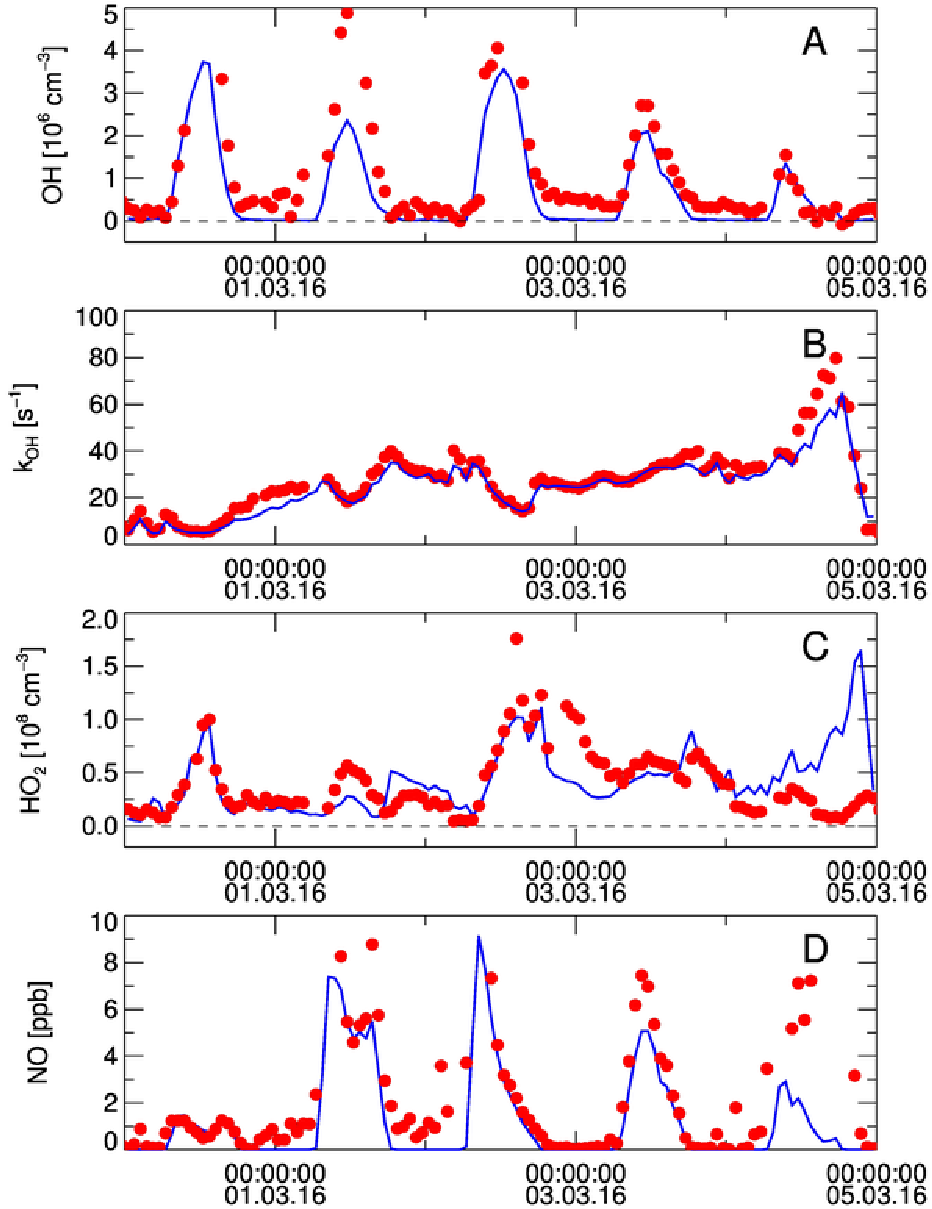


Fast photochemistry: missing RO_X sources

For both Winter and Summer



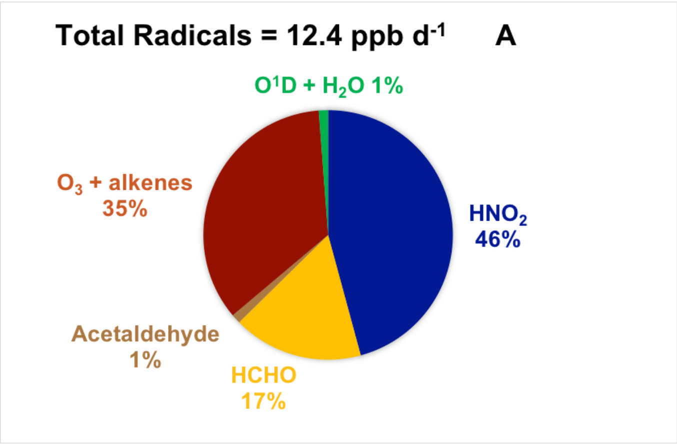
Photolysis of $ClNO_2$ and ozonolysis of alkenes



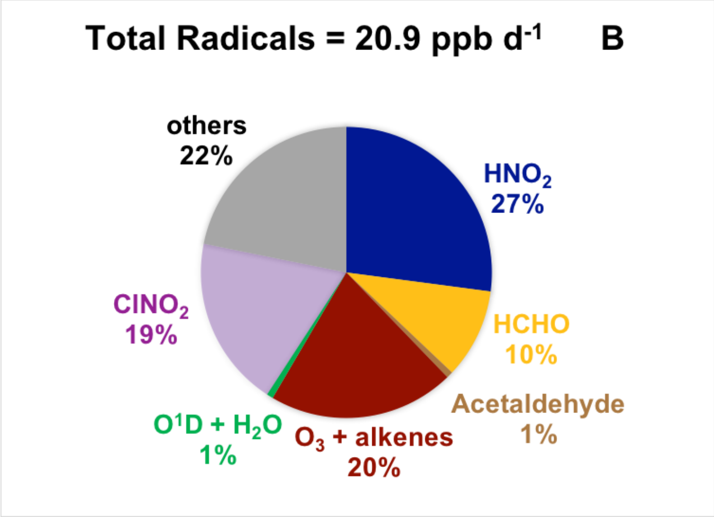
Model: RACM2 updated by LIM

and **Chlorine chemical module**

Experimentally determined



Modelled



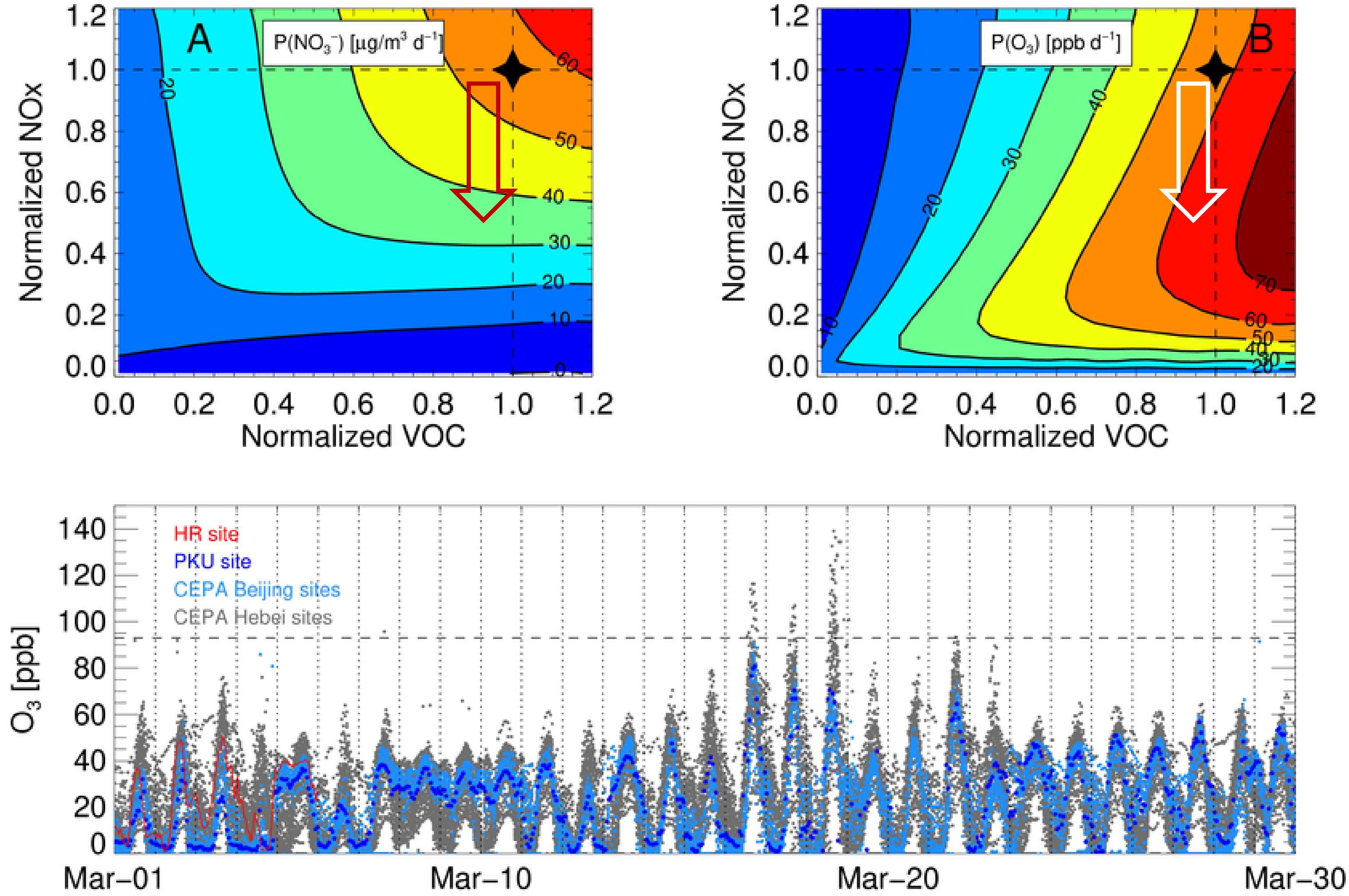
Suggested specific measurement parameters

To explore the missing ROx sources in winter or more general at high NOx regime, the following parameters may be of importance:

1. Photolysis of reactive nitrogen compounds
   - Measurement of $ClNO_2$: CIMS
   - Measurement of ANs/PNs: TD-LIF, **TD-CEAS**, CIMS
2. Ozonolysis of alkenes
   - Measurement of criegee radicals: CIMS
   - Measurement of speciated produced RO_2: **PTR3**

Instruments PKU may contribute

Policy Implications: control strategies for Beijing



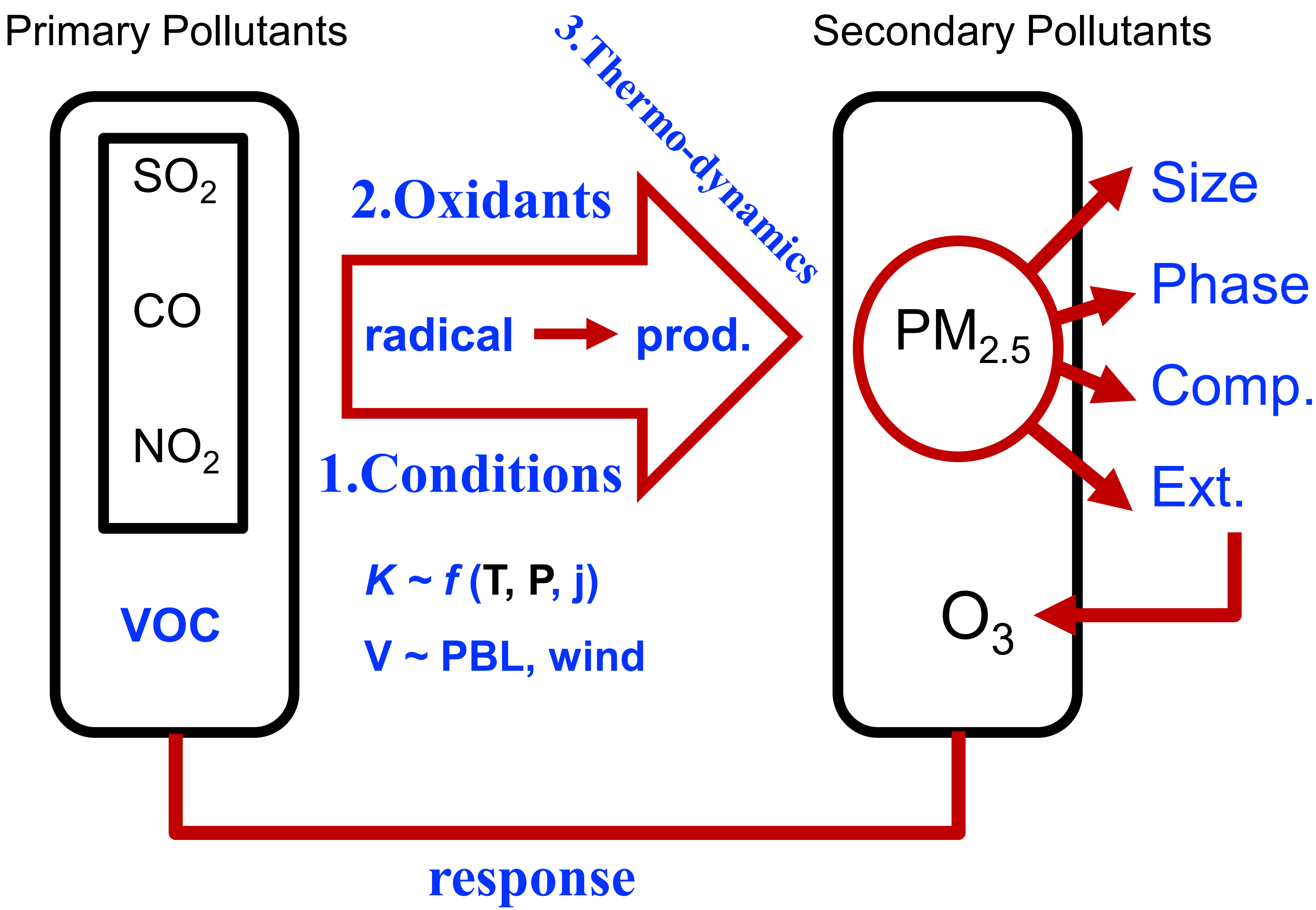
Winter Photochemical Smog

- **Beijing and Utah Winter Air Pollution**
  - **High loads of VOCs and NOx**
  - Low temperatures
  - Large daily UV dose of UVA but small UVB
  - Intense photochemical conversion of primary pollutants into photo-oxidants and aerosol

- **London Smog**
  - Characterized by high loads of SO_2, particles and soot
  - Low temperatures

- **Los Angeles Photochemical smog**
  - **High loads of VOCs and NOx**
  - High temperatures
  - Large daily UV dose

Measurement Concept for Winter Photochemical smog



To consider O_3 and PM formation in the same time !!!

Thanks!
Questions & Comments