Supplementary Materials

of

Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes

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1. VOC measurements, categorization and reactivity analysis

The VOC measurements were made by taking whole air samples with subsequent laboratory analyses. Generally, one sample was collected at noon each day during the field campaigns. (Note that the sampling was not made consecutively at Lanzhou.) In addition, multiple samples were taken on selected ozone episode days, normally one sample every two hours from 7:00 to 19:00 LT. Such a sampling strategy aimed at facilitating both a thorough evaluation of VOC pollution for the campaigns and a comprehensive modeling analysis for the high ozone events. In total, 130, 68, 76, and 24 VOC samples were collected in Beijing, Shanghai, Guangzhou, and Lanzhou, respectively.

Two-litre electro-polished stainless steel canisters, previously cleaned and evacuated at the University of California, Irvine (UCI), were used for the sampling. Details of the preparation and pre-conditioning of the canisters are described elsewhere (Blake et al., 1994). During the sampling, a stainless steel bellows valve was opened slightly and the canister was filled to ambient pressure in 2-3 minutes. After each campaign, the canisters were shipped to UCI's laboratory for the chemical analysis. A 5-column multiple gas chromatograph (GC) system equipped with flame ionization detection (FID), electron capture detection (ECD) and mass spectrometer detection (MSD) was employed to identify and quantify the VOCs species, including C_1-C_{10} hydrocarbons, C_1-C_2 halocarbons, and C_2-C_5 alkyl nitrates. Detailed descriptions of the analysis, quality assurance and quality control, measurement precision and accuracy for each species are given by Colman et al. (2001) and Simpson et al. (2010). Only the hydrocarbon data were analyzed in the present study (note that the oxygenated VOCs were not measured but simulated within the MCM model).

To facilitate analysis of the VOC speciation, the measured hydrocarbon species were grouped into anthropogenic hydrocarbons (AHC) and biogenic hydrocarbons (BHC). The AHC were further grouped into four sub-categories, namely, reactive aromatics (R-AROM), alkenes, alkanes with ≥4 carbons (C4HC), and low reactivity hydrocarbons (LRHC). The measured hydrocarbon species and the categorization are listed in Table S1.

Analysis of the VOC reactivity is critical for understanding the ozone photochemistry at a given location. In the present study, we analyzed the OH reactivity of CO and hydrocarbons, which is calculated based on the following equation.

$$R_{VOCi} = k_{OH+VOCi}*[VOC_i] \qquad \text{(Equation S1)}$$

where, the k_{OH+VOC} is the rate constant of the reaction between a VOC species and OH, and [VOC] is the measured concentration of the VOC species. The rate constants were taken from the Master Chemical Mechanism (v3.2; http://mcm.leeds.ac.uk/MCM/). As the OH reactivity takes both atmospheric abundances and reactivity towards OH into account, it is a better proxy than the concentration alone to predict the ozone formation potential of a given species.

Table S1. The quantified hydrocarbon species and the categorization

Category		**Species**
AHC	**LRHC**	methane, ethane, propane, ethyne, benzene
	C4HC	*n*-butane, *i*-butane, *n*-pentane, *i*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane[*], *2,2*-dimethylbutane, *2,3*-dimethylbutane, *2*-methylpentane, *3*-methylpentane, *2,2*-dimethylpentane[=], *2,3*-dimethylpentane[=], *2*-methylhexane, *3*-methylhexane, *2,2,4*-trimethylpentane, *2,3,4*-trimethylpentane[#,=,&], cyclopentane[=,&], methylcyclopentane[#,&], cyclohexane[&], methylcyclohexane[#,=,&]
	alkenes	ethene, propene, *1*-butene, *i*-butene, *trans*-*2*-butene, *cis*-*2*-butene, *1,3*-butadiene, *1*-pentene, *trans*-*2*-pentene[=], *cis*-*2*-pentene[=], *3*-methyl-*1*-butene[&], *2*-methyl-*1*-butene[#,=,&], *2*-methyl-*2*-butene[#,=,&]
	R-AROM	toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, *n*-propylbenzene[&], *i*-propylbenzene[#,&], *m*-ethyltoluene[&], *p*-ethyltoluene[&], *o*-ethyltoluene[&], *1,2,3*-trimethylbenzene, *1,2,4*-trimethylbenzene, *1,3,5*-trimethylbenzene, styrene[#,=,&]
BHC		isoprene, α-pinene, β–pinene[&]

[*] Species that were not measured in Beijing;
[#] Species that were not measured in Shanghai;
[=] Species that were not measured in Guangzhou;
[&] Species that were not measured in Lanzhou.

2. List of reactions describing ozone production and destruction

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (R1)$$

$$RO_2 + NO \xrightarrow{O_2} NO_2 + RO \qquad (R2)$$

$$O_3 + h\nu\ (\lambda < 320\ \mathrm{nm}) \rightarrow O(^1D) + O_2 \qquad (R3a)$$

$$O(^1D) + H_2O \rightarrow OH + OH \qquad (R3b)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (R4)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (R5)$$

$$O_3 + \textit{unsat.}\ \mathrm{VOCs} \rightarrow \mathrm{carbonyls} + \mathrm{Criegee\ biradicals} \qquad (R6)$$

$$OH + NO_2 \rightarrow HNO_3 \qquad (R7)$$

$$RO_2 + NO_2 \rightarrow RO_2NO_2 \qquad (R8)$$

$$NO_3 + \mathrm{VOCs} \rightarrow \mathrm{products} \qquad (R9)$$

$$N_2O_5 + \text{particle} \rightarrow (2-\emptyset) * NO_3^- + \emptyset * ClNO_2 \qquad (R10)$$

$$NO_3 + \text{particle} \rightarrow \text{products} \qquad (R11)$$

3. Ozone episodes

In the present study, twelve high ozone events were selected out and subject to the comprehensive modeling analysis to understand the formation of ozone episodes at the four cities. These episodes include 9, 26, 30 July 2005 in Beijing, 7, 8, 22 May 2005 in Shanghai, 18, 23, 24 May 2004 in Guangzhou, and 5, 11, 12 July 2006 in Lanzhou. Figures S1-S4 show the time series of ozone and related parameters observed during these episodes.

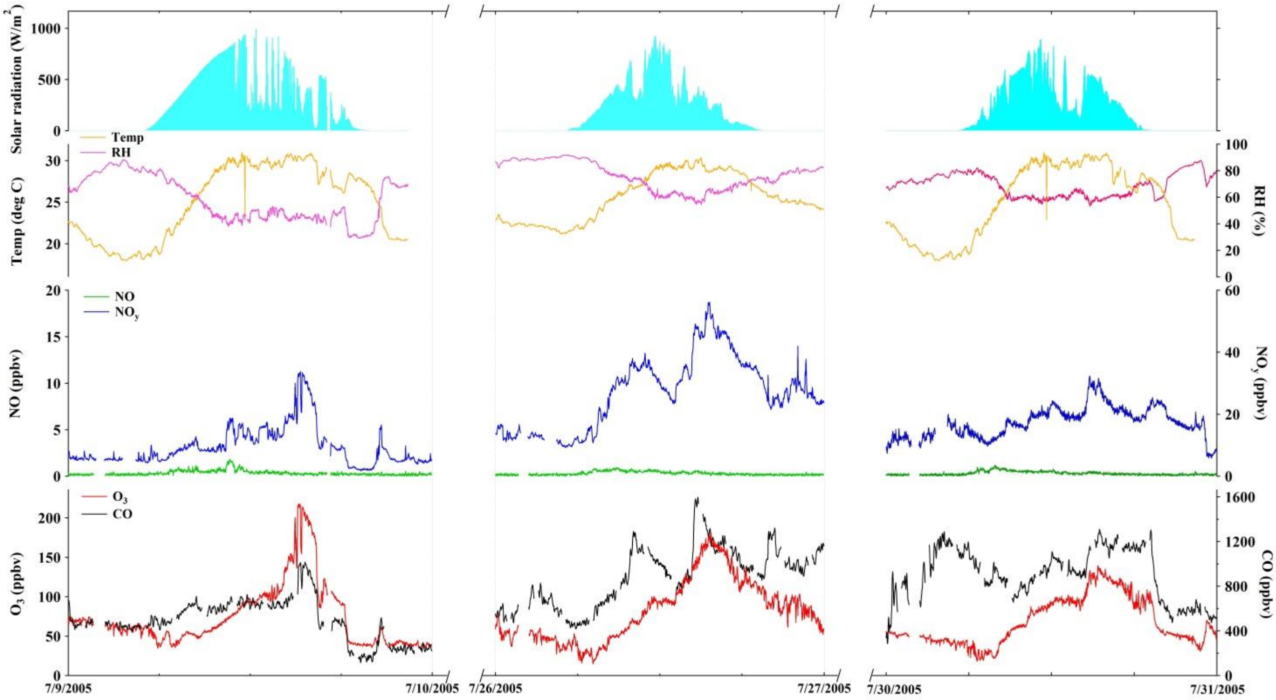

Figure S1. Time series of trace gases and meteorological parameters observed during the selected ozone episode days in Beijing in summer 2005

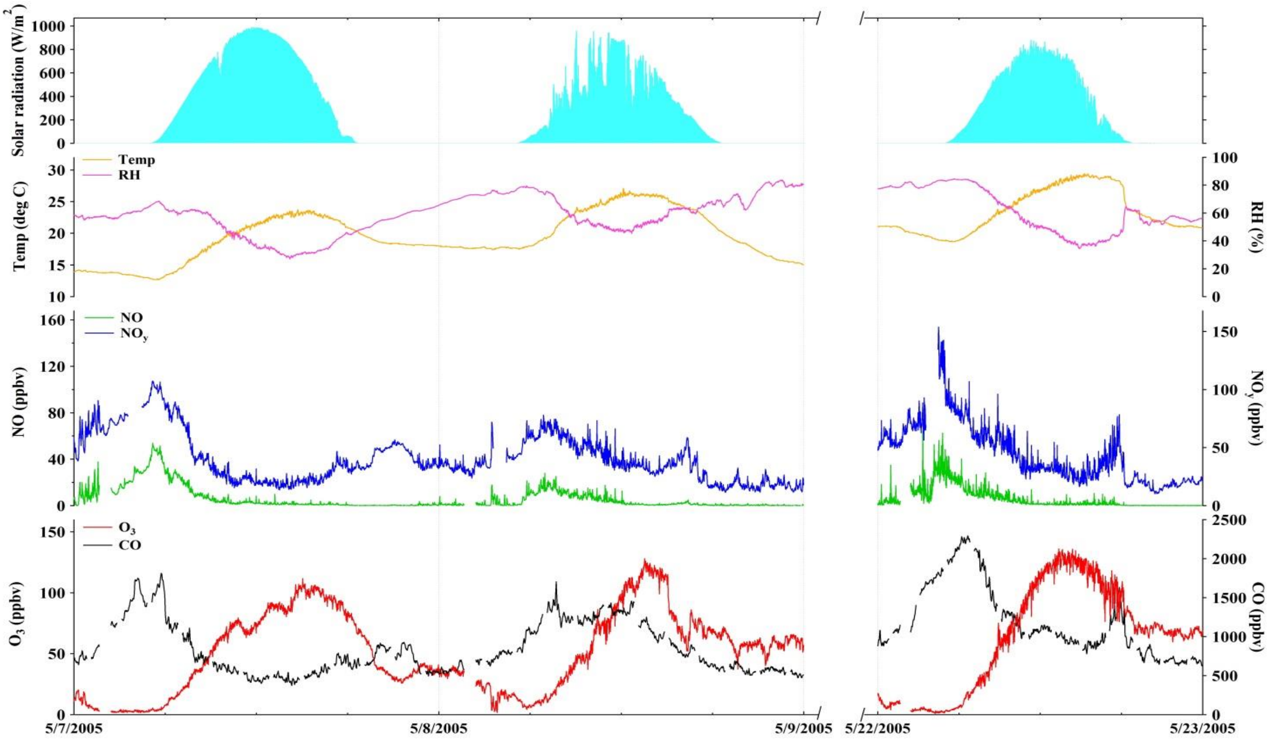

Figure S2. Time series of trace gases and meteorological parameters observed during the selected ozone episode days in Shanghai in late spring/early summer 2005

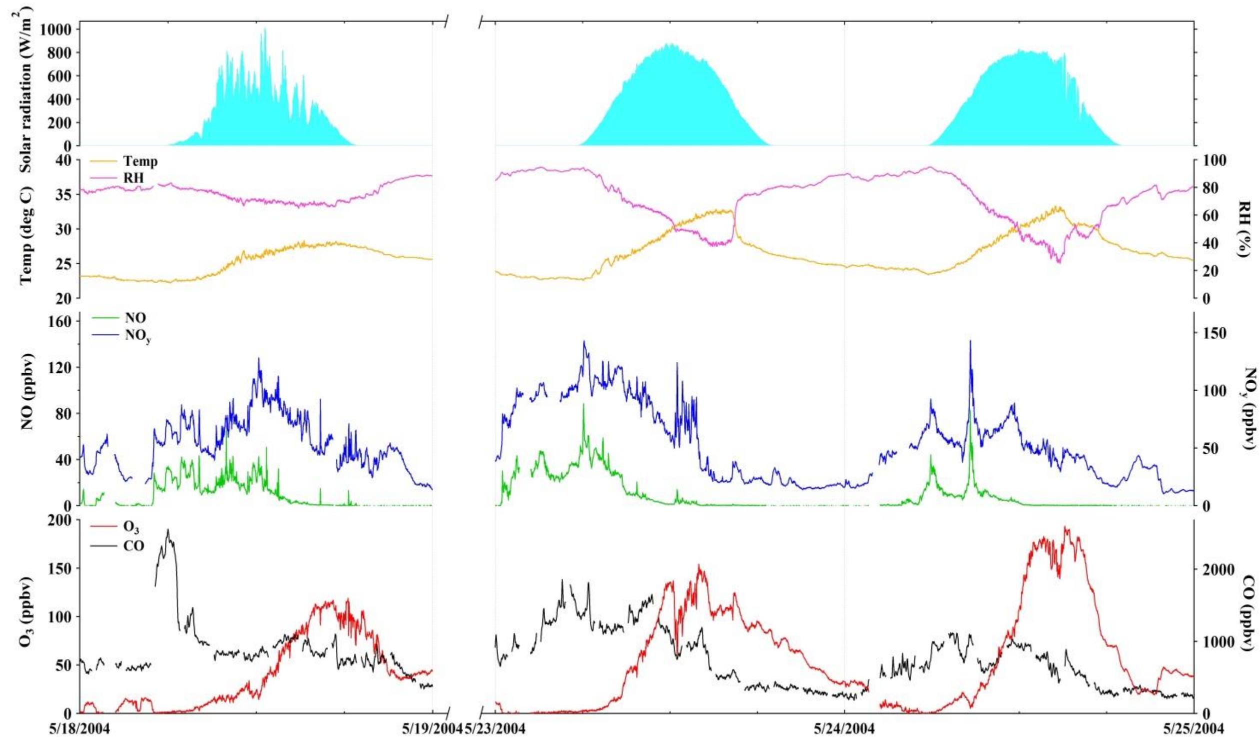

Figure S3. Time series of trace gases and meteorological parameters observed during the selected ozone episode days in Guangzhou in late spring 2004

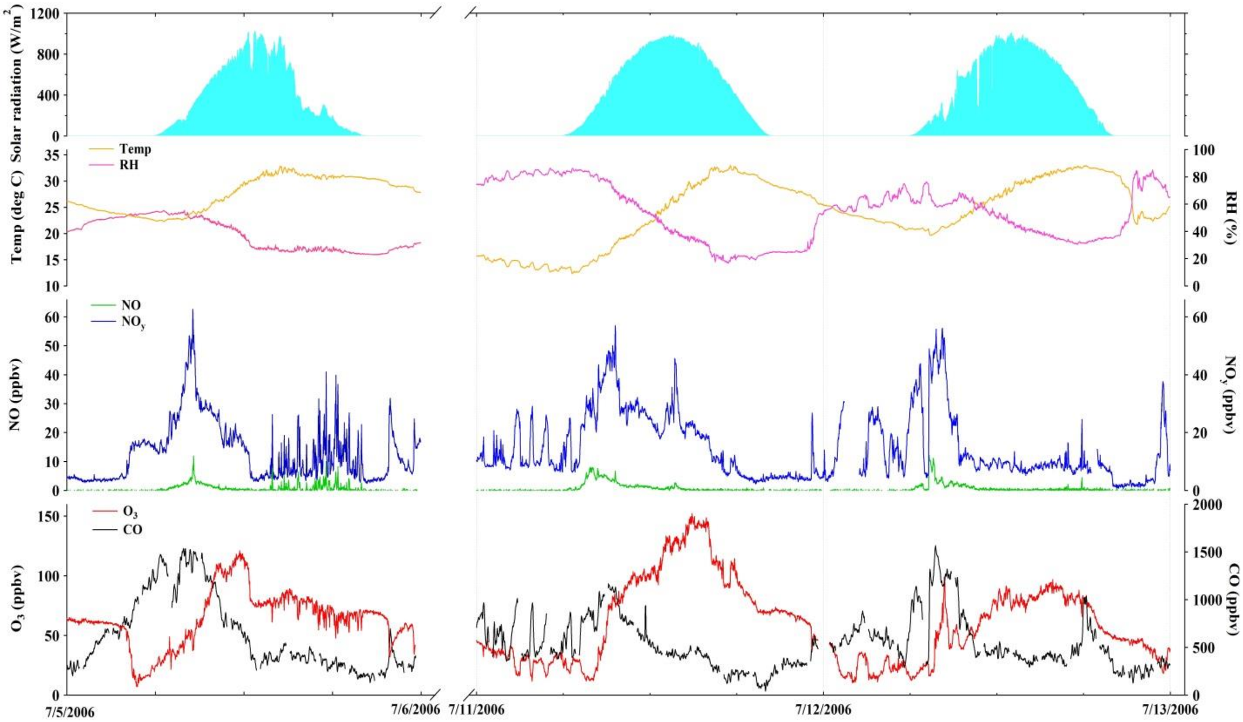

Figure S4. Time series of trace gases and meteorological parameters observed during the selected ozone episode days in Lanzhou in summer 2006

References

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