### Unexpectedly fast photochemistry in wintertime haze: Consequences for pollution mitigation strategies.

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#### **Supplementary Methods**

#### Description of the instrument for OH and HO<sub>2</sub> concentration measurements

OH and HO<sub>2</sub> radical concentrations were measured by the laser-induced fluorescence (LIF) instrument previously used in the 2014 summer campaign in Wangdu south of Beijing (Tan et al., 2017). Separate detection cells for OH and HO<sub>2</sub> were operated at a pressure of 4 hPa. Approximately 20mW of 308nm laser radiation generated by a pulsed, frequency-doubled tunable dye laser was sequentially passed through the two cells. Ambient air was sampled into each cell through 0.4 mm nozzles with flow rates of 1 slpm (slpm = standard litres per minute). The OH measurement is based on the detection of the OH resonance fluorescence induced by the incident 308 nm laser radiation. As recently reported (e.g. Mao et al., 2012), OH detection by LIF in a lowpressure cell can potentially suffer from interferences by internally produced OH, which can be quantified by chemical modulation (Feiner et al., 2016). This concept has been implemented in the instrument previously (Fuchs et al, 2011; Fuchs et al., 2016) and was used in the present campaign on several days (January 9th, 13th, 25th and March 1st). No significant OH interference signals were found for the conditions of this winter campaign (Tan et al., 2018). HO<sub>2</sub> measurements were achieved by chemical conversion of HO<sub>2</sub> to OH in the reaction with added NO. The converted OH was then detected by LIF. When high concentrations of NO are added for best possible conversion efficiencies, part of the atmospheric RO<sub>2</sub> radicals from long-chain alkanes, alkenes and aromatics can also be converted to OH, thereby producing a significant interference (Fuchs et al., 2011). In the present campaign, this interference was avoided by adding only small concentrations of NO. The HO<sub>2</sub> cell was operated alternatingly at HO<sub>2</sub> conversion efficiencies of 5% for 1 minute and 25% for 5 minutes, showing no difference in the HO<sub>2</sub> concentrations obtained for the two conversion efficiencies. This result suggests that interferences from RO<sub>2</sub> were negligible. The detection limits (signalto-noise ratio of 2) for 30 s time resolution were  $0.8 \times 10^6$  cm<sup>-3</sup> and  $0.2 \times 10^8$  cm<sup>-3</sup> for OH and HO<sub>2</sub>, respectively. The accuracies of the radical concentrations were calculated from the reproducibility of the calibrated sensitivities and the inherent systematic uncertainties of the calibration method, yielding  $2\sigma$  accuracies of 28% and 34% for OH and HO<sub>2</sub>, respectively.

#### Description of the instrument for total OH reactivity measurements

The total OH reactivity  $(k_{OH})$  of air is equivalent to the inverse atmospheric OH lifetime. In this study,  $k_{OH}$  was measured with an instrument based on laser photolysis – laser induced fluorescence (LP-LIF) (Hofzumahaus et al., 2009; Lou et al., 2010; Fuchs et al., 2017a,b). Ambient air was passed at a flow rate of 19 L min<sup>-1</sup> through a flow tube and part of the air was drawn into an OH fluorescence detection cell. A large concentration of OH radicals (about 10<sup>9</sup> molecules cm<sup>-3</sup>) was produced within a few nanoseconds in the flow tube by flash photolysis of  $O_3$  with subsequent reaction of  $O(^1D)$  atoms with water vapor (O<sub>3</sub> + hv (266 nm)  $\rightarrow$  O<sub>2</sub> + O<sup>1</sup>D, O<sup>1</sup>D + H<sub>2</sub>O  $\rightarrow$  2OH). The 266 nm radiation was provided by a quadrupled Nd:YAG laser pulse, which was operated at a low repetition rate of 1 Hz. Pseudo first-order decays of OH were recorded between to photolysis laser shots by LIF. Atmospheric  $k_{OH}$  was determined from the lifetime of the exponential decay and corrected for OH wall loss having a value of  $(3.0 \pm 0.3)$  s<sup>-1</sup> in the flow tube. The time resolution of the  $k_{OH}$  measurements was 90 seconds with a limit of detection of 0.3 s<sup>-1</sup>. The resulting accuracy of  $k_{OH}$  is (5-10) % ± 0.7 s<sup>-1</sup> at NO mixing ratios below 20 ppby. At higher ambient NO concentrations, which were observed from time to time during the campaign, the OH decays in the flow tube show deviations from a mono-exponential behavior, caused by OH recycling from the reaction of HO<sub>2</sub> with NO. In these cases, a bi-exponential fit allows the determination of  $k_{OH}$  with an overall accuracy of  $20\% \pm 0.7 \text{ s}^{-1}$  (Lou et al., 2010).

The OH reactivity of VOCs (total VOC reactivity) was estimated as the difference of the measured total OH reactivity and the calculated reactivity of measured inorganic compounds (CO, NO, NO<sub>2</sub>). The SO<sub>2</sub> contribution to  $k_{OH}$  was not significant in this campaign.

#### Description of the instrument for N2O5 concentration measurements

 $N_2O_5$  was measured by thermal decomposition – cavity enhanced absorption spectroscopy (CEAS) (Wang et al., 2017a). In the custom-built instrument,  $N_2O_5$  is converted to NO<sub>3</sub> at a temperature of 120 °C and then detected as NO<sub>3</sub> at its UV-VIS absorption maximum around 662 nm at 80 °C. The particle filter at the beginning of the inlet tube was exchanged once per hour under polluted conditions. The limit of detection (LOD) was estimated to be 2.7 pptv (1 $\sigma$ ) with an uncertainty of 19 % for a

time resolution of 60 s.

#### Description of the instrument for HONO concentration measurements

HONO was measured by two customized, in-house designed instruments from Peking University (PKU) and Forschungszentrum Juelich (FZJ) using the LOPAP (long path absorption photometer) technique (Li et al., 2014; Liu et al., 2016). Both instruments utilize a sampling unit consisting of two stripping coils in series. HONO reacts with 60 mM sulfanilamide in 1 mM HCl as adsorption solution and is converted to an azo dye with an aqueous solution of 0.8 mM N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA). The formed azo dye is photometrically measured in a Liquid Core Waveguide. For both LOPAP instruments, the time resolution was 5 minutes, detection limits were 10 pptv, measurement uncertainties were 12%, and sampling efficiencies were larger than 99.9%. The measurements of the two LOPAP instruments were averaged, yielding a combined HONO dataset with an uncertainty of  $\pm 20\%$  (Tan et al., 2018).

#### Description of the instrument for HCHO concentration measurements

HCHO was measured by Hantzsch Fluorimetry with a commercial instrument (AL4021, Aerolaser GmbH, Germany). The sensitivity of the instrument was calibrated using liquid HCHO standards. The standards were added to the stripping coil instead of the stripping solution while HCHO-free air was passed through the coil. The calibration was performed at three concentration levels of liquid HCHO standards. The concentrations corresponded to gas-phase mixing ratios of 2 ppbv, 10 ppbv, and 35 ppbv. HCHO-free air was generated by passing the sampled air through a catalyst (Hopkalit, Draeger) at room temperature. The HCHO-free air was also used to determine the background signal of the instrument. Calibrations for the sensitivity of the instrument, as well as for the measured flow rates were performed in the beginning and in the end of the campaign. Determined sensitivities agreed within 2%. The accuracy of the HCHO measurements was around 5% mainly due to the uncertainty of the calibration. The  $1\sigma$  precision derived from the HCHO-free air measurements was around 25 pptv at a time resolution of 2 min.

#### Description of the instrument for PAN concentration measurements

Peroxyacetyl nitrate (PAN) was measured by an on-line monitoring system using low temperature gas chromatography (GC) – electron capture detection (ECD) technology. Automatic calibrations were routinely achieved through photosynthesis of a PAN standard from acetaldehyde followed by the further reaction with NO (Huang et al., 2017). The lower detection limit of this instrument was 50 pptv and the time resolution of measurements was 5 min.

#### Description of the instrument for HNO<sub>3</sub>, NO<sub>3</sub>- and NH<sub>3</sub> concentration

#### measurements

Nitric acid (HNO<sub>3</sub>), particulate nitrate (NO<sub>3</sub><sup>-</sup>) and Ammonia (NH<sub>3</sub>) were measured by a Gas and Aerosol Collector coupled with two Ion chromatographic systems (GAC-IC) (Dong et al., 2012). A wet denuder system was used in the instrument with pure water as its absorption solution. Ambient air was sampled with a flowrate of 16.7 L/min through a 3/8" Teflon tube and absorbed by pure water. A cyclone filter is installed in front of the 3/8" Teflon tube and the aerosol cut off size is 2.5  $\mu$ m. Thereafter, the solution was automatically transferred through a filter, injected into the cation IC and measured. The lower detection limit of this instrument was 65 ppt, 0.034  $\mu$ g/m<sup>3</sup> and 30 pptv for HNO<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and NH<sub>3</sub>, respectively and the time resolution was 30 min. The measurement of HNO<sub>3</sub> concentrations may be negatively biased the due to the uptake at the inlet walls for the part of the inlet outside the heated lab while positively biased due to the decomposition of NH<sub>4</sub>NO<sub>3</sub> for the part of inlet inside the heated lab. Similar bias will also take place for the measurement of NH<sub>3</sub>. The measurement accuracy for HNO<sub>3</sub> and NH<sub>3</sub> were estimated to be 30% due to the intercomparsion of NH<sub>3</sub> performed in the previous campaigns and the measurement accuracy for NO<sub>3</sub><sup>-</sup> was estimated to be 10%.

#### Description of the instrument for VOC concentration measurements

The online measurements of ambient VOC concentrations ( $C_2$ – $C_{12}$  hydrocarbons) were done by a gas chromatography system coupled with a flame ionization and mass spectrometer detection (GC-MS/FID). Measurements had a time resolution of one hour during the campaign. VOCs were pre-concentrated in an ultralow temperature, cryogenfree pre-concentration device. Detailed analytical methods and quality-assurance quality-control (QA–QC) procedures for this system have been described elsewhere (Yuan et al., 2012). Detection limits for various compounds were in the range of (0.005–0.070) ppbv with an uncertainty of measurements was (10-15) %.

# Description of the instruments for aerosol surface area concentration measurements

Particle number size distributions (PNSD) were measured by a scanning mobility particle sizer (SMPS) (Long-DMA3081 + CPC3775) and a Nano-SMPS (Nano-DMA3085 + UCPC3776). The multiple charge correction, condensation particle counter (CPC) counting efficiency, and particle loss correction were applied to the measurements. An aerodynamic particle sizer (APS, TSI model 3321, TSI Inc., St. Paul, MN, USA) measured the particle-number size distribution between 500 nm and 10 mm (aerodynamic diameter). The APS results were transformed from aerodynamic to Stokes diameters using a particle density of 1.5 g cm<sup>-3</sup>. The dry-state aerosol surface area was calculated based on the dry-state particle number and geometric diameter in each size bin (<2.5  $\mu$ m) with a time resolution of 5 min.

Dry-state aerosol surface area was calculated based on PNSD, and corrected to ambient (wet) particle aerosol surface area accounting for particle hygroscopic growth. The growth factor was estimated by the ISORROPIA-II aerosol thermodynamics model (Clegg et al., 1998). The model input included water-soluble ions, along with simultaneously measured RH and T. The aerosol solutions were assumed to be metastable. Firstly, the model calculated the mass of aerosol liquid water content (ALWC), then determined the growth factor by taking the cube root of the ratio of the wet to the dry aerosol mass. The overall accuracy for the deduced ambient particle aerosol surface area was estimated to be 30%.

#### Description of the instruments for aerosol chemical composition measurements

Aerosol chemical composition ( $\langle PM_{1.0} \rangle$ ) was measured using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; short: AMS) (DeCarlo et al., 2006). Only specific parameters and settings for the described set-up will be given here. The AMS is capable of measuring the non-refractory fraction of ambient aerosol particles (NR-PM<sub>1</sub>) including organics (Org), ammonium (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>) and chloride (Cl<sup>-</sup>) in a size range of 60 – 600 nm (Liu et al., 1995). The AMS used for this study was modified by a quadrupole filter between the ionization region and the mass spectrometer. Fragmentation patterns of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> indicated that the quadrupole did not influence the transmission in the investigated m/z range (12 – 250 amu). Therefore, standard AMS data evaluation procedures could be applied. The detection limits for each species were determined from measuring particle free air for 14 times throughout the full campaign. The detection limit for organic (Org.), NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup> mass concentrations were 0.424 µg/m<sup>3</sup>, 0.005 µg/m<sup>3</sup>, 0.029 µg/m<sup>3</sup>, 0.011 µg/m<sup>3</sup>, 0.023 µg/m<sup>3</sup>, respectively.

The AMS was calibrated regularly (approximately every 7-10 days; except during the 19 days of the Spring Festival break) using size selected (350 nm) and dried NH<sub>4</sub>NO<sub>3</sub> particles and a CPC (TSI model 3786) as a reference (Jayne et al., 2000; Jimenez et al, 2003). From all calibrations, an average ionization efficiency (i.e. total response factor including transfer efficiency of the ToF-MS) of  $1.61 \pm 0.26 \times 10^{-08}$  was obtained by this procedure and was subsequently used for the determination of aerosol mass concentrations. Compound specific relative ionization efficiencies (RIE) for NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> were determined during the standard calibration procedure. The RIE of Org, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> were 1.4, 2.71 ± 0.12, 1.1, 1.54 ± 0.04, 1.3, respectively.

To correct for non-unity collection efficiencies of the AMS, a composition dependent correction factor was applied (Middlebrook et al., 2012). A comparison to PM<sub>1</sub> concentration values measured by a collocated scanning mobility particle sizer (SMPS) system showed that the total mass measured by the AMS on average accounts for 84 % and 73 % of the mass measured by the SMPS assuming an effective aerosol density of 1.4 g cm<sup>-3</sup> and 1.6 g cm<sup>-3</sup>, respectively. The density is expected to be within this range based the fact that the aerosol mass consists of at least 50 % NH<sub>4</sub>NO<sub>3</sub> and organics (both 1.4 g cm<sup>-3</sup>) and up to 50 % (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (1.77 g cm<sup>-3</sup>) and NH<sub>4</sub>HSO<sub>4</sub> (1.78 g cm<sup>-3</sup>). Taking into account that, (i) the AMS can only detect the non-refractory part of the aerosol and (ii) slight differences in the size ranges are covered by AMS and SMPS, the agreement of PM<sub>1</sub> masses measured by the two instruments is reasonable and assures that the AMS data can be quantitatively interpreted.

The AMS was located inside the building and sampled through a 0.18' inner diameter (ID) stainless steel inlet line (2 m length) that was further connected to a 0.255' ID

stainless steel line coated with Silcoinert® (7.3m length). Including the 0.06 L min<sup>-1</sup> withdrawal of the AMS, the total sampling flow was 1.82 L min<sup>-1</sup> and the residence time of the sampling air in the inlet line was approximately 10 s. While the outside temperature was varying from -19.2 °C to 19.0 °C, the temperature at the AMS inlet was rather constant with temperatures between 20.0 °C and 26.5 °C. Directly in front of the AMS the inlet flow was dried using a Nafion drier (RH < 6 %) and subsequently the flow was split to a CPC (TSI 3786, flow rate: 0.60 L min<sup>-1</sup>). In front of the Nafion drier an optical particle counter (OPC; Grimm model 1.129) took a subsample of 1.16 L min<sup>-1</sup>.

#### Description of the instruments for determining photolysis frequencies

Photolysis frequencies were calculated from spectral actinic flux densities measured with a spectroradiometer (Meteorologie Consult). The instrument employed a quartz receiver, a monolithic single monochromator and a photodiode-array. The setup was calibrated with a PTB-traceable irradiance standard before and after the campaign (Hofzumahaus et al., 2009). The accuracy of the actinic flux measurements was estimated 10% in the UV range at solar zenith angles smaller than 80°, which is the estimated accuracy for  $J(O^1D)$  and  $J(NO_2)$  as well.

#### Description of the instruments for measuring meteorological parameters

Meteorological parameters including wind speed, wind direction, relative humidity (RH), temperature (T) and pressure (p) were measured with a commercial Met One Meteorological Sensors & Systems. Wind speed and wind direction were measured by Met One 014A and 024A, respectively. RH and T were measured by a multi-parameter sensor system (Met One 083E). The air pressure was measured by Met One 092.

#### **Supplementary Figures**



**Figure S1.** Locations of the Huairou (HR) site, the Peking University (PKU) site and the monitoring sites of the Chinese Environmental Protection Agency (CEPA) in Beijing.



**Figure S2.** Time series of  $PM_{2.5}$ ,  $O_3$ ,  $O_3+NO_2$ ,  $O_3+NO_2+NO_2$ , PAN,  $j(O^1D)$  and  $j(NO_2)$  during the campaign. Several 1-2 day long pollution episodes were observed indicated by  $PM_{2.5}$  mass concentrations between 100 and 200 µg m<sup>-3</sup>. The strong pollution episode from February 29<sup>th</sup> to March 5<sup>th</sup> showed an even higher increase of  $PM_{2.5}$  reaching values of up to 360 µg m<sup>-3</sup>. The ozone mixing ratio was approximately 40 ppbv in clean episodes and showed frequently short-term drops to lower concentrations due to its reaction with emitted NO, which forms NO<sub>2</sub>. The concentration of Ox (O<sub>3</sub> + NO<sub>2</sub>) was remarkably stable. During the pollution episodes, however, Ox and other gaseous pollutants (NOz, and PAN) became photochemically enhanced and increased concurrently with  $PM_{2.5}$ , even though the photolysis frequencies  $j(O^1D)$  and  $j(NO_2)$  decreased considerably.



**Figure S3.** Time series of SO<sub>2</sub>, NO, NO<sub>2</sub>, CO and NH<sub>3</sub> concentrations and of the OH reactivity from VOCs during the campaign.



Figure S4. Time series of OH,  $HO_2$ ,  $k_{OH}$  and HONO concentrations during the campaign.



**Figure S5.** Time series of the wind direction (WD), wind speed (WS), temperature (Temp), pressure, relative humidity (RH) and water vapor mixing ratios ( $H_2O$ ) during the campaign.



**Figure S6.** Atmospheric measurements at Huairou from January 13<sup>th</sup> to January 17<sup>th</sup> 2016: Aerosol (PM<sub>1</sub>) chemical composition (a), ozone and nitrogen oxide species resulting from ozone oxidation of NO emissions (NO<sub>2</sub>, higher gaseous oxidation products NOz, particulate nitrate NO<sub>3</sub><sup>-</sup>) (b), OH concentrations and solar UV-A intensity represented as NO<sub>2</sub> photolysis frequency ( $j_{NO2}$ ) (c), partitioning of the total OH reactivity ( $k_{OH}$ ) to contribution from CO, NO<sub>x</sub> and organics (d), OH removal rate ( $k_{OH}$ ×[OH]) (e), ozone production rate (P(O<sub>3</sub>)) from the reaction of HO<sub>2</sub> with NO that is equivalent to the OH recycling rate (f). Gaps in the time series (a-f) indicate missing data.



**Figure S7.** Same as Figure S6 but for the haze event from January 19<sup>th</sup> to January 22<sup>nd</sup> 2016.



**Figure S8.** Same as Figure S6 but for the haze event from January 27<sup>th</sup> to January 31<sup>st</sup> 2016.



**Figure S9.** Same as Figure S6 but for the haze event from February 20<sup>th</sup> to February 23<sup>rd</sup> 2016.



**Figure S10.** The comparison of the experimentally determined gas phase oxidized nitrogen compounds – NOz (= $NOy - NOx - NO_3^-$ ) with the detailed measurements of NOz such as PAN, N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> for the analyzed five haze events experienced during this campaign.



**Figure S11.** Upper panel: Observed  $PM_{2.5}$  and total oxidant concentrations as characterized by the regional monitoring network and observed  $PM_{2.5}$  concentrations at HR site, PKU site and the CEPA sites in Beijing. Lowe panel: Observed  $O_3+NO_2+NO_2$  concentrations at HR site and PKU site and the  $O_3+NO_2*$  ( $NO_2* = NO_2 +$  interferences from NOz compounds) concentrations at the CEPA sites. The NO<sub>2</sub> observations at CEPA sites are performed by chemiluminescence instruments using a Mo-converter which is known to have significant interference from NOz (e.g., Dunlea et al., 2007). Therefore,  $O_3+NO_2*$  measurements at the CEPA sites are compared to the  $O_3+NO_2+NO_2$  concentrations at HR.



**Figure S12.** The observed  $O_3$  concentrations from the CEPA sites in both Beijing and Hebei in March 2016. The dashed line marks the 1hr Air Quality Standard for  $O_3$  in China.



**Figure S13.** The observed  $PM_1$  particulate nitrate (NO<sub>3</sub><sup>-</sup>) concentrations by AMS and the experimentally determined NO<sub>3</sub><sup>-</sup> formation potential (accumulated production since Feb 29<sup>th</sup>) according to Eq. 2 of the main text. The dashed line denotes the experimentally determined NO<sub>3</sub><sup>-</sup> formation potential from the reaction between OH and NO<sub>2</sub>.

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