Particle-phase photo-reactions of HULIS and TMIs establish a strong source of H₂O₂ and particulate sulfate in the winter North China Plain

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S1: Gas-phase measurements and instrumentation

During the field campaign, an AL2021- H_2O_2 analyzer was employed to measure atmospheric H_2O_2 . The AL2021- H_2O_2 analyzer is based on dual-channel enzyme fluorescence techniques and widely used in the world for the detection of atmospheric H_2O_2 .

 NO_x (NO/NO₂), O₃, SO₂ and CO were measured by a series of Thermo Scientific monitors including a chemiluminescence NO_x analyzer (Model 42i,), a UV-absorption O₃ analyzer (Model 49i), a pulsed fluorescence SO₂ analyzer (Model 43i) and an IR-absorption CO analyzer (Model 48i). The analyzer of NO_x , O₃ and SO₂ were calibrated once a week, while the CO analyzer was calibrated every three days because of its shifting baseline.

HONO was measured by a commercial long-path absorption photometer instrument (LOPAP-O3, QUMA).¹ Ambient air was sampled by using two same stripping coils in series. Because HONO is highly soluble, almost all the ambient HONO was absorbed in the solution of the first stripping coil, while possibly interfering species were sampled in the first as well as the second stripping coil. Thus, the signal difference between the two channels can largely eliminate the possible influence of the interfering species for the HONO measurement. The instrument has a detection limit of 10 pptv.

The ambient NH_3 concentration was measured by a custom-made active Differential Optical Absorption Spectroscopy (DOAS). Its transmitting and receiving telescope are designed within one unit, which was placed on the roof of one building 5 m above the ground. To fold the beam back to the telescope, a retro-reflector was mounted at the other side on the roof with a distance of 15 m. Consequently, the light travels 30 m between the transmitting/receiving telescope and the retro-reflector. The DOAS system consists of a telescope with a diameter of 210 mm as transmitter and receiver, a 35 W Deuterium lamp as a light source and a spectrograph. The calibration of the DOAS system was performed individually by inserting a cell with quartz glass windows into the optical path between the light source and the receiver assuming a constant value of the product of concentration and distance. Besides, standard gases with different concentration were filled into the cell in sequence to calibrate the responses of corresponding differential optical absorption. More details and verification of NH_3 measurement with DOAS can be found in Wang, et al.².

Online GC-MS/FID

The VOCs were measured online by gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID, ZF-PKU-VOC1007, Beijing Pengyuchangya) with a time resolution of 1 hour.³⁻⁴ Briefly, the air samples (600 ml in total) were first enriched in two different capillary columns at -150 °C for 5 min, then transferred into the dual-channel GC system through flash heating desorption. A deactivated quartz capillary column (15 cm \times 0.53 mm ID) for MS analysis and a PLOT capillary column (15 cm \times 0.53 mm ID) for FID analysis were used for enrichment. CO₂ and O₃ were removed by Ascarite II before running into the FID channel. The GC-FID channel measured C₂-C₅ hydrocarbons with a PLOT Al₂O₃ column (15 m \times 0.32 mm ID) whilst the GC-MS channel detected C₅-C₁₀ hydrocarbons with a DB-624 column (60 m \times 0.25 mm ID).⁵ The two channels have separate inlets and GC separation columns, while they shared the

same temperature program. A series of standards of different concentrations (0.4 - 4 ppbv) was selected to get a calibration curve for each compound, whose R² values were all above 0.99. 56 non-methane hydrocarbons (NMHCs, Spectra Gases Inc., USA), 13 oxygenated VOCs (OVOCs) and 27 halocarbons (Apel-Riemer Environmental Inc., USA) were identified and quantified, of which the detection limits ranged from 0.001 to 0.015 ppbv. An internal method with 4 specific compounds (bromochloromethane, 1,4-diflurobenzene, chlorobenzene, and 4bromoflurobenzene) has been used for the calibration of the GC/MS quantification for each sample, while an external method with 56 NMHCs was applied to the calibration of the GC/FID quantification every week. More detailed information about the instrument is described in previous studies.⁶⁻⁷ A discussion of the VOC and OVOC measurements is given in Zhang, et al.⁸ and Wang, et al.⁹.

DNPH-Cartridge-HPLC

Atmospheric carbonyls were collected by Sep-Pak silica gel cartridges (Waters, USA) coated with 2,4-dinitrophenylhenylhydrazine (DNPH) at a flow rate of $1.2 \text{ L} \text{min}^{-1}$ for a sampling duration of 2-hours. A KIO₃-scrubber was placed in front of the DNPH- cartridges to prevent interference from O₃ during the sampling and the DNPH-cartridges were wrapped by aluminum foil to avoid light irradiation. They were sealed in the bags and stored in the refrigerator before and after the sampling further on. The DNPH-cartridges were eluted with 5 mL acetonitrile and the extracts were analyzed by a High Performance Liquid Chromatography (HPLC) method. More details are given in a previous study.¹⁰

S2: Field measurements of particulate matter and instrumentation

Online measurements

Three different instruments—a standard Tapered Element Oscillating Microbalance system (TEOM 1400A, Thermo Scientific), a Synchronized Hybrid Ambient Real-time (Sharp 5030i, Thermo Scientific) and a Beta Attenuation Mass Monitor (BAM 1020, Met one) measured the mass concentration of $PM_{2.5}$ during the SRE-CAS campaign. The present paper deal with $PM_{2.5}$ measured by the TEOM since data from the Sharp and BAM instruments were only available since Nov. 14th. It should be noted that the $PM_{2.5}$ concentrations measured by TEOM were underestimated by ~ 28% in comparison with those by the Sharp instrument due to the evaporation of particulate matter at 50 °C heating.

A Time of Flight-Aerosol Chemical Speciation Monitor (Tof-ACSM, Aerodyne Inc.), a semicontinuous Organic/Elemental Carbon (OC/EC) analyzer (Model-4, Sunset Lab. Inc.) and an energy dispersive X-ray fluorescence (Xact 625i, CES) measured the concentration of nonrefractory particulate matter, OC and EC, as well as elements heavier than Aluminum in PM_{2.5} respectively. The time resolution was 10 min for the Tof-ACSM and 1 h for the others. The Tof-ACSM was equipped with a PM_{2.5} aerodynamic lens and a standard vaporizer heated to 600 °C.¹¹ The OC/EC analyzer was operated according to the NIOSH protocol and the split point of OC and EC was determined by a laser of 650 nm.

Offline measurements

 $PM_{2.5}$ was continuously collected on quartz fiber filters (90 mm diameter, Munktell) by a medium volume PM sampler (at a flow rate of 0.1 m³ min⁻¹) with a collection duration of 2 hours. The samples were stored in dish-like containers (90 mm, Millipore) in a refrigerator at -20 °C until analysis, where a quarter of each filter was ultrasonically extracted with 10 mL of ultrapure water for 30 min. The solutions were percolated through a microporous membrane (pore size, 0.45 μ m; diameter, 13mm), and the water-soluble ions (WSIs, i.e. Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, Mg²⁺, Ca²⁺ and K⁺) were analyzed by ion chromatography (IC, WAYEE IC6200). More details are given in previous studies.¹²⁻¹³

 $PM_{2.5}$ samples were collected on 203 mm × 254 mm quartz microfiber filters (Whatman) with a high-volume air sampler (HIVOL-CVALD, Thermal Scientific) at a flow rate of 1.13 m³ min⁻¹ during daytime (from 8 am to 7 pm) and night-time (from 8 pm to 7 am), respectively. 55 daysamples and 55 night-samples were collected from Nov. 4th to Dec. 29th in 2017. Quartz fiber filters (20 × 25 cm, Whatman) were pre-heated at 650 °C for 4 hours to remove any absorbed organics and inorganics before sampling. The filters were wrapped in aluminum foil after sampling and immediately stored at -20 °C until analysis. WSIs, OC/EC and water-soluble organic carbon (WSOC) were analyzed and employed for the evaluation of the fraction of humic-like substances (HULIS) in the modeling.

WSIs. A punched-out section (47mm in diameter) of each filter was submerged in a small beaker with 10 mL ultrapure water and sealed and sonicated for 15 min. The extract was filtered with a 0.45 μ m Teflon filter to remove any insoluble species. The extracts were analyzed via an ion

chromatograph (940 Professional IC, Metrohm) equipped with a Metrosep, a supp 16-250 separation column and a Metrosep C6 analytical column. The corresponding detection limits for major inorganic ions were in the range of 0.47-3.33 ng mL⁻¹.⁷

OC and EC. According to the IMPROVE protocol, a thermal/optical carbon analyzer (DRI Model 2015, Magee Scientific) examined another fraction of the filters (16 mm in diameter). Four OC fractions (OC1, OC2, OC3, and OC4 acquired at 140, 280, 480, and 580 °C in a helium atmosphere) and three EC fractions (EC1, EC2, and EC3 evolved at 580, 740, and 840 °C in 98 % He/2% O₂ atmosphere) were produced. The detection limit for OC determined by using the thermal/optical carbon analyzer was $0.18 \pm 0.06 \ \mu g \ cm^{-2}$, while it was $0.04 \pm 0.01 \ \mu g \ cm^{-2}$ for EC.⁷ Light at the wavelength $\lambda = 635$ nm was used for pyrolysis correction.

WSOC. A 47mm diameter section punched from the filter was cut into pieces and extracted with 20 mL ultrapure water in a small beaker. The extracts were filtered through a membrane filter of 0.22 μ m pore size. WSOC was analyzed on a Total Organic Carbon Analyzer (TOC-VCPN, Shimadzu Corp.). The extracted samples were acidified in pH = 2 to convert carbonates into CO₂. The remaining extracts were injected into the combustion tube for analysis. The detection limit is 0.5 μ g mL⁻¹ for WSOC.

S3: Verification and harmonization for chemical composition of PM_{2.5}

Tof-ACSM has been calibrated as introduced in a recent study¹⁴ to determine the Ionization Efficiency and Relative Ionization Efficiency (IE/RIE) for the quantification of non-refractory chloride, nitrate, sulfate and ammonium.

Since the Tof-ACSM is only able to measure non-refractory components (NR) evaporable at 600 °C, refractory sulfates and chlorides with higher melting points (CaSO₄, CaCl₂, MgCl₂, NaCl among others) were not detectable. Consequently, the concentration of sulfate and chloride ions affected by soil dust and/or sea spay aerosol might be underestimated. The SRE-CAS site was not influenced significantly neither by dust (indicated by the low concentration of the tracer elements Si, Ti and Ca) nor by sea spay aerosol (indicated by the trajectories) during the campaign. Hence, the WSIs (sulfate, chloride, nitrate and ammonium ions) measured from the 2-hour 90 mm filters by IC can be considered equal with the NR measured by the Tof-ACSM. A study reported that the agreement between NR by the aerosol mass spectrometer and WSIs by IC for chloride, nitrate, sulfate and ammonium was good when a collection efficiency (CE) of 0.5 for standard vaporizer was assumed.¹⁵ Accordingly, this CE was also applied throughout the present study.

The 2-hour averaged concentrations of chloride, nitrate, sulfate and ammonium measured by the Tof-ACSM were plotted against the corresponding WSIs derived from 2-hour filters, which resulted in harmonization factors of 0.85, 1.15, 1.05 and 1.2, respectively. The harmonized and sequentially 1-hour averaged concentrations of chloride and sulfate concentrations fairly matched with these of the element measurements of Cl and S by the Xact instrument with regression slopes of 1.05 ± 0.01 and 0.36 ± 0.00 , respectively, both of which were in a reasonable range. The lower harmonization factor for chloride was mostly due to the interferences from the organic fragments at m/z 35 at the site with extremely high organic matter. After the harmonization, the regression slope of predicted ammonium (by chloride, nitrate and sulfate) against the measured ammonium was 1.11 ± 0.01 with an $R^2 = 0.971$.

Sulphur oxidation ratios (SOR). SORs are calculated by the following equation:

$$SOR = \frac{n - SO_4^{2-}}{n - SO_4^{2-} + n - SO_2}$$

The n represents the molar concentration in the atmosphere.¹⁶⁻¹⁷ SOR was used to estimate the degree of the secondary formation of SO_4^{2-} , which can eliminate the interference of meteorological factors.

S4: Detailed observations during the SRE-CAS field campaign

Key trace gases

During the two-month SRE-CAS campaign, NO, NO₂, O₃, CO, SO₂ showed overall averaged concentrations of 52.9 ± 66.2 ppbv, 27.8 ± 13.4 ppbv, 8.6 ± 9.3 ppbv, 1869 ± 1406 ppbv and 11.57 ± 9.9 ppbv, respectively. Mixing ratios of SO₂, NO and CO are elevated after Nov. 10^{th} because of coal combustion and biomass burning near the rural site. In the Beijing-Tianjin-Hebei region, the SO₂ concentration rises during winter mainly because of the heating;¹⁸ however, it showed a sharp decline since 2016 due to the 'ban' of coal policy.¹⁹ In general, the trace gas pollutants (NO_x, CO, SO₂) showed distinct variations (Figure S2), which could be mainly ascribed to variation of atmospheric mixing condition from day to day. They also exhibited very similar diurnal profiles with high concentrations in the night and morning (low mixing layer height; MLH), and a broad valley in the early afternoon (high MLH).

NO showed high values throughout the campaign (Figure S2b, left axis), especially during both the morning and evening under stagnant conditions. Then NO showed a rapid drop due to the growing MLH. Huge NO concentrations suppress the gas-phase oxidation capacity. For instance, it suppresses the gas-phase recombination of HO_2 radicals which is regarded as the classical gasphase formation of atmospheric H_2O_2 .

 O_3 exhibited a pronounced diurnal course with a mid-afternoon maximum and an evening minimum (Figure S2c, right axis). O_3 closely followed the solar radiation pattern, suggesting its photochemical generation. The global radiation (Figure S2a, right axis) represents the total shortwave solar radiation received on a horizontal surface on the ground which includes both the direct solar radiation and the diffuse radiation resulting from reflected or scattered sunlight. The maximum peak value of O_3 during the measurement period was less than 40 ppbv, indicating considerably reduced photochemical activity in the winter of NCP. The low values of O_3 in the night (partly close to zero), were mainly due to the titration by NO related to traffic and heating in the winter. In fact, a negative correlation between NO and O_3 was observed throughout the campaign. Furthermore, the very low O_3 concentrations during the night imply also a minor gasphase formation of NO₃ radicals under SRE-CAS conditions.

High concentrations of CO were observed especially after Nov. 14th (Figure S2b, right axis) suggesting strong anthropogenic pollution (coal combustion and biomass burning events) during the winter season at this site.

In general, SO_2 is a useful indicator for regional air pollution originating from coal combustion, which exhibited high concentrations during the whole measurement period (Figure S2e, left axis). Evident increases of SO_2 in winter were attributed to coal combustion for residential heating during this season. High SO_2 concentrations together with the availability of effective oxidants, e.g. H_2O_2 , will favor the formation of sulfate at the site, leading to the increase of $PM_{2.5}$ loadings.

 H_2O_2 exhibited a significant day-to-day variation with a daily maximum concentration between 0.2-1.2 ppbv (Figure S2d, left axis). In winter, the solar radiation intensity was low (Figure S2A, right axis) whereas the gas-phase H_2O_2 concentrations were high and could reach 1.2 ppbv. Both the gas-phase concentration of H_2O_2 and O_3 followed the solar radiation with time lags of 2 and 3 hours, respectively. The high H_2O_2 mixing ratios are closely related to the intensity of solar radiation. The increase of the H_2O_2 mixing ratio begins around 8 am, reaching a median value of 0.46 ppby; afterwards it quickly decays and remains near zero overnight.

Main PM_{2.5} constituents

The average concentrations of $PM_{2.5}$ were $103.8 \pm 89.7 \ \mu g \ m^{-3}$ during the SRE-CAS campaign and are indicated by strong combustion-related pollution.

After the start of the residential heating, i.e. after Nov. 10^{th} , more SO₂ was emitted and particulate sulfate was measured with an average concentration of $8.0 \pm 12.0 \ \mu\text{g} \ \text{m}^{-3}$. Sulfate contributed with 0.18 ± 0.10 to the inorganic components on average and reaches a maximum ratio of 0.70 during heavily polluted events, especially under high RH conditions (Figure S2).

OC was measured online by a Sunset OC/EC analyzer with an average concentration of $61.7 \pm 58.0 \ \mu g \ m^{-3}$. As the main contributor of PM_{2.5} OC was significantly positive correlated to CO (R² = 0.63). Thus, OC should be mainly originated from biomass burning and coal combustion. Filter measurement of OC and WSOC indicated a ratio of WSOC to OC of $33 \pm 9\%$.

Partitioning and reaction mechanism of H_2O_2

The partitioning of H_2O_2 in both the liquid-phase and the gas-phase is calculated according to the Henry's Law. The temperature-dependent Henry's Law constant is defined as follows:

H(T)=H(T₀)exp $\left[-\frac{\Delta H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$

where $T_0 = 298$ K and $H(T_0) = 1.0 \times 10^5$ M atm⁻¹ for H_2O_2 .²⁰ With - $\Delta H/R = 7297.1$ K, Henry's law coefficient for H_2O_2 is sensitive to ambient temperature. The mean temperature is 271 K during the campaign. Thus, $H(271K) = 1.2 \times 10^6$ M atm⁻¹ is one order of magnitude higher than H(298 K). A high Henry's law coefficient at low temperature favors the partitioning of H_2O_2 towards the aqueous aerosol-phase leading to comparable H_2O_2 concentration levels in either phase. The mean concentrations of H_2O_2 in the aqueous and gas phase are illustrated in Figure S5a. With high ALW and low temperature (i.e., a high Henry's law coefficient) in the morning, the aqueous-phase H_2O_2 accounts for 69% of the total H_2O_2 , which is higher than the gas-phase concentration. In contrast at noon, with low ALW and high temperature (i.e., a low Henry's law coefficient), the aqueous-phase H_2O_2 only accounts for 21% of the total H_2O_2 .

When H_2O_2 is dissolved in aqueous aerosol particles and cloud/fog droplets, it can effectively oxidize S(IV) leading to the formation of sulfate. The reaction sequence of the S(IV) oxidation by H_2O_2 is shown below:

 $HSO_{3}^{-}+H_{2}O_{2}\rightarrow HOOSO_{2}^{-}+H_{2}O$ $HOOSO_{2}^{-}+H^{+}(HA)\rightarrow HOOSO_{2}H$

The oxidation rate is expressed as:

 $-d[H_2O_2]/dt = k[H^+][H_2O_2][HSO_3^-]/(1+K[H^+])$

with k = 7.5 \pm 1.16 \times 10⁷ M⁻² s⁻¹ and K = 13 M⁻¹ at T =298 K. Because H₂O₂ is a very weak electrolyte, and $[H^+][HSO_3^-]=H_{SO_2}K_{s1}p_{SO_2}$, and, for pH > 2, 1 + K[H⁺] \approx 1, the rate of this reaction is practically pH independent over the pH range of atmospheric interest.²⁰ H_{SO2}, K_{s1} and p_{SO2} represents the Henry's law coefficient, the equilibrium coefficient and the partial pressure of SO₂.

S5: Dependency of the measured diurnal PM_{2.5} concentration pattern on MLH

The near-ground air pollution in the winter NCP is strongly influenced by the diurnal boundary layer mixing, i.e., the mixing layer height (MLH). The MLH is an important factor affecting the diffusion of pollutants in the lower troposphere.²¹⁻²² Typically, an increase or uplift of the MLH during daytime is often linked to a decrease of air pollutants mixing ratios, whereas shallow MLHs during night and early morning hours are often accompanied by high air pollution levels. Accordingly, the measured diurnal concentration profiles, e.g. of PM_{2.5} and particulate sulfate (see Figure 1), are immensely affected by the diurnal variation of the MLH. Therefore, PM_{2.5} sulfate concentration profiles show lower values during midday when the MLH is high. They also show higher values during the evening to morning because of the low MLH.

However, in order to examine potential daytime PM2.5 sulfate formations, the effect of the diurnal change of the MLH should be removed from the raw measurement data to allow for a more straightforward interpretation. Unfortunately, no vertical profiling of the MLH, e.g., by a ceilometer, was performed during the SRE-CAS campaign directly at the measuring site. Nevertheless, daytime MLH profiles are measured by a ceilometer at Shijiazhuang (capital city of Hebei province), with a distance of 100 km to SRE-CAS. Due to the strong stable weather situation at the whole NCP during the campaign these measurements can be regarded valid also for SRE-CAS. In Figure S17a, the median MLH profile for polluted days ($PM_{2.5, daily} > 75 \ \mu g \ m^{-3}$) is shown. Unfortunately, measured MLH values are available for daytime only. No MLH values are available between 4 pm and 8 am when often shallow MLHs are present under high-pressure weather conditions during winter in the NCP. However, it is noted that ceilometer-measured backscatter profiles are applied to estimate MLHs, which are known to be limited in detecting shallow MLHs.²³⁻²⁵ Nevertheless, measured radiosonde data in Beijing suggests at times quite low BLHs measurement during the campaign period (radiosonde data available at: http://weather.uwyo.edu/upperair/sounding.html).

In order to overcome the lack in the measured MLH profile data, a minimum MLH value of 70 m in the morning hours was estimated based on the radiosonde data. An adjusted night-time MLH profile was obtained by linear interpolation. Figure S17a shows the deduced and measured MLH profile together with the median temperature for the polluted days.

The diurnal MLH profile for Nov. and Dec. 2017 agrees reasonably with the typical diurnal MLH profile for winter NCP conditions in 2014 reported in the recent literature,²² but shows with about 400 m a bit lower maximum (see Figure S17a). Furthermore, the deduced MLH profile correlates well with the measured temperature profile with an R² of 0.86. This implies that the deduced MLH profile is reasonable as the diurnal mixing is mainly a function of the local diurnal heating of the lower tropospheric layers under stable high-pressure conditions. The displayed variation of the MLH (\approx factor 5.7) suggests a substantial mixing impact throughout the day.

Instead of the MLH, the normalization could have also been performed with ratio quantities of stable trace gases such as CO. However, CO is an important tracer for biomass burning and the location was under high biomass burning influence. Therefore, the CO concentration is more or less affected by local burning and traffic sources. The CO concentrations (see Figure S2b, right

axis) show not always a typical mixing pattern which would be expected due to entrainment through shrinking or increase of the MLH.

By means of the deduced diurnal MLH profile, normalized concentration profiles of $PM_{2.5}$ as well as its constituents were determined in order to artificially exclude the diurnal mixing interaction. Figure S17b displays the normalized diurnal profile of the median $PM_{2.5}$ mass and $PM_{2.5}$ sulfate mass, together with the normalized MLH profile. On the one hand, the normalized median $PM_{2.5}$ sulfate concentration profile shows a diurnal pattern with a variation factor about 3 (Figure S17b). On the other hand, the normalized MLH profile (see Figure 1 and Figure S17b) shows larger diurnal variations (> 5). Thus, a sulfate formation or entrainment (emission or entrainment from atmospheric layers above) is needed to compensate the larger diurnal mixing.

In detail, the multiplication of the diurnal normalized PM_{2.5} sulfate profile with the normalized MLH profile (see Figure S17c) should allow to identify potential productions and/or emissions of sulfate during the morning. The main productions/emissions should be present between 8 am and 10 am in order the explain the rapid sulfate increase observed in the field. Besides the rapid morning increase, Figure S17c shows a rather constant sulfate mass until noon, a decrease after noon and a small increase/stabilization of the concentration during the later afternoon and subsequent night.

The stabilized sulfate mass concentrations between 10 am and 12 pm implies conditions with a comparable normalized sulfate production and loss rates. Contrary to that, after 12 pm the observed decrease of the normalized sulfate indicates a decreasing S(VI) production in the aerosols which dry more and more until around 3 pm (lowest RH conditions), which might emphasize the importance of depositions during this period. During the later afternoon and later on, the MLH normalized sulfate stabilizes with increasing RH and ALW content. This most likely suggests that the sulfate production is as high as loss processes, i.e. deposition. The constant normalized sulfate concentration occurs during the continuous loss of H_2O_2 (see Figure 1). Together with the increasing ALW content, this indicates that during this time the sulfate formation is partly triggered by H_2O_2 .

S6: Sulfate formation linked to the MLH evolution, H₂O₂, and HONO

Figure 1e shows (i) the diurnal course of the MLH adjusted sulfate aerosol mass concentration (in μ g m⁻³), (ii) the MLH adjusted sulfate formation rate (in μ g m⁻³ h⁻¹) and (iii) the diurnal course of the most important S(IV) oxidants (incl. precursors), e.g. H₂O₂ (observed hourly gas-phase concentration change, ppbv h⁻¹) and HONO (MLH adjusted gas-phase concentration, µg m⁻³) on high PM2.5 days. A correlation of the increase of the MLH-corrected HONO concentration and the MLH-corrected sulfate concentration at sunrise was observed. Usually, HONO is fast photolyzed with sunrise. Thus, this result directs to an important HONO source related to sunrise. However, the strong HONO increase correlates also very well with the strong MLH growth. The latter grows because of the surface warming. Hence, the MLH is strongly affected but not the atmospheric layers above. The radiosonde profiles from Beijing indicate that during late autumn and winter the North China Plain is characterized by multiple inversion layers above the ground. So, the rapid elevation of the MLH can induce an entrainment from the air layers above. It is expected that particularly at night within and around the Hebei province chimneys can emit into air layers above the MLH. This leads to a high input of pollutants, e.g. SO₂, HONO, particulate sulfate and PM_{2.5}, into these layers. Due to the very stable weather conditions, these pollutants will not be mixed into the free troposphere. Hence, with rapid MLH increase in the morning, these polluted layers will be entrained into the MLH (lower air layers) and can represent a potential source for HONO and particulate sulfate during the morning.

Furthermore, Figure 1e shows a distinct increase of the sulfate concentration and the differential change (dS(VI)/dt) in the morning. Later on, dS(VI)/dt lowers with decreasing relative humidity and is nearly zero in the afternoon and evening. Moreover, the MLH adjusted sulfate aerosol mass concentration is nearly constant. This means that during this latter period the formation and loss (mainly deposition) of particulate sulfate is equal.

In addition to the observed rapid increase of the sulfate mass and the production in the morning hours, Figure 1e reveals also a substantial increase of the H_2O_2 formation and the HONO concentration in the morning. This indicates that both H_2O_2 and HONO can possibly be involved in the sulfate formation during the morning. Beyond that, the formation rate of gas-phase H_2O_2 increases during daytime and decreases in the late afternoon, which is related to both the decrease in relative humidity during the morning and the subsequent increase during late afternoon. This suggests that the H_2O_2 increase is caused by the degassing of H_2O_2 from the particles.

The H₂O₂-based S(VI) oxidation can be also important at mornings as the aqueous H₂O₂ could be consumed in the early morning and is only released to the gas phase later when the relative humidity decreases. In the later afternoon, when $d(H_2O_2)/dt$ is negative, the sulfate concentration gets stabilized. The negative values correspond with increasing relative humidity and the decreasing temperature in the later afternoon. Overall, the temporal behavior observed indicates an enhanced H₂O₂ uptake at late afternoon and subsequent particulate sulfate formation.

HONO photolysis is known to be a significant primary source of OH radicals in winter, particularly in polluted areas with high NO_x concentration.²⁶⁻²⁷ During the SRE-CAS campaign,

high concentrations of HONO with maximum values of 10.2 ppbv were found, suggesting that HONO photolysis might contribute substantially to (i) the atmospheric oxidation capacity via the formation of OH and (ii) indirectly to the S(VI) formation via the reaction of OH and SO₂ in the gas phase. The R^2 between HONO and particulate sulfate is 0.64. Hence, photolysis of HONO could be considered as important for the particulate sulfate formation during the SRE-CAS campaign. However, the correlation is positive, which means that HONO photolysis leads to sulfate depletion; sulfate production, in turn, is related to HONO formation. Still, regarding the strong increase in HONO with sunset and its fast photolysis afterwards, together with the MLH effect on sulfate concentration, HONO photolysis can be a potential source for morning sulfate formation in addition to other OH sources.

S7: Chamber experiments setup

Experimental Procedures of Chamber Runs

The aerosol chamber is a cylindrical, 19 m³ Teflon bag with a surface-to-volume ratio of 2 m⁻¹. Trace gases (i.e., O_3 , NO_x and SO_2) were monitored continuously throughout the experiments with gas monitors consisting of a NOx analyzer (42i TL Trace Level NOx Analyzer, Thermo Scientific, USA), an ozone analyzer (Model 49c, Thermo Environmental Instruments) and an SO₂ analyzer (Model 43B, Thermo Environmental Instruments). Hydrogen peroxide concentrations were monitored with an H₂O₂ monitor (AL2021, Aerolaser, Germany) further on. Particle number concentration was monitored with a TROPOS-style Mobility Particle Size Spectrometer²⁸. Prior to each experiment, the chamber was flushed with clean air for minimum of 18 hours at a flow rate of 200 L min⁻¹. Then, the humidification started. A Merck L-6200A HLPC pump was used to nebulize ultrapure water (Milli-Q gradient A 10, $R > 18 M\Omega$ cm, 3 ppbv TOC, Millipore, USA) at a flow rate of 3 mL min⁻¹ into a heated transfer line (T $\approx 300^{\circ}$ C), resulting in an RH of 52 $\pm 3\%$ within less than three hours. SO₂ and NO were added to the chamber, yielding final concentrations of 25 and 50 ppby, respectively. While SO₂ was used to simulate urban background, NO (50 ppby) prevented potential gas-phase formation of H₂O₂ by HO₂ radical recombination. The temporal profiles of relevant signals for a typical experiment are given in fig. S8A. After injecting seed particles by nebulizing the particle stock solution and an equilibration time of 15 minutes, particles were sampled for 30 minutes on filters (borosilicate glass fiber filter coated with fluorocarbon, 47 mm in diameter, PALLFLEX T60A20, PALL, NY, USA) at a flow rate of 30 L min⁻¹ (i.e., a total volume of 0.6 m^3) for all experiments. Detailed average particle volume concentrations for the filter sampling periods of each experiment are provided in Table S1. Afterwards, the UV lamps (Cleo Advantage 140W-R XPT, total irradiance = 42.36 W m^{-2}) were turned on for 1 hour. After 15 minutes of irradiation, particles were sampled again for 30 minutes on a filter as before. Both filter samples of each experiment were subsequently analyzed by ion chromatography (IC) coupled to conductivity detection to determine total concentrations of SO₄^{2–}and NH₄⁺ ions.

Seed composition

To produce various seed particles, different types of inorganic sulfate salts, SRFA and EDTA were dissolved in water and nebulized into the chamber. The experiments were conducted at pH = 1, 3, 4 and 5. The pH-value was determined with a pH electrode (SI Analytics, Lab 855) in the seed solution before nebulization into the chamber. The composition of the seed solutions and the resulting pH values are given in Table S1.

The experiments were either conducted with ammonium sulfate ((NH₄) $_2$ SO₄, Merck Millipore, Experiments 1–4, 7, 11 and 12), ammonium bisulfate (NH₄HSO₄, Carl Roth GmbH, Experiments 8 and 10), or sodium sulfate (Na $_2$ SO₄ × 10 H₂O, PanReac AppliChem, Experiments 5, 6 and 12) in general. The concentration of the inorganic salt in the seed solution was adjusted to ensure a comparable particle size distribution and sulfate content for all experiments. If necessary, the pH-value of the seed solution was adjusted by the addition of an NaOH solution (1 M NaOH, Merck Millipore) to the desired pH-values, as can be seen in Table S1.

As a proxy for particulate HULIS, SRFA (International Humic Substances Society, added amount can be found in Table S1), was used (experiments 1–12). The concentration of SRFA was chosen to mimic HULIS concentrations during the SRE-CAS campaign, yielding a fraction of 1

w% of SRFA in the seed particles, according to the water insoluble organic carbon (WISOC)/WSOC*/HULIS-C ratio of 65/20/15 w%, which was obtained through the treatment described in section S12. Note that WSOC* denotes WSOC without the contribution of HULIS.

To support the hypothesis of the photochemical H_2O_2 production from HULIS-TMI complexes, dedicated chamber experiments were performed to suppress the formation of such metal complexes by adding a strong metal-chelating agent. Because of its large complex formation constant, EDTA (Titriplex II, ACS, Merck Millipore) was chosen and added to the seed solution (experiments 11–13). Here, the amount of EDTA was varied between 0.08 and 0.008 g L⁻¹ to simulate different extents of complexations. To ensure a complete complexation of TMIs, the mixture was stirred for 4 hours prior to the injection into the chamber. Blank experiments (experiments 16–18) were conducted by introducing inorganic seed particles without the addition of SRFA, metals or EDTA into the chamber.

To investigate the formation of H_2O_2 from authentic aerosol particles in ACD-C, particles collected at two different locations at the North China Plain (Wuqing and Wangdu, SRE-CAS) were extracted and the resulting solutions were used as seed particle solutions. The filter extracts were prepared as follows: a quarter of 17 single filters from the HaChi field campaign²⁹ in Wuqing (39°23''N, 117°0'E, 07/12–08/14/2009) were extracted (experiment 14). The 17 filter aliquots were cut into pieces and extracted in 150 mL water (Milli-Q gradient A 10, R > 18 M Ω , 3 ppbv TOC, Millipore, USA) for one hour using an orbital shaker (420 rpm). To remove insoluble parts, the extract was centrifuged (6000 rpm, 10 min) and the supernatant filtrated with a syringe filter (0.2 µm, Acrodisc Pall, USA). A total volume of about 100 mL was obtained from this extraction procedure. For filter samples from SRE-CAS (38°39' 37.36" N, 115°15' 16.05" E, experiment 14 and 15), the same procedure was used for quarters of 5 filter samples with 100 mL was obtained.

To maintain a comparable particle size distribution throughout all chamber experiments, 0.8 g and 0.53 g (NH₄)₂SO₄ were added to the extract from the HaChi campaign and to the one from the SRE-CAS campaign, respectively. After addition of ammonium sulfate, the solution was nebulized into the chamber and experiments were done as described above.

Data acquisition and calibration of H_2O_2 measurements by AL2021

Hydrogen peroxide concentrations were measured based on the peroxidase-catalyzed reaction of p-hydroxyphenyl acetic acid with peroxides forming a fluorescent dimer. After the excitation of the dimer at 325 nm, the resulting fluorescence is recorded at 400–420 nm³⁰⁻³¹.

The applied H_2O_2 monitor provides two different signals: Signal A corresponds to the sum of H_2O_2 and organic peroxides present in the sampled air. For signal B, H_2O_2 is decomposed by catalase prior to the excitation, and the signal is further corrected by an internal calibration factor. Thus, signal B accounts solely for peroxides other than H_2O_2 (hydroperoxides, peracids etc.). The internal calibration factor was determined once a day prior to each experiment throughout the instrument calibration. Total concentrations of H_2O_2 were calculated by subtraction of signal B from signal A. Although catalases are generally known to have a high selectivity towards H_2O_2 and a weak reactivity towards organic peroxides³², we cannot completely exclude a contribution

of smaller organic peroxides to the signal A that would result in an underestimation of organic peroxides and thereby in an overestimation of H_2O_2 . Such a contribution, however, is limited by the selectivity of the enzyme and therefore regarded as a minor effect. Furthermore, the resulting concentrations were smoothed using a running average over 10 minutes, which was roughly the delay time of the instrumental response to compositional changes in the chamber. We note that despite this slow response the instrument gives concentration values in 4 second intervals, resulting in a rather noisy signal. Additionally, since the observed H_2O_2 concentrations were close to the lower limit of the instrumental measuring range, further averaging was necessary to enhance signal-to-noise ratios. Remarkably, for all experiments a negative response for both signals upon injection of particles and NO was observed, which is likely caused by an unknown cross-sensitivity of the method and instrument. Therefore, the signal was re-adjusted to zero after a stabilization time of a few minutes.

The H_2O_2 formation potential of a seed solution was calculated by the difference between the 20 minutes averaged raw H_2O_2 Signal before UV-radiation and the averaged raw H_2O_2 Signal from 20 to 40 minutes after starting the UV-radiation.

To prove the performance of the H₂O₂ monitor and to determine the response factor, a calibration experiment was performed. For this purpose, a 0.03% H₂O₂ solution was injected with a microliter syringe corresponding to a mixing ratio in the chamber in the range of 70 – 500 pptv. The response curve ($R^2 = 0.99$) was recorded and the results are shown in Figure S8b. Further on, the response of the total peroxide Signal A of the instrument was calibrated to H₂O₂-equivalents to estimate the total peroxide concentration for experiments 10-12.

Quantification of WSOC

Water-soluble organic carbon from aqueous extracts was measured as non-purgeable organic carbon³³ with a commercially available TOC-V_{CPH} analyzer (Shimadzu, Japan). For the Wuqing (HaChi) and SRE-CAS filter extracts, a 1 mL aliquot was taken and diluted to 20 mL. The solution was then acidified with hydrochloric acid and purged with nitrogen to drive out dissolved inorganic carbon. The remainder was then injected into a combustion tube to oxidize all carbon to CO₂, which was subsequently monitored by an infrared detector.

Quantification of metal content by total reflection X-ray fluorescence

To obtain naturally abundant trace metal concentrations in SRFA, an aliquot of an SRFA extract was analyzed by total reflection X-ray fluorescence (TXRF) using an S2 PICOFOX (Bruker, Germany). For the analysis, a 50 μ L (2 × 25 μ L) aliquot of the seed solution were brought onto a quartz sample carrier surface and 10 μ L of a 1 mg/L Ga/Y standard solution added to the aliquot as an internal standard. The carrier was heated to 100 °C for about 5 minutes and afterwards cooled to room temperature and measured.

The calibration and quality assurance were accomplished using a multi-element standard solution (Lot N: N15521, C.P.A. Ltd, Bulgaria) that contained the following elements: Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn. The obtained

results were in good agreement (with a deviation of ± 5 %) with the values provided by the manufacturer, thus, validating the applied procedure. The error of the determined metal concentrations is estimated to be less than 7% except for metals with low concentrations such as Sr, Ni, As, Ba, Pb, for which the error is less than 15%. Further details on the technique can be found elsewhere³⁴.

IC analysis of sulfate and ammonium ions

The amount of SO_4^{2-} and NH_4^+ was determined offline by IC-CD from filter samples. For the offline analysis, ¹/₄ filters were cut into small pieces and placed in plastic tubes (Centrifuge tube, 15 mL, Labsolute). The filter pieces were extracted using 10 mL of a formaldehyde-water mixture (0.5 mL formaldehyde (37%) in 1L water) and agitated with an orbital shaker (420 rpm) for 1 h. The extracts were purified with a 0.45 µm syringe filter (Acrodisc Pall, USA). The total amount of sulfate was analyzed within 48 hours after sample preparation by IC with conductivity detector (ICS 6000, Thermo Fisher Scientific). The cations were analyzed with a CS16-4 µm column combined with a CG16-4 µm guard column (both Thermo Scientific Dionex) using methanesulfonic acid (MSA; 36 mM) as eluent at 40°C. Anions were separated by an AS18 column combined with an AG18 guard column (both Thermo Scientific Dionex) using an eluent gradient of aqueous KOH at 23°C (Table S2).

The calibration of the target anion and cation was done in the range of 0.2–5.0 mg L⁻¹ for NH₄⁺ and 0.2–5.0 for SO₄^{2–} mg L⁻¹. Single-element IC standard solutions were used for quantification SO₄^{2–} (1000 mg L⁻¹, Sigma-Aldrich) and NH₄⁺ (1000 mg L⁻¹, Sigma-Aldrich). The concentration of ammonium and sulfate was calculated as difference between the filter taken in the dark and during UV irradiation. The values for ammonium were taken as reference for any loss processes that might occur during chamber experiment (e.g., wall losses) and sample preparation. SO₄^{2–} was corrected for those losses by applying losses of NH₄^{+ 35}.

S8: Additional results from simulation chamber experiments

Influence of particle-phase acidity and seed composition

As investigated in experiments 2–9 (Figure S7b and S7c), neither particle-phase acidity nor the inorganic seed composition significantly affected photochemical H_2O_2 production in the chamber (Figure S18b and S18c). Therefore, the photochemical H_2O_2 production of these experiments was lumped together, yielding an average ΔH_2O_2 of 116.4 ± 83.3 pptv.

Complexation of TMIs with EDTA

As shown in Table S3, TXRF analysis of the SRFA-containing seed solution showed considerable amounts of metal ions being naturally present in SRFA. So, no further metal ions were added to the seed solutions to generate the required metal complexes. Moreover, such metal ions were also highly abundant in filter samples from both the HaChi campaign and the SRE-CAS measurements.

To evaluate the role of naturally abundant TMIs on photochemical H_2O_2 production, EDTA was added to mask any metal ions, and thus, strongly limited any contributions from TMI-SRFA complexes on H_2O_2 formation. As shown in Figure S8c, the addition of EDTA resulted in a strongly reduced H_2O_2 production, yielding merely a mixing ratio of 28.5 ± 9.5 pptv (experiment 10–12), which resembles H_2O_2 mixing ratios of blank experiments without any SRFA addition (i.e. 11–26 pptv, experiment 16 and 17).

To further support the hypothesis of a reduction in H_2O_2 production due to the complexation of TMIs by EDTA, a control experiment with a reduced amount of EDTA was conducted. Although EDTA was still in excess, in this experiment a significant production of H_2O_2 of 111 pptv was observed, which is comparable to experiments without EDTA addition. The H_2O_2 formation is attributed to a combination of the following factors: The measured complex stability constant of the Fe(II)–SRFA complex³⁶ is with logK = 5 about 9 orders of magnitudes lower than the stability constant of the Fe(II)–EDTA complex logK = 14.3³⁷. Therefore, from a thermodynamic point of view, even a much smaller EDTA addition should sufficiently suppress the formation of Fe(II)– SRFA complexes in the seed solution. However, note that the seed solution was freshly prepared before each experiment, and thus, did not reach thermodynamic equilibrium. Moreover, SRFA contains a large number of various complexation sites with a large range of stability constants that might partially exceed the stability constant of Fe(II)–EDTA. In addition to the complex stability, TMI–EDTA complexes are known to decompose rapidly under UV-radiation for lower TMI:EDTA ratios, as reported previously³⁸. Hence, only a large excess of EDTA efficiently suppressed TMI–SRFA complex formation, and thus, H_2O_2 formation upon irradiation.

Evaluation of sulfate production

Chamber experiments indicated a change in sulfate concentrations in the seed particles upon irradiation. As depicted in Figure S9a, experiments with SRFA and the resuspended aerosol collected during the SRE-CAS campaign and the HaChi campaign resulted in an increase of the sulfate fraction, suggesting a production of sulfate from oxidation of SO₂ through in-particle generated H_2O_2 .

Experiments investigating particle-phase acidities indicated a pH-dependency of the sulfate formation (Figure S9b). For experiments at pH 1 and pH 3 no significant increase in the sulfate fraction could be observed, whereas experiments at pH 5 resulted in a significant increase in the SO_4^{2-}/NH_4^+ ratio. This pH-dependency might be a result of the pH-dependent partitioning behavior of SO₂, favoring SO₂ uptake at higher pH values. In contrast, the decrease in sulfate concentrations under more acidic conditions might indicate the formation of organosulfates, which was shown to be favored at lower pH values³⁹⁻⁴².

In addition, also for experiments using EDTA as complexing agent an increase in the SO_4^{2-} to NH_4^+ ratio was observed. However, as for these experiments no H_2O_2 formation was observed, other oxidants have to drive such a sulfate production. Consistently, the H_2O_2 monitor indicated the formation of other organic peroxides in the presence of EDTA, which are potentially capable to oxidize SO_2 (Figure 6a).

S9: Model initialization of the water-soluble organic mass

During all periods, the organic mass contributes almost 50% to PM_{2.5}. During the SRE-CAS field campaign, the total organic carbon (OC) and the WSOC were measured. However, the amount of water-soluble HULIS as part of the WSOC was not determined. Hence, an average split of WISOC/WSOC*/HULIS-C was determined based on available literature data to initialize the model. A detailed literature overview of the measured fraction in ambient samples including quantified HULIS contents is given in Table S15.43-77 The resulting average and median values for different seasons and areas are as well summarized in Table S9. From the literature survey, the following findings were derived: During winter in China, the contribution of WISOC to OC is around 65 %, which is in good agreement with the average WSOC/OC ratio of 33 ± 9 % from the filter measurements during the SRE-CAS field campaign. The contribution of HULIS-C to WSOC is around 42 %. It is noteworthy that good correlations between the HULIS and K⁺ concentrations have been widely reported, particularly in the region where biomass burning is regarded as the dominant source of ambient organic aerosol matter.^{70, 74, 78} Correspondingly, also in the present study, a very good correlation ($r^2 = 0.78$) has been found between K⁺ and WSOC from the filter measurement. Hence, the HULIS/K⁺ ratio was also taken as a valid proxy for the HULIS-C/WSOC ratio. According to the literature survey, the average ratio of HULIS/K⁺ is about 6.5 during winter in China. From this value, an average HULIS-C/WSOC ratio of 32 ± 9 % was derived from the filter measurements, which is somewhat smaller but still comparable to the HULIS-C/WSOC ratio of 42 % resulting from the review. Overall, the ratios of WSOC/OC and HULIS-C/WSOC from the review lead to a WISOC/WSOC*/HULIS-C split of 65/20/15 (w%), which was applied within the model for the organic aerosol initialization. This results into an initial HULIS concentration of 10.3, 12.4, 13.1, and 14.4 µg m⁻³ for the first, second, third and fourth modelling period, respectively. Additionally, 1% contribution of oxalic acid to organic mass was adopted to consider iron interactions with dicarboxylic acids.

S10: Meteorological simulation setup

The general weather situation was characterized by descending air masses (descending backward trajectories new Figure S3 in the supplement) indicating high pressure conditions in winter together with advection of cold and dry continental air. Those weather conditions are not preferring cloud formation, actually it even suppresses cloud or fog formation. During the descend of the air mass from higher altitudes, the RH is decreasing because of adiabatic warming. Additionally, in the last 24 hours, the approaching air parcels mainly originate from the surrounding area and reside within the rather dry continental boundary layer (Figure S3). This indicates that cloud/fog chemistry has not influenced measured aerosol. Besides all this, an O₃ LIDAR was operated during the campaign. From the Figure S4, it can be seen that cloud formation occurs only above 3000 meters, and thus, did not affect the measurement site as the air parcels reside almost exclusively below 2000 meters for the preceding 72 hours (Figure S3). In conclusion, cloud chemistry was unlikely to affect the measured aerosol composition.

Local fog occurrence can alter the particle composition significantly. However, it is known that during haze events fog does usually not occur.⁷⁹⁻⁸⁰ However, no instrument was operated during the campaign enabling the microphysical detection of fog. To distinguish whether fog or an extreme haze event occurred, the campaign data were screened for periods with RH \ge 90% (Figure S2). From this analysis, two periods were identified. One between the 6th to 7th Nov. and the other one between 29th to 30th of Dec.

In the next step, we investigated the concentration time profile of soluble gases during this period, i.e., SO_2 , HONO, NH_3 and H_2O_2 (Figure S2). Fog occurrence would imply a strong reduction of these water-soluble gases due to the significantly higher liquid water content and occurring aqueous-phase chemistry in this less acidic solution in comparison to haze.

The analysis showed quite high ammonia concentrations during period 1 (6^{th} to 7^{th} Nov.) above 40 ppb as well as stable SO₂ concentrations. Therefore, this period was excluded to be affected by fog conditions.

For the second period (29th to 30th of Dec.), no ammonia data were available from 28th Dec 20:00 to 29th Dec. 13:00, because of an instrument failure. Interestingly, a strong SO₂ increase and rapid decrease was observed for a very short period at 29. Dec. (10 a.m. to 2 p.m.). During this time, also the gas-phase H₂O₂ was not high indicating a strong SO₂ oxidation by H₂O₂. But, for HONO, no significant concentration variation was observed. Fog would have led to a significant observable reduction in the HONO concentrations, because of the increase in the liquid water content and pH. Furthermore, the PM_{2.5} concentration was still high (\geq 75 µg m⁻³). Such high concentrations are not typical for fog occurrence as a substantial fraction of the PM_{2.5} is part of the fog droplet spectra with typically larger sizes above the PM_{2.5} inlet cutoff. Additionally, a fog formation would activate CCNs (diameter usually \geq 200nm) causing an observable reduction in the data. Accordingly, no fog occurrence was expected and thus no fog interaction was considered in the model studies for this period.

S11: Development of the HONO multiphase chemistry mechanism

For HONO, it is suggested that the uptake and hydrolysis of NO₂ dimers might be important.⁸¹ Accordingly, the multiphase chemistry mechanism was extended to treat the multiphase chemistry of N₂O₃ and N₂O₄, respectively. These additions are classical high-NO_x chemistry which is adequate for the situation at SRE-CAS but should be further extended by more recent finding for HONO formation pathways in future mechanism development.

The gas-phase chemical mechanism was extended with reactions, which might be relevant under the very high NO_x mixing ratios as observed at the SRE-CAS. Overall, the advanced scheme consists of 16 gas-phase reactions, two phase transfer processes and four aqueous-phase equilibria (Tables S10-S12).

S12: Development of the TMI-HULIS chemistry mechanism

Reactions of $[Fe^{(II)}HULIS]^+$ complex with aqueous O₂ and OH and the reaction of $[Fe^{(III)}HULIS]^{2+}$ complex with O_2^{-} were implemented based on Miller, et al. ⁸². Recent studies revealed that the oxidation rates for Fe complexed by HULIS were substantially higher than the reported value for inorganic iron(II) oxidation by O₂.⁸³ Available kinetic data in the literature for the reaction of iron(II)-organic complexes with aqueous O2 vary strongly with second-order rate constants between 2 and 347 M⁻¹ s⁻¹.⁸²⁻⁸⁶ The implemented value based on Miller, et al. ⁸² of 74 M⁻¹ s⁻¹ is a rate constant in the middle range of the available kinetic data. The reaction of the $[Fe^{(II)}HULIS]^+$ complex with O_2^- is based on the kinetic data compilation of Bielski, et al. ⁸⁷, in which the reaction rate constant of iron(II)-organo complexes with O2⁻ range from 1.0×10^5 L mol⁻¹ s⁻¹ to 1.0×10^7 L mol⁻¹ s⁻¹. Accordingly, the implemented value of 1.0×10^5 L mol⁻¹ s⁻¹ corresponds to the lower limit and is a conservative choice. Furthermore, the Fenton-like chemistry of [Fe^(II)HULIS]⁺ has been considered using the same kinetic data as for the Fenton reaction of Fe²⁺ with H₂O₂ because of the lack of more adequate kinetic data. It was shown that Fenton-like chemistry of Fe^(II)-SRFA is slower than the original Fenton of Fe²⁺ reactions, ^{82,} ⁸⁴ whereas for dopamine it was found to be comparable.⁸⁸ Therefore, the rate constant implemented here represent an upper limit. Therewith, this approach considers the highest H₂O₂ depletion and lowest depletion of [Fe^(II)HULIS]⁺ complexes preserving the most conservative H₂O₂ source and loss yield. These approaches enable a slightly robust mechanisms, because the H₂O₂ production from $[Fe^{(II)}HULIS]^+$ is lowest, whereas the H₂O₂ consumption by $[Fe^{(II)}HULIS]^+$ is highest.



Figure S1. Location of SRE-CAS site in the North China Plain (a) The locations of the North China Plain and Wangdu County (b) Dongbaituo village (https://www.openstreetmap.org) (c) SRE-CAS site, picture taken by unmanned aerial vehicle.



Figure S2. Campaign data (11/01to 12/31/2017). Time series of (top to bottom): (a, Left), relative humidity (RH). (a, Right), global radiation intensity. (b, Left), NO concentration. (b, Right), CO concentration. (c, Left), NO₂ concentration. (c, Right), O₃ concentration. (d, Left), H₂O₂ concentration. (d, Right), HONO concentration. (e, Left), SO₂ concentration. (e, Right), OC concentration. (f, Left), PM_{2.5} concentration. (f, Right), sulfate concentration. (g, Left) aerosol liquid water content predicted by ISORROPIA II model, (g, Right), pH of fine particles predicted by ISORROPIA II model. (h, left), NH₃ concentration. (h, right), NH₄⁺ concentration. The color of the sulfate concentration curve represents the sulfate fraction of the secondary inorganic aerosol. The purple squares indicate the four modeling periods (MP1-4).



Figure S3. Calculated backward trajectories for polluted days. Calculated 24- (a) and 72-hours (b) backward trajectories using HYSPLIT for polluted days during the measurement campaign. All trajectory heights are below 2500 m.



Figure S4. Vertical extinction coefficient measured by an ozone Lidar at the measurement site during the field campaign for the modeling periods. Light layer above 3000 m indicated clouds.



Figure S5. Calculated rates of sulfate formation in aerosol particles during polluted days ($PM_{2.5} \ge 75 \ \mu g \ m^{-3}$). The formation rates have been calculated by using the average value over all polluted days of SO₂ (13.26 ppbv), H₂O₂ (0.17 ppbv), O₃ (5.96 ppbv), NO₂ (33.76 ppbv) and dissolved iron (1e-9 mol 1⁻¹). The iron concentration has not been measured, but is derived from our simulations of the base case. The yellow area represents the daytime pH of the aerosols calculated with ISOROPPIA (see Figure S5 b). Red line: calculated sulfate formation rates by H₂O₂ related S(IV) oxidation. Green line: calculated sulfate formation for the low reaction rate coefficient determined from Spindler et al. (2003). Blue dashed line: calculated sulfate formation rates by NO₂ related S(IV) oxidation et al. (1988). Magenta line: calculated sulfate formation rates by dissolved free iron related S(IV) oxidation.



Figure S6. Time-resolved dependence of the net H_2O_2 production/degradation rates from the relative humidity and solar radiation. (a) Dependence from the relative humidity. (b) Dependence from the global radiation. Orange symbols: morning data (7 am to 12 am). Blue symbols: afternoon data (1 pm to 5 pm).



Figure S7. Diurnal profiles of the H₂O₂ concentrations in the gas-phase (a, H₂O₂ (g)), H₂O₂ concentrations in the liquid-phase (a, H₂O₂ (aq)) calculated by Henry Law, aerosol liquid water content (b, left), pH (b, right), temperature (c) and relative Humidity (d) during polluted episodes (daily averaged PM_{2.5} > 75 μ g m⁻³). The solid lines represent the medians and the shadow area represent the 25% - 75% range.



Figure S8. Experimental overview of aerosol chamber experiments. (a) Generalized scheme of ACD chamber as used in the present experiments. Detailed observations for each experimental run are displayed in panels (b), (c), and (d), showing the temporal evolution of H_2O_2 and SO_2 mixing ratios as well as the sulfate/ammonium ratios determined from filter samples; the yellow shaded region indicates the irradiation period.



Figure S9. Total peroxide signal and effect of ETDA addition on H_2O_2 formation in chamber experiments. (a) Temporal evolution of gas-phase H_2O_2 and total peroxides during experiments in the presence and absence of EDTA. (b) Response curve of the H_2O_2 calibration experiment. Between two injections, the system was allowed to stabilize for 20 minutes. (c) Effect of the addition of a complexing agent (i.e., EDTA) on photochemical H_2O_2 production.



Figure S10. Results of the chamber experiment series. (a) Change of the sulfate fraction in seed particles determined as difference between the sulfate content during dark period and during UV irradiation. Values are normalized to the change of ammonium to compensate for losses during sample preparation. (b) pH-dependent change of the sulfate fraction in seed particles determined as in Figure A.



Figure S11. Comparison of the multiphase modeling results with the observed (top) gas-phase H_2O_2 concentrations and the (bottom) PM_{2.5} sulfate for the first, third and fourth selected modeling period. Comparison of the measured and modeled H_2O_2 gas-phase concentrations during the first (a), third (b) and fourth (c) modeling period. Black dots: One-hour averaged gas-phase H_2O_2 concentrations measured. Cyan line: First base case simulations. Blue line: Simulation with added iron-HULIS interaction chemistry. Orange and red line: Runs with a low and high TMI soluble fraction. Green line: Run w/o TMI chemistry. Comparison between the modeled and measured sulfate concentration normalized to the diurnal variation of the MLH for the first (d), third (e) and fourth (f) modeling period. Red line: Modeled sulfate concentration. Blue line: Measured sulfate concentration. Black line: MLH. The grey areas represent night-time periods.



Figure S12. Simulated gas-phase HO₂ (a) and gas-phase H₂O₂ (b) concentrations during the second model period (Nov. $25^{th}-29^{th}$). Cyan line: First base case simulations without new iron-HULIS chemistry. Brown Line: base case simulations without new iron-HULIS chemistry, but model constraint for higher production of gas-phase HO₂. Blue line: Simulation with added iron-HULIS aerosol chemistry mechanism.



Figure S13. Diurnal profiles of the HONO (left axis) and CO (right axis) concentrations in the gas-phase during polluted episodes (daily averaged $PM_{2.5} > 75 \ \mu g \ m^{-3}$). The solid lines represent the medians and the shadow area represent the 25% - 75% range.


Figure S14. Modeled chemical sink and source rates of HO_2/O_2^- in the particle phase. Modeled multiphase chemical sink and source rates of HO_2/O_2^- (base case) during the second day of the first (a), second (b), third (c) and fourth (d) modeling period. The grey areas represent night-time periods. Further chemical production/loss processes include formation/loss processes that contribute less than 5% to the fluxes averaged over the full simulation period. These include also iron-oxalate photolysis, that contributes 0.7%, 0.6%, 0.7% and 1.5% to HO_2/O_2^- formation on the first, second, third and fourth simulation, respectively



Figure S15. Modeled multiphase chemical sink and source rates of H_2O_2 . Modeled multiphase chemical sink and source rates of H_2O_2 (base case) during the second day of the first (a), second (b), third (c) and fourth (d) modeling period. The grey areas represent night-time periods. Further chemical production/loss processes include formation/loss processes that contribute less than 5% to the fluxes averaged over the full simulation period.



Figure S16. Modeled diurnal sulfate formation (left) and calculated diurnal sulfate formation scaled by the MLH (right). Modeled diurnal sulfate formation during the first (a), second (b), third (c) and fourth (d) modeling period. Modeled diurnal sulfate formation normalized by using the MLH height during the first (e), second (f), third (g) and fourth (h) modeling period. Orange line: overall modeled sulfate production rate. Blue line: modeled sulfate formation rate from gas-phase oxidation of SO₂ by OH. Red line: modeled sulfate formation rate from aqueous-phase oxidation of HSO₃⁻ by H₂O₂. The grey shaded areas represent night-time periods. For more clarity, Figures (e), (f), (g) and (h) are without error bars.



Figure S17. Description of the mean mixing layer height (MLH) during periods with high PM_{2.5} concentrations and its effect on the measured sulfate and PM_{2.5} concentration. (a) Diurnal MLH profile during the SRE-CAS campaign at periods with high PM_{2.5} concentrations. High PM_{2.5} concentrations are defined as periods with PM_{2.5} \geq 75 µg m⁻³. Dots: measured values. Blue line: adjusted MLH profile based on the measured data and an estimated minimum MLH of 70 m at 7 am. Dashed red line: median diurnal temperature profile. R² represents the correlation coefficient between the MLH and temperature. (b) Diurnal normalized S(VI) and PM_{2.5} concentrations by daily maximum S(VI) and PM_{2.5} concentrations. Furthermore, the normalized MLH is presented. (c) Product ratio of the normalized S(VI) and PM_{2.5} concentration with the normalized MLH.



Figure S18. Results of the chamber experiment series. (a) Typical time profile of H_2O_2 , NO, O_3 , SO_2 and particle volume recorded during experiment 9. (b) Experiments #2, #8 and #11 are exemplary for the effect of particle-phase acidity on H_2O_2 formation in the dark (0-60 min) and under UV-irradiation (60-120 min). (c) Effect of different inorganic seed particle compositions on H_2O_2 formation in the dark (0-60 min) and under UV-irradiation (60-120 min). (c) Effect irradiation (60-120 min).

Tables

Table S1.

Experimental overview of the chamber experiments. All experiments were conducted in the presence of inorganic seed particles (40–50 μ g m⁻³), 25 ppbv SO₂ and 50 ppbv NO at 53 ± 3% RH and T = 293 K. The temporal evolution of single experiments can be found in Figure S9.

Numbor	Composition of the seed solution ^{<i>a</i>} / g L ⁻¹				Part. V	ΔH_2O_2
Number	Inorganic seed	SRFA	EDTA	— рн ["]	/ µm³ cm⁻³	/ \mathbf{pptv}^d
	pH dependency ex	periments				
1	(NH ₄) ₂ SO ₄ , 7.8	0.08	-	5	37.5	e
2	(NH ₄) ₂ SO ₄ , 7.8	0.08	-	5	44.7	60
3	(NH ₄) ₂ SO ₄ , 7.8	0.08	-	5	43.0	31
4	(NH ₄) ₂ SO ₄ , 7.8	0.08	-	5	36.7	34
5	$Na_2SO_4, 14.7^c$	0.08	-	5	32.8	296
6	$Na_2SO_4, 14.7^c$	0.08	-	5	44.7	154
7	(NH4) ₂ SO4, 7.8	0.08	-	3	38.7	110
8	NH ₄ HSO ₄ ,7.9	0.08	-	1	41.9	144
9	NH4HSO4,7.9	0.08	-	1	40.1	152
	Complexation with	EDTA				
10	(NH ₄) ₂ SO ₄ , 7.8	0.08	0.08	5	44.1	38
11	(NH ₄) ₂ SO ₄ , 7.8	0.08	0.08	4	40.6	19
12	$Na_2SO_4, 14.7^a$	0.08	0.008	4	39.0	111
	Redispersion of au	thentic ambi	ent particles	5		
	Wuqing (HaChi)					
13	17 Filter aliquots	-	-	5	42.7	31
	SRE-CAS campaig	<i>gn</i>				
14	5 Filter aliquots	-	-	5	41.8	43
15	5 Filter aliquots	-	-	5	41.0	49
	Blank measureme	nts				
16	(NH ₄)HSO ₄ , 7.8	-	-	1	34.4	11
17	(NH ₄) ₂ SO ₄ , 7.8	-	-	5	39.5	26
18	(NH ₄) ₂ SO ₄ , 7.8	-	-	5	54.1	_e

^{*a*} Concentrations were adjusted to ensure a similar particle size distribution for all experiments

^b Measured in seed solution

^c Na₂SO₄ was used as decahydrate

^{*d*} Values were calculated as described in section S7 "Data acquisition and calibration of H₂O₂ measurements by AL2021"

^{*e*} Instable flow of reagent solution

Table S2.

Gradient for anion separation on an ICS 6000 system with CS16-4 µm column at 23 °C.

Time / min	0–4	8	13.5–17.4	20-21.5	21.5-23.1	23.1-26.8
KOH / mM	4	20	28	40	55	4

Table S3.

Concentrations of metal ions determined by TXRF analysis. The standard deviation was calculated from triplicate measurements.

Samples Metal	Redispersion HaChi / μmol L ⁻¹	Redispersion SRE-CAS campaign / μmol L ⁻¹	Seed solution of experiment 3 / µmol L ⁻¹
К	31.58 ± 1.58	299.67 ± 1.14	6.19 ± 0.89
Ca	22.69 ± 0.97	144.98 ± 4.76	17.01 ± 0.26
Ti	1.16 ± 0.12	1.36 ± 0.13	4.44 ± 0.10
Cr	0.08 ± 0	0.26 ± 0.02	nd
Mn	1.44 ± 0.04	1.95 ± 0.09	nd
Fe	5.15 ± 0.09	2.82 ± 0.11	2.18 ± 0.07
Ni	0.23 ± 0.01	0.08 ± 0.01	0.09 ± 0.02
Cu	5.71 ± 0.11	0.50 ± 0.02	0.03 ± 0.01
Zn	26.89 ± 0.96	38.61 ± 1.57	0.93 ± 0.01
As	0.59 ± 0.16	0.48 ± 0.03	0.02 ± 0
Se	0.32 ± 0.02	0.30 ± 0.01	nd
Rb	0.26 ± 0.01	0.31 ± 0.02	0.05 ± 0
Sr	0.13 ± 0.04	0.51 ± 0.02	0.16 ± 0.09
Mo	102.59 ± 9.38	16.64 ± 1.77	79.73 ± 7.02
Ba	1.90 ± 0.57	3.91 ± 0.07	0.98 ± 0.17
La	0.13 ± 0	nd	0.96 ± 0.08
Pb	2.00 ± 0.26	0.27 ± 0.06	0.01 ± 0

nd: not detected

Table S4.

WSOC, number of aliquots and amount of (NH₄)₂SO₄ added for redispersion experiments.

Sampling location	Number of aliquots	Resulting WSOC / µg L ⁻¹	$(NH_4)_2SO_4$ addition / g
Wuqing (HaChi)	17	39.780	0.53 g in 0.07 L
SRE-CAS campaign	5	141.040	0.80 in 0.1 L

Table S5.

Overview of the implemented meteorological parameters applied in SPACCIM for the four modeling periods. The parameters represent mean measured values during the campaign periods.

Meteorological data	1 st Period	2 nd Period	3 rd Period	4 th Period
Temperature (K)	275	274	273	270
Pressure (hPa)	1021.2	1019.2	1020.7	1024.4
Relative humidity (%)	50	50	57	73
Wind speed (m s^{-1})	1 m s ⁻¹			
Maximum measured j _{NO2}	0.005	0.0046	0.0038	0.002
$PM_{2.5} (\mu g m^{-3})$	117	122	178	201

Table S6.

Implemented initial concentrations for the four modeling periods.

Compound	Initial conce	ntration / molecules cm	1 ⁻³	
Compound	1 st Period	2 nd Period	3 rd Period	4 th Period
H ₂	1.28×10^{13}	1.28×10^{13}	1.28×10^{13}	1.28×10^{13}
Methane	4.33×10 ¹³	4.33×10 ¹³	4.33×10 ¹³	4.33×10 ¹³
CO ₂	9.10×10 ¹⁵	9.10×10 ¹⁵	9.10×10 ¹⁵	9.10×10 ¹⁵
H ₂ O ₂	9.20×10^{08}	2.40×10^{09}	1.30×10^{09}	4.00×10^{09}
NO	1.15×10^{12}	2.29×10^{12}	1.96×10^{12}	2.26×10^{12}
NO ₂	9.54×10 ¹¹	8.17×10^{11}	1.10×10^{12}	1.13×10^{12}
O ₃	1.71×10^{11}	2.24×10^{11}	1.57×10^{11}	8.46×10^{10}
CO	6.44×10^{13}	6.16×10 ¹³	8.72×10^{13}	1.06×10^{14}
SO ₂	3.95×10 ¹¹	3.97×10 ¹¹	3.88×10 ¹¹	3.37×10 ¹¹
HONO	4.72×10^{10}	5.09×10 ¹⁰	7.85×10^{10}	1.39×10 ¹¹
NH ₃	1.18×10^{12}	1.13×10 ¹²	1.13×10 ¹¹	7.88×10^{11}
Ethane	3.64×10 ¹¹	3.43×10 ¹¹	4.77×10 ¹¹	2.91×10 ¹¹
Ethylene	5.06×10 ¹¹	3.95×10 ¹¹	6.05×10 ¹¹	2.92×10 ¹¹
Propane	1.34×10^{11}	1.33×10^{11}	1.93×10 ¹¹	1.18×10^{11}
Propylene	1.24×10^{11}	9.70×10^{10}	1.56×10^{11}	1.61×10^{11}
Isobutane	3.25×10^{10}	2.79×10^{10}	4.03×10 ¹⁰	6.02×10^{10}
n-Butane	6.92×10^{10}	6.04×10^{10}	8.96×10 ¹⁰	1.24×10^{11}
Acetylene	1.74×10^{11}	1.36×10 ¹¹	2.14×10^{11}	2.04×10 ¹¹
trans-2-Butene	5.86×10^{09}	7.29×10^{09}	7.82×10^{09}	1.53×10^{10}
1-Butene	1.69×10^{10}	1.32×10^{10}	2.24×10^{10}	2.39×10 ¹⁰
cis-2-Butene	4.30×10^{09}	3.30×10^{09}	4.02×10^{09}	8.48×10^{09}
Isopentane	4.90×10^{09}	3.99×10 ⁰⁹	5.56×10^{09}	1.02×10^{10}
n-Pentane?	2.72×10^{10}	2.43×10^{10}	3.42×10^{10}	7.64×10^{10}
Chloromethane	1.22×10^{10}	8.39×10^{09}	1.36×10^{10}	1.31×10^{10}
Vinvlchloride	1.76×10^{09}	7.60×10^{08}	1.64×10^{09}	1.28×10^{09}
1.3-Butadiene	6.37×10^{09}	5.63×10 ⁰⁹	8.73×10^{09}	8.48×10^{09}
Bromomethane	2.08×10^{08}	1.85×10^{08}	6.41×10^{08}	8.70×10^{10}
Chloroethane	2.39×10^{09}	8.63×10^{08}	1.53×10^{09}	1.21×10^{09}
1-Pentene	3.86×10 ⁰⁹	3.72×10^{09}	5.41×10^{09}	7.15×10 ⁰⁹
Isoprene	3.84×10^{09}	3.07×10^{09}	3.96×10 ⁰⁹	4.55×10 ⁰⁹
Acrolein	8.14×10^{09}	6.55×10^{09}	1.19×10^{10}	7.92×10^{09}
Propanal	1.04×10^{10}	8.32×10^{09}	1.43×10^{10}	1.10×10^{10}
1.1-Dichloroethene	4.16×10^{07}	3.24×10^{07}	1.16×10^{08}	1.84×10^{08}
2.2-Dimethylbutane	1.10×10^{09}	9.52×10^{08}	1.34×10^{09}	1.80×10^{09}
Acetaldehyde	8.27×10^{10}	6.23×10^{10}	9.37×10 ¹⁰	9.37×10 ¹⁰
Dichloromethane	4.08×10^{10}	3.96×10 ¹⁰	5.99×10 ¹⁰	5.43×10 ¹⁰
2.3-Dimethylbutane	1.25×10^{09}	1.10×10^{09}	1.73×10^{09}	2.80×10^{09}
2-Methylpentane	1.05×10^{10}	9.43×10 ⁰⁹	1.26×10^{10}	1.78×10^{10}
3-Methylpentane	6.75×10^{09}	6.12×10 ⁰⁹	8.64×10 ⁰⁹	1.31×10^{10}

Compound	Initial conce	-3		
Compound	1 st Period	2 nd Period	3 rd Period	4 th Period
MTBE	4.62×10^{09}	3.52×10^{09}	6.05×10^{09}	4.68×10^{09}
1-Hexene	5.54×10^{09}	5.24×10^{09}	7.36×10^{09}	8.36×10^{09}
n-Hexane	1.25×10^{10}	1.23×10^{10}	1.76×10^{10}	2.41×10^{10}
Methacrolein	1.01×10^{09}	8.39×10^{08}	1.47×10^{09}	8.66×10^{08}
1,1-Dichloroethane	2.31×10^{08}	2.56×10^{08}	5.02×10^{08}	6.72×10^{08}
n-Butanal	1.85×10^{09}	1.58×10^{09}	2.81×10^{09}	1.70×10^{09}
Methylvinylketone	3.62×10^{09}	3.04×10^{09}	4.70×10^{09}	3.75×10^{09}
cis-1,2-Dichloroethene	2.43×10^{07}	1.92×10^{07}	4.07×10^{07}	6.09×10^{07}
Methylethylketone	2.33×10^{10}	1.91×10^{10}	2.75×10^{10}	2.64×10^{10}
Chloroform	1.94×10^{10}	1.41×10^{10}	2.12×10^{10}	2.32×10^{10}
1,1,1-Trichloroethane	1.06×10^{08}	1.30×10^{08}	1.42×10^{08}	1.94×10^{08}
2-Methylhexane	2.20×10^{09}	1.96×10^{09}	2.89×10^{09}	3.74×10^{09}
Cyclohexane	2.89×10^{09}	3.07×10^{09}	4.69×10^{09}	6.30×10^{09}
3-Methylhexane	2.04×10^{09}	1.73×10^{09}	2.36×10 ⁰⁹	3.63×10^{09}
Benzene	1.21×10^{11}	8.80×10^{10}	1.33×10^{11}	1.38×10^{11}
1,2-Dichloroethane	2.07×10^{10}	1.07×10^{10}	2.18×10^{10}	1.99×10^{10}
n-Heptane	5.21×10 ⁰⁹	5.06×10 ⁰⁹	7.27×10^{09}	9.97×10^{09}
Trichloroethylene	1.82×10^{09}	1.98×10^{09}	3.91×10 ⁰⁹	2.74×10^{09}
2-Pentanone	2.46×10^{09}	1.80×10^{09}	2.92×10^{09}	2.49×10^{09}
1,2-Dichloropropane	1.98×10^{10}	8.54×10^{09}	1.81×10^{10}	1.43×10^{10}
n-Pentanal	1.39×10^{09}	1.07×10^{09}	1.85×10^{09}	1.01×10^{09}
3-Pentanone	1.04×10^{09}	8.65×10^{08}	1.47×10^{09}	1.33×10^{09}
Toluene	7.72×10^{10}	7.15×10^{10}	1.07×10^{11}	1.09×10^{11}
n-Octane	4.10×10 ⁰⁹	3.47×10^{09}	5.17×10^{09}	6.72×10^{09}
1,1,2-trichloroethane	1.51×10^{09}	6.83×10^{08}	1.65×10^{09}	1.16×10^{09}
Tetrachloroethylene	4.32×10 ⁰⁹	2.56×10^{09}	3.15×10^{09}	3.13×10^{09}
n-Hexanal	1.13×10^{10}	9.76×10^{09}	1.69×10^{10}	1.10×10^{10}
1,2-Dibromoethane	9.61×10 ⁰⁶	6.08×10^{06}	3.91×10^{07}	5.23×10^{07}
Ethylbenzene	1.39×10^{10}	1.20×10^{10}	1.83×10^{10}	2.27×10^{10}
n-Nonane	4.46×10 ⁰⁹	3.02×10^{09}	4.82×10^{09}	5.54×10^{09}
m-Xylene	6.20×10^{09}	5.10×10 ⁰⁹	7.11×10^{09}	8.56×10^{09}
p-Xylene	2.48×10^{10}	2.04×10^{10}	2.84×10^{10}	3.42×10^{10}
o-Xylene	1.16×10^{10}	9.45×10^{09}	1.42×10^{10}	1.32×10^{10}
Styrene	1.09×10^{10}	1.26×10^{10}	1.66×10^{10}	1.60×10^{10}
iso-Propylbenzene	7.54×10^{08}	6.36×10^{08}	1.22×10^{09}	1.38×10^{09}
n-Propylbenzene	1.61×10^{09}	1.22×10^{09}	1.88×10^{09}	1.73×10^{09}
m-Ethyltoluene	4.07×10^{09}	3.23×10^{09}	4.87×10^{09}	5.00×10^{09}
p-Ethyltoluene	2.81×10^{09}	2.18×10^{09}	3.15×10^{09}	3.53×10^{09}
n-Decane	3.46×10^{09}	2.79×10^{09}	4.16×10 ⁰⁹	4.01×10^{09}
1,3,5-Trimethylbenzene	1.86×10^{09}	1.54×10^{09}	2.24×10^{09}	2.68×10^{09}
o-Ethyltoluene	2.04×10^{09}	1.62×10^{09}	2.49×10^{09}	2.56×10 ⁰⁹
1,2,4-Trimethylbenzene	5.17×10 ⁰⁹	4.45×10 ⁰⁹	6.49×10^{09}	6.27×10 ⁰⁹

Compound	Initial concer	ntration / molecules cm	1 ⁻³	
Compound	1 st Period	2 nd Period	3 rd Period	4 th Period
1,2,3-Trimethylbenzene	2.17×10^{09}	1.85×10^{09}	2.66×10^{09}	2.77×10^{09}
n-Undecane	3.26×10 ⁰⁹	2.83×10^{09}	4.71×10^{09}	5.23×10^{09}
n-Dodecane	6.16×10^{09}	6.00×10^{09}	1.02×10^{10}	1.63×10^{09}
Formaldehyde	1.68×10^{11}	1.25×10^{11}	1.68×10^{11}	1.68×10^{11}
Acetone	1.68×10^{11}	1.25×10 ¹¹	1.68×10^{11}	9.37×10^{10}

Table S7.

Implemented emission values of the four modeling periods. VOC emission rates are obtained from an anthropogenic emission inventory⁸⁹. For NO, NO₂, SO₂, CO, and NH₃, emission rates are implemented from a recent study⁹⁰. Both emission inventory data (molecules cm⁻² s⁻¹) are divided by an estimated boundary layer height ($5 \cdot 10^4$ cm) to achieve box model emission rates (molecules cm⁻³ s⁻¹).

Compound	Emission rates / molecules cm ⁻³ s ⁻¹					
Compound	1 st Period	2 nd Period	3 rd Period	4 th Period		
NO	1.16×10^{07}	1.16×10^{07}	1.16×10^{07}	1.16×10^{07}		
NH ₃	3.54×10^{04}	3.54×10^{04}	3.54×10^{04}	3.54×10^{04}		
СО	4.86×10^{07}	4.86×10^{07}	4.86×10^{07}	4.86×10^{07}		
SO ₂	8.64×10^{06}	8.64×10^{06}	8.64×10^{06}	8.64×10^{06}		
Ethane	6.31×10^{05}	6.31×10^{05}	7.57×10^{05}	7.57×10^{05}		
2,3-Butanedione	1.09×10^{04}	1.09×10^{04}	1.69×10^{04}	1.69×10^{04}		
Benzaldehyde	1.78×10^{03}	1.78×10^{03}	2.25×10^{03}	2.25×10^{03}		
Acetaldehyde	8.44×10^{04}	8.44×10^{04}	1.15×10^{05}	1.15×10^{05}		
o-Cresol	6.73×10^{03}	6.73×10^{03}	1.13×10^{04}	1.13×10^{04}		
Ethylene	1.02×10^{06}	1.02×10^{06}	1.28×10^{06}	1.28×10^{06}		
Glyoxal	1.07×10^{05}	1.07×10^{05}	1.87×10^{05}	1.87×10^{05}		
Formaldehyde	1.47×10^{05}	1.47×10^{05}	1.93×10^{05}	1.93×10^{05}		
Isoprene	2.20×10^{04}	2.20×10^{04}	1.08×10^{04}	1.08×10^{04}		
Methacrolein	1.46×10^{04}	1.46×10^{04}	2.19×10^{04}	2.19×10^{04}		
Methanol	1.67×10^{05}	1.67×10^{05}	2.68×10^{05}	2.68×10^{05}		
Methylglyoxal	3.95×10^{04}	3.95×10^{04}	6.91×10^{04}	6.91×10^{04}		
Methylvinylketone	9.85×10^{02}	9.85×10^{02}	1.09×10^{03}	1.09×10^{03}		
Phenol	3.66×10^{03}	3.66×10 ⁰³	5.87×10^{03}	5.87×10^{03}		
Propane	2.09×10^{05}	2.09×10^{05}	2.57×10 ⁰⁵	2.57×10^{05}		
Acetylene	8.42×10^{04}	8.42×10^{04}	8.64×10^{04}	8.64×10^{04}		
n-Butane	1.84×10^{05}	1.84×10^{05}	1.89×10^{05}	1.89×10^{05}		
Isobutane	1.84×10^{05}	1.84×10^{05}	1.89×10^{05}	1.89×10^{05}		
Tetrachloroethene	4.99×10^{03}	4.99×10^{03}	5.12×10^{03}	5.12×10 ⁰³		
Trichloroethylene	8.40×10^{02}	8.40×10^{02}	8.62×10^{02}	8.62×10^{02}		
1.2-Dichloroethane	3.17×10^{02}	3.17×10^{02}	3.25×10^{02}	3.25×10^{02}		
Ethyl acetate	8.57×10^{01}	8.57×10^{01}	8.79×10^{01}	8.79×10^{01}		
Methyl acetate	2.40×10^{03}	2.40×10^{03}	2.46×10^{03}	2.46×10^{03}		
Ethylene oxide	1.06×10^{03}	1.06×10^{03}	1.08×10^{03}	1.08×10^{03}		
Ethanol	3.52×10^{02}	3.52×10^{02}	3.62×10^{02}	3.62×10^{02}		
Isopropyl Acetate	1.43×10^{05}	1.43×10^{05}	1.46×10^{05}	1.46×10^{05}		
Dimethyl ether	1.18×10^{04}	1.18×10^{04}	1.21×10^{04}	1.21×10^{04}		
2-Methylbutane	1.19×10^{05}	1.19×10^{05}	1.22×10^{05}	1.22×10^{05}		
n-Hexane	6.80×10^{04}	6.80×10^{04}	6.99×10^{04}	6.99×10^{04}		
n-Pentane	6.72×10^{04}	6.72×10^{04}	6.91×10^{04}	6.91×10^{04}		
2-Methylpentane	8.79×10^{04}	8.79×10^{04}	6.47×10^{04}	6.47×10^{04}		
3-Methylpentane	1.99×10 ⁰⁴	1.99×10^{04}	2.05×10^{04}	2.05×10^{04}		

Compound	Emission rates / molecules cm ⁻³ s ⁻¹					
Compound	1 st Period	2 nd Period	3 rd Period	4 th Period		
2,3-Dimethylbutane	1.22×10^{04}	1.22×10^{04}	1.26×10^{04}	1.26×10^{04}		
Isopropanol	1.16×10^{05}	1.16×10^{05}	1.19×10^{05}	1.19×10^{05}		
Butyl acetate	3.88×10^{04}	3.88×10^{04}	3.99×10^{04}	3.99×10^{04}		
Propyl acetate	1.08×10^{04}	1.08×10^{04}	1.11×10^{04}	1.11×10^{04}		
Vinylchloride	8.41×10^{03}	8.41×10^{03}	8.64×10^{03}	8.64×10^{03}		
n-Butanol	2.37×10^{03}	2.37×10^{03}	2.44×10^{03}	2.44×10^{03}		
n-Propanol	4.31×10^{02}	4.31×10^{02}	4.43×10^{02}	4.43×10^{02}		
Heptane	2.32×10^{05}	2.32×10^{05}	2.56×10^{05}	2.56×10^{05}		
Octane	4.99×10^{04}	4.99×10^{04}	5.51×10^{04}	5.51×10^{04}		
3-Methylhexane	4.33×10 ⁰⁴	4.33×10^{04}	4.78×10^{04}	4.78×10^{04}		
Undecane	4.17×10^{04}	4.17×10^{04}	4.61×10^{04}	4.61×10^{04}		
Cyclohexane	3.61×10^{04}	3.61×10^{04}	3.99×10^{04}	3.99×10^{04}		
Nonane	2.09×10^{04}	2.09×10^{04}	2.31×10^{04}	2.31×10^{04}		
Decane	1.53×10^{04}	1.53×10^{04}	1.69×10^{04}	1.69×10^{04}		
Methyl glycol	4.43×10^{04}	4.43×10^{04}	4.89×10^{04}	4.89×10^{04}		
Propylene glycol	2.43×10^{04}	2.43×10^{04}	2.69×10^{04}	2.69×10^{04}		
Ethylene glycol	8.25×10^{03}	8.25×10^{03}	9.12×10^{03}	9.12×10 ⁰³		
Ethyl ether	3.04×10^{03}	3.04×10^{03}	3.36×10^{03}	3.36×10 ⁰³		
2-Butanol	4.34×10^{02}	4.34×10^{02}	4.80×10^{02}	4.80×10^{02}		
Cyclohexanol	4.34×10^{02}	4.34×10^{02}	4.80×10^{02}	4.80×10^{02}		
Benzene	7.27×10^{04}	7.27×10^{04}	7.74×10^{04}	7.74×10^{04}		
Styrene	4.92×10^{04}	4.92×10^{04}	5.63×10^{04}	5.63×10 ⁰⁴		
Toluene	5.48×10^{05}	5.48×10^{05}	5.83×10^{05}	5.83×10 ⁰⁵		
Ethylbenzene	5.98×10 ⁰³	5.98×10 ⁰³	6.36×10^{03}	6.36×10^{03}		
n-Propylbenzene	1.73×10^{03}	1.73×10^{03}	1.84×10^{03}	1.84×10^{03}		
i-Propylbenzene	4.76×10^{02}	4.76×10^{02}	5.07×10^{02}	5.07×10^{02}		
o-Xvlene	8.60×10^{04}	8.60×10^{04}	9.44×10^{04}	9.44×10^{04}		
p-Xylene	1.16×10^{05}	1.16×10^{05}	1.27×10^{05}	1.27×10^{05}		
1.2.5-Trimethylbenzene	7.37×10^{04}	7.37×10^{04}	8.09×10^{04}	8.09×10^{04}		
1.3.5-Trimethylbenzene	6.80×10^{04}	6.80×10^{04}	7.47×10^{04}	7.47×10^{04}		
mXvlene	3.15×10^{04}	3.15×10^{04}	3.46×10^{04}	3.46×10^{04}		
1,2,3-Trimethylbenzene	2.09×10^{04}	2.09×10^{04}	2.29×10^{04}	2.29×10^{04}		
o-Ethyltoluene	1.31×10^{04}	1.31×10^{04}	1.43×10^{04}	1.43×10^{04}		
m-Ethyltoluene	8.37×10^{03}	8.37×10^{03}	9.18×10^{03}	9.18×10^{03}		
Acetone	2.89×10^{04}	2.89×10^{04}	3.29×10^{04}	3.29×10^{04}		
Cvclohexanone	2.44×10^{02}	2.44×10^{02}	2.78×10^{02}	2.78×10^{02}		
2-Hexanone	2.44×10^{02}	2.44×10^{02}	2.78×10^{02}	2.78×10^{02}		
methylethylketone	2.66×10^{04}	2.66×10^{04}	3.03×10^{04}	3.03×10^{04}		
Propylene	3.20×10^{05}	3.20×10^{05}	3.96×10 ⁰⁵	3.96×10 ⁰⁵		
1-Butene	6.82×10^{04}	6.82×10^{04}	8.44×10^{04}	8.44×10^{04}		
1-Pentene	4.58×10^{04}	4.58×10^{04}	5.67×10^{04}	5.67×10 ⁰⁴		
1-Hexene	4.34×10^{04}	4.34×10^{04}	5.63×10^{04}	5.63×10 ⁰⁴		

Compound	Emission rates / molecules cm ⁻³ s ⁻¹				
Compound	1 st Period	2 nd Period	3 rd Period	4 th Period	
3-Isopentene	3.86×10^{05}	3.86×10^{05}	4.39×10^{05}	4.39×10^{05}	
Isobutene	7.24×10^{04}	7.24×10^{04}	8.22×10^{04}	8.22×10^{04}	
2-Isopentene	2.41×10^{04}	2.41×10^{04}	2.74×10^{04}	2.74×10^{04}	
Acrolein	1.99×10^{04}	1.99×10^{04}	2.72×10^{04}	2.72×10^{04}	
p-Tolualdehyde	6.65×10^{03}	6.65×10^{03}	9.07×10^{03}	9.07×10^{03}	
Propionaldehyde	4.43×10^{03}	4.43×10^{03}	6.05×10^{03}	6.05×10^{03}	
Butyraldehyde	4.43×10^{03}	4.43×10^{03}	6.05×10^{03}	6.05×10^{03}	
Crotonaldehyde	2.22×10^{03}	2.22×10^{03}	3.02×10^{03}	3.02×10^{03}	
α-Pinene	1.55×10^{04}	1.55×10^{04}	1.67×10^{04}	1.67×10^{04}	
β-Pinene	1.03×10^{04}	1.03×10^{04}	1.11×10^{04}	1.11×10^{04}	
1,3-Butadiene	1.63×10^{05}	1.63×10^{05}	1.63×10^{05}	1.63×10^{05}	

Table S8.

Implemented aerosol composition for the four modeling periods. In the lower part, the varied aerosol mass fractions of TMIs in the two different sensitivity runs are described.

A	Aerosol mass fraction				
Aerosol compound	1 st Period	2 nd Period	3 rd Period	4 th Period	
NO ₃ -	0.1243140	0.0788835	0.1711622	0.1243460	
SO ₄ ²⁻	0.0328486	0.0202418	0.0788484	0.1712704	
$\mathrm{NH_4}^+$	0.0766199	0.0496608	0.0980244	0.1075742	
Cl ⁻	0.0602846	0.0460149	0.0639886	0.0365715	
Br ⁻	0.0004645	0.0006073	0.0006159	0.0005376	
I-	0.0004645	0.0006073	0.0006159	0.0005376	
Other Cations ⁺	0.0455057	0.0341588	0.0462366	0.0268712	
Other Cations ²⁺	0.0036509	0.0033969	0.0023701	0.0011734	
Fe ³⁺	0.0003550	0.0004081	0.0004036	0.0003117	
Mn^{3+}	0.0001208	0.0002149	0.0001328	0.0001604	
Cu^{2+}	0.0000427	0.0000635	0.0000159	0.0000368	
METAL	0.0106051	0.0046300	0.0124519	0.0034442	
BC	0.0851680	0.1011802	0.0654303	0.0641444	
WISOC	0.3600743	0.4246663	0.2958190	0.2979537	
WSOC	0.1107921	0.1306665	0.0910212	0.0916781	
HULIS	0.0830941	0.0979999	0.0682659	0.0687585	
Oxalic Acid	0.0055956	0.0065993	0.0045970	0.0046302	
Low soluble TMI fraction					
Fe ³⁺	0.0001065	0.0001224	0.0001211	0.0000935	
Mn^{3+}	0.0000345	0.0000614	0.0000380	0.0000458	
Cu^{2+}	0.0000213	0.0000318	0.0000080	0.0000184	
METAL	0.0109612	0.0051009	0.0128373	0.0037954	
High soluble TMI fraction					
Fe ³⁺	0.0012424	0.0014283	0.0014125	0.0010909	
Mn^{3+}	0.0001726	0.0003070	0.0001898	0.0002292	
Cu^{2+}	0.0001280	0.0001905	0.0000477	0.0001103	
METAL	0.0095806	0.0033907	0.0113542	0.0025227	

Table S9.

Average and median values of HULIS fractions and HULIS/K ⁺ ratios in China (winter/annual) and Worldwide. Averag	e
and median values have been calculated based on data provided in Table S10.	

China (winter)				China (annual)					Worldwide (annual)			
	WISOC	HULIS-C	HULIS	HULIS	WISOC	HULIS-C	HULIS	HULIS	WISOC	HULIS-C	HULIS	HULIS
	/OC (%)	/WSOC (%)	/K+	/PM (%)	/OC (%)	/WSOC (%)	/K ⁺	/PM (%)	/OC (%)	/WSOC (%)	/K+	/PM (%)
n	8	10	6	6	28	36	14	36	35	82	26	38
Average	66.6	44.5	6.5	7.6	58.1	48.0	7.66	7.7	54.7	42.4	7.2	7.4
Median	64.1	42.9	6.2	7.6	58.1	47.1	6.26	7.9	54.9	42.0	6.2	7.1
σ	10.0	11.6	0.8	2.1	13.9	11.8	3.11	3.5	15.3	14.6	3.2	3.4

Table S10.

Reaction	$k / (cm^{-3})^{(1-n)} s^{-1}$		Reference
$NO_2 + h\nu \rightarrow NO_2^*$	$3.067 \cdot 10^{-2} \cos(X)^{0.134} \exp(-0.242/\sec(X))$		Calculated
$N_2O_3 + h\nu \rightarrow NO + NO_2$	estimated as N ₂ O ₅		
$N_2O_4 + hv \rightarrow NO_2 + NO_2$	estimated as N_2O_5		01
$N_2O_5 + hv \rightarrow NO_2 + NO_3$	$7.083 \cdot 10^{-3} \cos(X)^{0.88} \exp(-0.237/\sec(X))$		91
$NO_2^* + N_2 \rightarrow NO_2 + N_2$	$2.70 \cdot 10^{-11}$		92
$NO_2^* + O_2 \rightarrow NO_2 + O_2$	$3.00 \cdot 10^{-11}$		92
$NO_2^* + H_2O \rightarrow HONO + OH$	$1.20 \cdot 10^{-14}$		92
$NO_2 + NO + H_2O \rightarrow HONO + HONO$	$2.00 \cdot 10^{-35}$		93
2 2			94
			95
$HONO + HONO \rightarrow NO_2 + NO + H_2O$	$1.00 \cdot 10^{-20}$		95
$HNO_3 + NO \rightarrow HONO + NO_2$	$3.40 \cdot 10^{-22}$		96
$NO_2 + NO_2 + H_2O \rightarrow HONO + HNO_3$	$1.52 \cdot 10^{-37}$		97
$HONO + HNO_3 \rightarrow NO_2 + NO_2 + H_2O$	$1.60 \cdot 10^{-17}$		95
$NO + NO_2 + M \rightarrow N_2O_3 + M$	$3.1 \cdot 10^{-34} (T/300)^{-7.7} [N_2]$	\mathbf{k}_0	91
	$7.9 \cdot 10^{-12} (T/300)^{1.4}$	\mathbf{k}_{∞}	
	0.6	F_{C}	
$N_2O_3 + M \rightarrow NO + NO_2 + M$	$1.9 \cdot 10^{-7} (T/300)^{-8.7} exp(-4880/T)[N_2]$	\mathbf{k}_0	91
	$4.7 \cdot 10^{15} (T/300)^{0.4} \exp(-4880/T)$	\mathbf{k}_{∞}	
	0.6	F_{C}	01
$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	$1.4 \cdot 10^{-33} (T/300)^{-3.8} [N_2]$	\mathbf{k}_0	91
	$1.0 \cdot 10^{-12}$	\mathbf{k}_{∞}	
	0.4	F_{C}	01
$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$	$1.3 \cdot 10^{-5} (T/300)^{-3.8} \exp(-6400/T) [N_2]$	\mathbf{k}_0	91
	$1.15 \cdot 10^{16} \exp(-6460/T)$	\mathbf{k}_{∞}	
	0.4	F _C	
Remarks: $X = $ solar zenith angle			

Gas-phase reactions implemented in the extended HONO chemistry module.

Table S11.Phase transfer data implemented in the extended HONO chemistry module.

Species	H _A / M atm ⁻¹	- ΔH/R / K	Reference	α	Reference	$D_{g} / m^{2} s^{-1}$	Reference
N_2O_3	25.3	3500	98	0.1	estimated	$1.4 \cdot 10^{-5}$	99
N_2O_4	1.62	3500	98	0.1	estimated	$1.3 \cdot 10^{-5}$	99

Table S12.

Equilibrium reacti	ions and sulfur	[,] oxidations	extended b	oy NO2 ai	nd HONO	implemented in
the extended HON	O chemistry m	odule.				

Equilibrium	K298	k298, forward	k298, backward	Reference
HONO + HONO \rightleftharpoons N ₂ O ₃	$3.03 \cdot 10^{-3}$	$6.06 \cdot 10^{-14}$	$5.00 \cdot 10^{10}$	100
$N_2O_3 \rightleftharpoons NO + NO_2$	3.30·10 ⁻⁵	$6.60 \cdot 10^{-16}$	$5.00 \cdot 10^{10}$	101
$N_2O_4 + H_2O \rightleftharpoons HONO + NO_3 + H^+$	$1.25 \cdot 10^5$	$8.68 \cdot 10^8$	$1.44 \cdot 10^{-4}$	101-102
$N_2O_4 \rightleftharpoons NO_2 + NO_2$	1.53.10-5		$4.50 \cdot 10^8$	101
Departion	1			
Reaction	k	K		102
Reaction $HSO_3^- + NO_2^- + H^+ \rightarrow NOH + HSO_4^- + A$	k H ⁺ 4	x .77·10 ³ ×exp(-610	0(1/T-1/298))	103
Reaction $HSO_3^- + NO_2^- + H^+ \rightarrow NOH + HSO_4^- + MOH + NOH \rightarrow N_2O + H_2O$	k H ⁺ 4 5	x 4.77·10 ³ ×exp(-610 5.00·10 ⁹	0(1/T-1/298))	103 103
Reaction $HSO_3^- + NO_2^- + H^+ \rightarrow NOH + HSO_4^- + HOH^+ + NOH^- +$	H ⁺ 4 5 1	x 4.77·10 ³ ×exp(-610 5.00·10 ⁹ .20·10 ⁷	0(1/T-1/298))	103 103 104

Table S13.

Contribution of different reactions to the chemical formation and loss pathways of H_2O_2 for all four periods. Contributions are averages over the whole modeling period. Only contributions over 5% are considered.

		1 st period	
	Low soluble TMI	Base case	High soluble TMI
	H ₂ O ₂ formation react	tions	
$HO_{2}/O_{2}^{-} + Cu^{+}$	91.0%	97.0%	99.0%
CH ₂ OO	5.3%	1.7%	0.5%
Other formation reactions ⁽¹⁾	3.7%	1.3%	0.5%
	H ₂ O ₂ loss reaction	18	
$H_2O_2 + Fe(II)HULIS^+$	31.4%	48.2%	57.1%
$H_2O_2 + HSO_3^-$	50.5%	24.4%	8.3%
$H_2O_2 + Cu^+$	15.1%	20.2%	24.6%
$H_2O_2 + MnOH^{2+}$	0.0%	5.4%	8.8%
Other loss reactions ⁽²⁾	4.0%	2.8%	1.2%
		2 nd period	
	Low soluble TMI	Base case	High soluble TMI
	H ₂ O ₂ formation react	tions	
$HO_2/O_2^- + Cu^+$	94.1%	98.1%	99.4%
CH ₂ OO	3.4%	1.1%	0.3%
Other formation reactions ⁽¹⁾	2.5%	0.8%	0.3%
	H ₂ O ₂ loss reaction	15	
$H_2O_2 + Fe(II)HULIS^+$	34.8%	50.6%	57.7%
$H_2O_2 + HSO_3^-$	43.2%	19.8%	6.4%
$H_2O_2 + Cu^+$	19.2%	24.6%	29.3%
$H_2O_2 + MnOH^{2+}$	0.0%	3.5%	5.7%
Other loss reactions ⁽²⁾	3.8%	0.5%	0.9%
		3 rd period	
	Low soluble TMI	Base case	High soluble TMI
	H ₂ O ₂ formation react	tions	
$HO_2/O_2^- + Cu^+$	93.3%	97.7%	99.1%
CH ₂ OO	3.9%	1.2%	0.3%
Other formation reactions ⁽¹⁾	3.8%	1.1%	0.6%
	H ₂ O ₂ loss reaction	15	
$H_2O_2 + Fe(II)HULIS^+$	29.9%	45.2%	54.1%
$H_2O_2 + HSO_3^-$	58.7%	27.5%	10.1%
$H_2O_2 + Cu^+$	7.4%	9.9%	12.3%
$H_2O_2 + MnOH^{2+}$	1.8%	15.3%	21.2%
Other loss reactions ⁽²⁾	2.2%	2.1%	2.3%
		4 th period	
	Low soluble TMI	Base case	High soluble TMI
	H ₂ O ₂ formation react	tions	
$HO_2/O_2^- + Cu^+$	92.6%	97.3%	99.0%
CH ₂ OO	3.6%	1.2%	0.4%
Other formation reactions ⁽¹⁾	3.8%	1.5%	0.6%

	H ₂ O ₂ loss reacti	ons	
$H_2O_2 + Fe(II)HULIS^+$	12.9%	26.5%	40.0%
$H_2O_2 + HSO_3^-$	77.7%	49.6%	23.2%
$H_2O_2 + Cu^+$	7.8%	13.6%	21.6%
$H_2O_2 + MnOH^{2+}$	0.5%	8.7%	12.9%
Other loss reactions ⁽²⁾	1.1%	1.6%	2.3%
⁽¹⁾ Includes the formation by reco	mbination of HO ₂ in gas	s and particle phase	

 $^{(2)}$ Includes H₂O₂ photolysis in gas and particle phase as well as consumption by organics

Table S14

	1 st period	2 nd period	3 rd period	4 th period
Gas phase				
OH	36.1%	39.1%	26.6%	18.6%
Criegee	0.5%	0.4%	0.3%	0.2%
Aqueous-phase				
H_2O_2	61.6%	57.7%	71.7%	70.3%
O ₃	0.0%	0.0%	0.0%	0.0%
HNO ₄	1.1%	0.5%	0.7%	6.6%
HONO	0.0%	0.0%	0.0%	0.0%
NO_2	0.1%	0.1%	0.1%	0.5%
OH	0.0%	0.0%	0.0%	0.0%
NO ₃	0.0%	0.0%	0.0%	0.0%
CO_3^-	0.0%	0.0%	0.0%	0.0%
CH ₃ OOH	0.0%	0.0%	0.0%	0.0%
CH ₃ COOOH	0.0%	0.0%	0.0%	0.0%
CH_3O_2	0.0%	0.0%	0.0%	0.0%
Cl_2	0.0%	0.0%	0.0%	0.0%
Br_2	0.0%	0.0%	0.0%	0.0%
HOX	0.4%	0.4%	0.1%	0.5%
(X = Cl, Br or I)				

Contribution of different reactions towards the formation of sulfate. Contributions are averages over the whole modeling period.

Table S15.

Summary of HULIS-C contribution to OC/WSOC and of HULIS/K $^+$ ratios in ambient aerosols reported in the literature.

Site	Site type	Sample type	Season	WISOC/WSOC* /HULIS-C (w%)	HULIS-C /WSOC (%)	HULIS /PM	HULIS/K ⁺	Ref ·
Lanzhou	Urban	PM2.5	Winter	76/13/11	45.8	6.0	6.14 ± 1.69	
			Winter haze	77/12/11	47.8	5.5	5.33	70
			Winter snow	64/21/15	41.7	5.7	6.33	
			Summer	73/15/12	44.4	6.3	5.66	
Guangzhou	Urban	PM2.5	Annual	61/19/20	48.0	8.6	5.27	105
	Suburban	PM2.5	Annual	57/16/27	57.0	10.7	6.02	
Beijing	Urban	PM2.5	Fall	59/17/24	58.7 ± 11.5			76
Beijing	Urban	PM2.5	Winter		21.8 ± 13.5			106
			Non-heating		27.4 ± 12.0			
Guangzhou	Suburban	PM2.5	Annual	66/16/18	49.0 ± 6.0	5.4	3.72 - 5.05	68
Changzhou	Suburban	PM2.5	Summer daytime	40/22/38	62.6	14.0	6.26	107
			Summer Nighttime	48/21/31	58.3	11.6	5.83	
Hong Kong	Coastal	PM3.2	Annual	70/18/12 ª	42.0 ± 13.0			73
	& urban		Winter		58.6			
Shanghai	Urban	PM2.5	Winter	58/18/24	67.3 ± 10.8	9.1	6.03	
			Spring	51/19/30	60.3 ± 14.6	7.9		67
			Summer	39/33/28	59.5 ± 11.6	6.6		
			Fall	46/32/22	64.7 ± 9.1	6.5		
Shanghai	Urban	PM2.5	Annual	45/29/26	48.2 ± 18.7	9.3	9.23	
			Winter	55/21/24	55.2 ± 16.5	9.6	7.49	108
			Spring	32/43/25	37.8 ± 14.2	7.8	6.2	
			Summer	32/3632	48.4 ± 16.5	10.1	12.62	
Shanghai	Urban	PM2.5	Fall	49/20/31	61.0 ± 19.9	12.5	12.37	108
Shanghai	Urban	PM1	Annual		39.9	8.4	9.29	
			Winter		41.7	9.8	7.49	
			Spring		48.5	6.0	9.62	66
			Summer		38.7	9.6	17.39	
			Fall		31.0	6.6	8.06	
Weizhou Island	Background	PM2.5	Spring	53/11/36	76.8 ± 12.9	15.4	9.43	77
Hong Kong	Urban	PM2.5	Annual			10.0 ± 5.0	4.08	
Guangzhou	Suburban	PM2.5	Annual			10.0 ± 4.0	4.73	109
Hong Kong	Coastal, rural	PM2.5	BB	51/20/29	60.0	11.7 ± 2.1	5.2 ± 0.7	60
Hong Kong	Coastal, suburban	PM9	Annual		46.3			49
Maofeng Mt.	Coastal, suburban	TSP	Summer		40.5	3.6		
			Winter		39.4	1.5		64
Guangzhou	Coastal, suburban	TSP	Summer		37.0	1.5		

			Winter		44.0	2.6		
Wushan Mt.	Coastal, urban	TSP	Summer		36.0	1.6		
			Winter		40.6	3.2		
Korea, Asia	Urban	PM10	Winter		33.5 ± 6.1			110
		PM1.8	Winter		44.9 ± 6.4	8.0		
Budapest, EU	Rural	PM2.5	Summer		33.0			62
Budapest	Urban	PM2.5	Spring		31.0 - 35.0			
Jungfraujoch,	High-alpine	PM2.5	Summer		55.0 - 60.0			111
Thessaloniki	Urban	TSP	Winter		32 - 43	0.6 - 7.8	2.3	
Mainz	Rural	TSP	Winter		32 - 43		5.65	72
Ostrava, EU	Urban	TSP	Winter		32-43	2.1 - 12.8	2.49	12
Kladno, EU	Suburban	TSP	Winter		32 - 43	4.3 – 15.1	4.39	
K-Puszta, EU	Rural	PM10	Summer		55 - 60			112
K-Puszta, EU	Rural	PM1.5	Jan. – Spet.		57.0			113
Near Aveiro	Coastal, rural	PM2.5	Annual		51.6			51
K-Puszta	Rural	PM1.5	Summer, Fall		41.0			43
Po Valley	Rural (polluted)	PM1.5	Summer, Fall		29.0			
Terceira Islands	Marine	PM2.5	Annual	52/37/11	21.0			114
Puy de Dome,	Highland	PM2.5	Annual	27/61/12	23.0			115
Schauinsland	Highland	PM2.5	Annual	22/70/8	14.0			
Sonnblick	Mountain peak	PM2.5	Annual	41/55/4	9			114
K-Puszta, EU	Rural	PM2.5	Annual	32/53/15	24			
Budapest, EU	Urban	PM2.5	Non-heating		25			
K-Puszta, EU	Rural	PM2.5	Spring		35			116
Budapest, EU	Urban	PM2.5	Summer		48			
Chamonix, EU	Rural	PM10	BB		23.4			
Paris, EU	Urban	PM10	Winter		38.6			117
South France	Urban	PM10	Summer		34.8			
Grenoble, EU	Urban	PM10	Spring, Fall		28.9			
Mace Head	Marine	PM1.5	Spring, Fall		22.0			118
Budapest, EU	Urban	PM2.5	Spring, Summer		47			119
Budapest, EU	Urban	PM2.5	Non-heating	71/11/18	62.0	7.1		55
Aveiro, EU	Coastal, rural	PM2.5	Annual	46/44/10	23.0			120
Mace Head, EU	Marine,	PM1.5	Summer, Fall		19			56
New York, NA	Rural nighttime	PM2.5	Summer		47			
	Rural daytime	PM2.5	Summer		39			63
	Rural	PM2.5	Fall		55			
Auckland, AU	Marine urban	PM10	Summer		51			
Christchurch, AU	Marine urban	PM10	Summer		34			56
Auckland, AU	Marine urban	PM10	Winter		47			
Christchurch, AU	Marine urban	PM10	Winter		45			

BB	PM2.5	BB daytime	40.0	62
BB	PM2.5	BB nighttime	61.0	
Pasture	PM2.5	Dry to wet transition	25.5	121
BB	PM2.5	BB daytime	63.0	116
BB	PM2.5	BB nighttime	76.0	
Pasture	PM10	Dry period	29.0	
Pasture	PM10	Dry to wet transition	20.8	122
Pasture	PM10	Wet period	12.5	
	BB Pasture BB BB Pasture Pasture Pasture	BBPM2.5BBPM2.5BBPM2.5BBPM2.5PasturePM10PasturePM10PasturePM10	BBPM2.3BB daylineBBPM2.5BB nightimePasturePM2.5Dry to wet transitionBBPM2.5BB daytimeBBPM2.5BB nightimePasturePM10Dry periodPasturePM10Dry to wet PasturePM10Wet period	BBPM2.5BB nighttime40.0BBPM2.5BB nighttime61.0PasturePM2.5Dry to wet transition25.5BBPM2.5BB daytime63.0BBPM2.5BB nighttime76.0PasturePM10Dry period29.0PasturePM10Dry to wet 20.8PasturePM10Wet period12.5

References

1. Kleffmann, J.; Lörzer, J. C.; Wiesen, P.; Kern, C.; Trick, S.; Volkamer, R.; Rodenas, M.; Wirtz, K., Intercomparison of the DOAS and LOPAP techniques for the detection of nitrous acid (HONO). *Atmos. Environ.* **2006**, *40* (20), 3640-3652.

2. Wang, S.; Nan, J.; Shi, C.; Fu, Q.; Gao, S.; Wang, D.; Cui, H.; Saiz-Lopez, A.; Zhou, B., Atmospheric ammonia and its impacts on regional air quality over the megacity of Shanghai, China. *Sci. Rep.* **2015**, *5*, 15842.

3. Guo, S.; Hu, M.; Zamora, M. L.; Peng, J.; Shang, D.; Zheng, J.; Du, Z.; Wu, Z.; Shao, M.; Zeng, L.; Molina, M. J.; Zhang, R., Elucidating severe urban haze formation in China. *Proc. Natl. Acad. Sci. USA* **2014**, *111* (49), 17373-17378.

4. Lelieveld, J.; Evans, J. S.; Fnais, M.; Giannadaki, D.; Pozzer, A., The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* **2015**, *525* (7569), 367-371.

5. Liu, Y.; Shao, M.; Fu, L.; Lu, S.; Zeng, L.; Tang, D., Source profiles of volatile organic compounds (VOCs) measured in China: Part I. *Atmos. Environ.* **2008**, *42* (25), 6247-6260.

6. Yuan, B.; Hu, W. W.; Shao, M.; Wang, M.; Chen, W. T.; Lu, S. H.; Zeng, L. M.; Hu, M., VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China. *Atmos. Chem. Phys.* **2013**, *13* (17), 8815-8832.

7. Wu, D.; Li, Q.; Ding, X.; Sun, J.; Li, D.; Fu, H.; Teich, M.; Ye, X.; Chen, J., Primary particulate matter emitted from heavy fuel and diesel oil combustion in a typical container ship: characteristics and toxicity. *Environ. Sci. Technol.* **2018**, *52* (21), 12943-12951.

8. Zhang, F.; Shang, X.; Chen, H.; Xie, G.; Fu, Y.; Wu, D.; Sun, W.; Liu, P.; Zhang, C.; Mu, Y.; Zeng, L.; Wan, M.; Wang, Y.; Xiao, H.; Wang, G.; Chen, J., Significant impact of coal combustion on VOCs emissions in winter in a North China rural site. *Sci. Total Environ.* **2020**, *720*, 137617.

9. Wang, J.; Sun, S.; Zhang, C.; Xue, C.; Liu, P.; Zhang, C.; Mu, Y.; Wu, H.; Wang, D.; Chen, H.; Chen, J., The pollution levels, variation characteristics, sources and implications of atmospheric carbonyls in a typical rural area of North China Plain during winter. *J. Environ. Sci.* **2020**.

10. Pang, X.; Mu, Y., Seasonal and diurnal variations of carbonyl compounds in Beijing ambient air. *Atmos. Environ.* **2006**, *40* (33), 6313-6320.

11. Xue, J.; Yuan, Z.; Griffith, S. M.; Yu, X.; Lau, A. K.; Yu, J. Z., Sulfate formation enhanced by a cocktail of high NO_x, SO₂, particulate matter, and droplet pH during haze-fog events in megacities in China: an observation-based modeling investigation. *Environ. Sci. Technol.* **2016**, *50* (14), 7325-7334.

Liu, P.; Zhang, C.; Mu, Y.; Liu, C.; Xue, C.; Ye, C.; Liu, J.; Zhang, Y.; Zhang, H., The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing. *Atmos. Chem. Phys.* **2016**, *16* (15), 10097-10109.
 Liu, P.; Zhang, C.; Xue, C.; Mu, Y.; Liu, J.; Zhang, Y.; Tian, D.; Ye, C.; Zhang, H.; Guan, J., The contribution of residential coal combustion to atmospheric PM2. 5 in northern China

during winter. Atmos. Chem. Phys. 2017, 17 (18), 11503-11520.

14. Fröhlich, R.; Cubison, M. J.; Slowik, J. G.; Bukowiecki, N.; Prévôt, A. S. H.; Baltensperger, U.; Schneider, J.; Kimmel, J. R.; Gonin, M.; Rohner, U.; Worsnop, D. R.; Jayne, J. T., The ToF-ACSM: a portable aerosol chemical speciation monitor with TOFMS detection. *Atmos. Meas. Tech.* **2013**, *6* (11), 3225-3241.

15. Takegawa, N.; Miyazaki, Y.; Kondo, Y.; Komazaki, Y.; Miyakawa, T.; Jimenez, J. L.; Jayne, J. T.; Worsnop, D. R.; Allan, J. D.; Weber, R. J., Characterization of an aerodyne aerosol mass spectrometer (AMS): intercomparison with other aerosol instruments. *Aerosol Sci. Technol.* **2005**, *39* (8), 760-770.

16. Sun, Y.; Zhuang, G.; Tang, A. A.; Wang, Y.; An, Z., Chemical characteristics of PM2.5 and PM10 in haze-fog episodes in Beijing. *Environ. Sci. Technol.* **2006**, *40* (10), 3148-3155.

17. Liu, P.; Zhang, C.; Mu, Y.; Liu, C.; Xue, C.; Ye, C.; Liu, J.; Zhang, Y.; Zhang, H., The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing. **2016**, *16* (15), 10097-10109.

18. Meng, K.; Xu, X.; Cheng, X.; Xu, X.; Qu, X.; Zhu, W.; Ma, C.; Yang, Y.; Zhao, Y., Spatiotemporal variations in SO₂ and NO₂ emissions caused by heating over the Beijing-Tianjin-Hebei Region constrained by an adaptive nudging method with OMI data. *Sci. Total. Environ.* **2018**, *642*, 543-552.

19. Sun, J.; Liu, L.; Xu, L.; Wang, Y.; Wu, Z.; Hu, M.; Shi, Z.; Li, Y.; Zhang, X.; Chen, J.; Li, W., Key role of nitrate in phase transitions of urban particles: implications of important reactive surfaces for secondary aerosol formation. *J. Geophys. Res.* **2018**, *123* (2), 1234-1243.

20. Seinfeld, J. H.; Pandis, S. N., *Atmospheric chemistry and physics: from air pollution to climate change*. John Wiley & Sons: 2016.

21. Tang, G.; Zhang, J.; Zhu, X.; Song, T.; Münkel, C.; Hu, B.; Schäfer, K.; Liu, Z.; Zhang, J.; Wang, L.; Xin, J.; Suppan, P.; Wang, Y., Mixing layer height and its implications for air pollution over Beijing, China. *Atmos. Chem. Phys.* **2016**, *16* (4), 2459-2475.

22. Zhu, X.; Tang, G.; Guo, J.; Hu, B.; Song, T.; Wang, L.; Xin, J.; Gao, W.; Münkel, C.; Schäfer, K.; Li, X.; Wang, Y., Mixing layer height on the North China Plain and meteorological evidence of serious air pollution in southern Hebei. *Atmos. Chem. Phys.* **2018**, *18* (7), 4897-4910.

23. Haeffelin, M.; Angelini, F.; Morille, Y.; Martucci, G.; Frey, S.; Gobbi, G. P.; Lolli, S.; O'Dowd, C. D.; Sauvage, L.; Xueref-Rémy, I.; Wastine, B.; Feist, D. G., Evaluation of mixing-height retrievals from automatic profiling lidars and ceilometers in view of future integrated networks in Europe. *Boundary-Layer Meteorol.* **2011**, *143* (1), 49-75.

24. Wiegner, M.; Madonna, F.; Binietoglou, I.; Forkel, R.; Gasteiger, J.; Geiß, A.; Pappalardo, G.; Schäfer, K.; Thomas, W., What is the benefit of ceilometers for aerosol remote sensing? An answer from EARLINET. *Atmos. Meas. Tech.* **2014**, *7* (7), 1979-1997.

25. Wiegner, M.; Mattis, I.; Pattantyús-Ábrahám, M.; Bravo-Aranda, J. A.; Poltera, Y.; Haefele, A.; Hervo, M.; Görsdorf, U.; Leinweber, R.; Gasteiger, J.; Haeffelin, M.; Wagner, F.; Cermak, J.; Komínková, K.; Brettle, M.; Münkel, C.; Pönitz, K., Aerosol backscatter profiles from ceilometers: validation of water vapor correction in the framework of CeiLinEx2015. *Atmos. Meas. Tech.* **2019**, *12* (1), 471-490.

26. Ren, X.; Brune, W. H.; Mao, J.; Mitchell, M. J.; Lesher, R. L.; Simpas, J. B.; Metcalf, A. R.; Schwab, J. J.; Cai, C.; Li, Y., Behavior of OH and HO₂ in the winter atmosphere in New York City. *Atmos. Environ.* **2006**, *40*, 252-263.

27. Tan, Z.; Rohrer, F.; Lu, K.; Ma, X.; Bohn, B.; Broch, S.; Dong, H.; Fuchs, H.; Gkatzelis, G. I.; Hofzumahaus, A.; Holland, F.; Li, X.; Liu, Y.; Liu, Y.; Novelli, A.; Shao, M.; Wang, H.; Wu, Y.; Zeng, L.; Hu, M.; Kiendler-Scharr, A.; Wahner, A.; Zhang, Y., Wintertime photochemistry in Beijing: observations of RO_x radical concentrations in the North China Plain during the BEST-ONE campaign. *Atmos. Chem. Phys.* **2018**, *18* (16), 12391-12411.

28. Birmili, W.; Stratmann, F.; Wiedensohler, A., Design of a dma-based size spectrometer for a large particle size range and stable operation. *J. Aero. Sci.* **1999**, *30* (4), 549-553.

29. Liu, H. J.; Zhao, C. S.; Nekat, B.; Ma, N.; Wiedensohler, A.; van Pinxteren, D.; Spindler, G.; Müller, K.; Herrmann, H., Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain. *Atmos. Chem. Phys.* **2014**, *14* (5), 2525-2539.

30. Lazrus, A. L.; Kok, G. L.; Lind, J. A.; Gitlin, S. N.; Heikes, B. G.; Shetter, R. E., Automated fluorometric method for hydrogen peroxide in air. *Anal. Chem.* **2002**, *58* (3), 594-597.

Lazrus, A. L.; Kok, G. L.; Gitlin, S. N.; Lind, J. A.; McLaren, S. E., Automated fluorimetric method for hydrogen peroxide in atmospheric precipitation. *Anal. Chem.* 2002, *57* (4), 917-922.
 Mhamdi, A.; Queval, G.; Chaouch, S.; Vanderauwera, S.; Van Breusegem, F.; Noctor, G., Catalase function in plants: a focus on Arabidopsis mutants as stress-mimic models. *J. Exp. Bot.*

2010, 61 (15), 4197-4220.

33. van Pinxteren, D.; Brüggemann, E.; Gnauk, T.; Iinuma, Y.; Müller, K.; Nowak, A.; Achtert, P.; Wiedensohler, A.; Herrmann, H., Size- and time-resolved chemical particle characterization during CAREBeijing-2006: Different pollution regimes and diurnal profiles. *J. Geophys. Res.- Atmos.* **2009**, *114*, D00G09.

34. Fomba, K. W.; Müller, K.; van Pinxteren, D.; Herrmann, H., Aerosol size-resolved trace metal composition in remote northern tropical Atlantic marine environment: case study Cape Verde islands. *Atmos. Chem. Phys.* **2013**, *13* (9), 4801-4814.

35. Keck, L.; Wittmaack, K., Effect of filter type and temperature on volatilisation losses from ammonium salts in aerosol matter. *Atmos. Environ.* **2005**, *39* (22), 4093-4100.

36. Bligh, M. W.; Waite, T. D., Role of heterogeneous precipitation in determining the nature of products formed on oxidation of Fe(II) in seawater containing natural organic matter. *Environ. Sci. Technol.* **2010**, *44* (17), 6667-6673.

37. Smith, R. M.; Martell, A. E.; Motekaitis, R. J.; Standard Reference Data, p., NIST critically selected stability constants of metal complexes database. Standard Reference Data Program, National Institute of Standards and Technology, U.S. Dept. of Commerce: Gaithersburg, MD, 2004.

38. Noradoun, C. E.; Cheng, I. F., EDTA degradation induced by oxygen activation in a zerovalent iron/air/water system. *Environ. Sci. Technol.* **2005**, *39* (18), 7158-7163.

39. Iinuma, Y.; Müller, C.; Böge, O.; Gnauk, T.; Herrmann, H., The formation of organic sulfate esters in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions. *Atmos. Environ.* **2007**, *41* (27), 5571-5583.

40. Surratt, J. D.; Gomez-Gonzalez, Y.; Chan, A. W.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H., Organosulfate formation in biogenic secondary organic aerosol. *J. Phys. Chem. A* **2008**, *112* (36), 8345-8378.

41. Chan, M. N.; Surratt, J. D.; Chan, A. W. H.; Schilling, K.; Offenberg, J. H.; Lewandowski, M.; Edney, E. O.; Kleindienst, T. E.; Jaoui, M.; Edgerton, E. S.; Tanner, R. L.; Shaw, S. L.; Zheng, M.; Knipping, E. M.; Seinfeld, J. H., Influence of aerosol acidity on the chemical composition of secondary organic aerosol from β-caryophyllene. *Atmos. Chem. Phys.* 2011, *11* (4), 1735-1751.

42. Riva, M.; Budisulistiorini, S. H.; Zhang, Z.; Gold, A.; Surratt, J. D., Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol. *Atmos. Environ.* **2016**, *130*, 5-13.

43. Zappoli, S.; Andracchio, A.; Fuzzi, S.; Facchini, M. C.; Gelencsér, A.; Kiss, G.; Krivácsy, Z.; Molnár, Á.; Mészáros, E.; Hansson, H. C.; Rosman, K.; Zebühr, Y., Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmos. Environ.* **1999**, *33* (17), 2733-2743.

44. Krivácsy, Z.; Gelencsér, A.; Kiss, G.; Mészáros, E.; Molnár, Á.; Hoffer, A.; Mészáros, T.; Sárvári, Z.; Temesi, D.; Varga, B.; Baltensperger, U.; Nyeki, S.; Weingartner, E., Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch. *J. Atmos. Chem.* **2001**, *39* (3), 235-259.

45. Krivacsy, Z., Role of organic and black carbon in the chemical composition of atmospheric aerosol at European background sites. *Atmos. Environ.* **2001**, *35* (36), 6231-6244.

46. Kiss, G.; Varga, B.; Galambos, I.; Ganszky, I., Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. *J. Geophys. Res.-Atmos.* **2002**, *107* (D21), ICC 1-1-ICC 1-8.

47. Mayol-Bracero, O. L.; Guyon, P.; Graham, B.; Roberts, G.; Andreae, M. O.; Decesari, S.; Facchini, M. C.; Fuzzi, S.; Artaxo, P., Water-soluble organic compounds in biomass burning aerosols over Amazonia 2. Apportionment of the chemical composition and importance of the polyacidic fraction. *J. Geophys. Res.-Atmos.* **2002**, *107* (D20), LBA 59-1-LBA 59-15.

48. Cavalli, F.; Facchini, M. C.; Decesari, S.; Mircea, M.; Emblico, L.; Fuzzi, S.; Ceburnis, D.; Yoon, Y. J.; O'Dowd, C. D.; Putaud, J.-P.; Dell'Acqua, A., Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic. *J. Geophys. Res.-Atmos.* **2004**, *109* (D24).

49. Yu, J. Z.; Yang, H.; Zhang, H.; Lau, A. K. H., Size distributions of water-soluble organic carbon in ambient aerosols and its size-resolved thermal characteristics. *Atmos. Environ.* **2004**, *38* (7), 1061-1071.

50. Decesari, S.; Fuzzi, S.; Facchini, M. C.; Mircea, M.; Emblico, L.; Cavalli, F.; Maenhaut, W.; Chi, X.; Schkolnik, G.; Falkovich, A.; Rudich, Y.; Claeys, M.; Pashynska, V.; Vas, G.;

Kourtchev, I.; Vermeylen, R.; Hoffer, A.; Andreae, M. O.; Tagliavini, E.; Moretti, F.; Artaxo, P., Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds. *Atmos. Chem. Phys.* **2006**, *6* (2), 375-402.

51. Duarte, R. M. B. O.; Santos, E. B. H.; Pio, C. A.; Duarte, A. C., Comparison of structural features of water-soluble organic matter from atmospheric aerosols with those of aquatic humic substances. *Atmos. Environ.* **2007**, *41* (37), 8100-8113.

52. Feczko, T.; Puxbaum, H.; Kasper-Giebl, A.; Handler, M.; Limbeck, A.; Gelencsér, A.; Pio, C.; Preunkert, S.; Legrand, M., Determination of water and alkaline extractable atmospheric humic-like substances with the TU Vienna HULIS analyzer in samples from six background sites in Europe. *J. Geophys. Res.-Atmos.* **2007**, *112* (D23).

53. Lukács, H.; Gelencsér, A.; Hammer, S.; Puxbaum, H.; Pio, C.; Legrand, M.; Kasper-Giebl, A.; Handler, M.; Limbeck, A.; Simpson, D.; Preunkert, S., Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe. *J. Geophys. Res.*-*Atmos.* **2007**, *112* (D23).

54. Pio, C. A.; Legrand, M.; Oliveira, T.; Afonso, J.; Santos, C.; Caseiro, A.; Fialho, P.; Barata, F.; Puxbaum, H.; Sanchez-Ochoa, A.; Kasper-Giebl, A.; Gelencsér, A.; Preunkert, S.; Schock, M., Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a westeast transect across Europe. *J. Geophys. Res.-Atmos.* **2007**, *112* (D23). 55. Salma, I.; Ocskay, R.; Chi, X.; Maenhaut, W., Sampling artefacts, concentration and chemical composition of fine water-soluble organic carbon and humic-like substances in a continental urban atmospheric environment. *Atmos. Environ.* **2007**, *41* (19), 4106-4118.

56. Krivácsy, Z.; Kiss, G.; Ceburnis, D.; Jennings, G.; Maenhaut, W.; Salma, I.; Shooter, D., Study of water-soluble atmospheric humic matter in urban and marine environments. *Atmos. Res.* **2008**, *87* (1), 1-12.

57. Salma, I.; Ocskay, R.; Láng, G. G., Properties of atmospheric humic-like substances – water system. *Atmos. Chem. Phys.* **2008**, *8* (8), 2243-2254.

58. Baduel, C.; Voisin, D.; Jaffrezo, J. L., Seasonal variations of concentrations and optical properties of water soluble HULIS collected in urban environments. *Atmos. Chem. Phys.* **2010**, *10* (9), 4085-4095.

59. Lin, P.; Engling, G.; Yu, J. Z., Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China. *Atmos. Chem. Phys.* **2010**, *10* (14), 6487-6500.

60. Lin, P.; Huang, X.-F.; He, L.-Y.; Zhen Yu, J., Abundance and size distribution of HULIS in ambient aerosols at a rural site in South China. *J. Aerosol Sci.* **2010**, *41* (1), 74-87.

61. Salma, I.; Mészáros, T.; Maenhaut, W.; Vass, E.; Majer, Z., Chirality and the origin of atmospheric humic-like substances. *Atmos. Chem. Phys.* **2010**, *10* (3), 1315-1327.

62. Claeys, M.; Vermeylen, R.; Yasmeen, F.; Gómez-González, Y.; Chi, X.; Maenhaut, W.; Mészáros, T.; Salma, I., Chemical characterisation of humic-like substances from urban, rural and tropical biomass burning environments using liquid chromatography with UV/vis photodiode array detection and electrospray ionisation mass spectrometry. *Environ. Chem.* **2012**, *9* (3), 273-284.

63. Pavlovic, J.; Hopke, P. K., Chemical nature and molecular weight distribution of the watersoluble fine and ultrafine PM fractions collected in a rural environment. *Atmos. Environ.* **2012**, *59*, 264-271.

64. Song, J.; He, L.; Peng, P. a.; Zhao, J.; Ma, S., Chemical and isotopic composition of humiclike substances (HULIS) in ambient aerosols in Guangzhou, south China. *Aerosol Sci. Technol.* **2012**, *46* (5), 533-546.

65. Kuang, B. Y.; Lin, P.; Huang, X. H. H.; Yu, J. Z., Sources of humic-like substances in the Pearl River Delta, China: positive matrix factorization analysis of PM_{2.5} major components and source markers. *Atmos. Chem. Phys.* **2015**, *15* (4), 1995-2008.

66. Qiao, T.; Zhao, M.; Xiu, G.; Yu, J., Seasonal variations of water soluble composition (WSOC, Hulis and WSIIs) in PM1 and its implications on haze pollution in urban Shanghai, China. *Atmos. Environ.* **2015**, *123*, 306-314.

67. Zhao, M.; Huang, Z.; Qiao, T.; Zhang, Y.; Xiu, G.; Yu, J., Chemical characterization, the transport pathways and potential sources of PM_{2.5} in Shanghai: Seasonal variations. *Atmos. Res.* **2015**, *158-159*, 66-78.

68. Fan, X.; Song, J.; Peng, P. a., Temporal variations of the abundance and optical properties of water soluble Humic-Like Substances (HULIS) in PM_{2.5} at Guangzhou, China. *Atmos. Res.* **2016**, *172-173*, 8-15.

69. Park, S.; Son, S. C., Size distribution and sources of humic-like substances in particulate matter at an urban site during winter. *Environ. Sci. Process Impacts* **2016**, *18* (1), 32-41. 70. Tan, J.; Xiang, P.; Zhou, X.; Duan, J.; Ma, Y.; He, K.; Cheng, Y.; Yu, J.; Querol, X., Chemical characterization of humic-like substances (HULIS) in PM2.5 in Lanzhou, China. **2016**,

573, 1481-1490.

Zhao, M.; Qiao, T.; Li, Y.; Tang, X.; Xiu, G.; Yu, J. Z., Temporal variations and source apportionment of Hulis-C in PM_{2.5} in urban Shanghai. *Sci. Total. Environ.* 2016, *571*, 18-26.
 Voliotis, A.; Prokeš, R.; Lammel, G.; Samara, C., New insights on humic-like substances associated with wintertime urban aerosols from central and southern Europe: Size-resolved chemical characterization and optical properties. *Atmos. Environ.* 2017, *166*, 286-299.
 Wang, N.; Yu, J. Z., Size distributions of hydrophilic and hydrophobic fractions of watersoluble organic carbon in an urban atmosphere in Hong Kong. *Atmos. Environ.* 2017, *166*, 110-

soluble organic carbon in an urban atmosphere in Hong Kong. *Atmos. Environ.* 2017, 166, 110-119.

74. Ye, Z.; Li, Q.; Ma, S.; Zhou, Q.; Gu, Y.; Su, Y.; Chen, Y.; Chen, H.; Wang, J.; Ge, X., Summertime day-night differences of PM_{2.5} components (inorganic ions, OC, EC, WSOC, WSON, HULIS, and PAHs) in Changzhou, China. *Atmosphere* **2017**, *8* (12), 189.

75. Ma, Y.; Cheng, Y.; Qiu, X.; Cao, G.; Fang, Y.; Wang, J.; Zhu, T.; Yu, J.; Hu, D., Sources and oxidative potential of water-soluble humic-like substances (HULISWS) in fine particulate matter (PM_{2.5}) in Beijing. *Atmos. Chem. Phys.* **2018**, *18* (8), 5607-5617.

76. Mo, Y.; Li, J.; Jiang, B.; Su, T.; Geng, X.; Liu, J.; Jiang, H.; Shen, C.; Ding, P.; Zhong, G.; Cheng, Z.; Liao, Y.; Tian, C.; Chen, Y.; Zhang, G., Sources, compositions, and optical properties of humic-like substances in Beijing during the 2014 APEC summit: Results from dual carbon isotope and Fourier-transform ion cyclotron resonance mass spectrometry analyses. *Environ. Pollut.* **2018**, *239*, 322-331.

77. Zhou, X.; Zhang, L.; Tan, J.; Zhang, K.; Mao, J.; Duan, J.; Hu, J., Characterization of humic-like substances in PM_{2.5} during biomass burning episodes on Weizhou Island, China. *Atmos. Environ.* **2018**, *191*, 258-266.

78. Lin, P.; Rincon, A. G.; Kalberer, M.; Yu, J. Z., Elemental composition of HULIS in the Pearl River Delta Region, China: results inferred from positive and negative electrospray high resolution mass spectrometric data. *Environ. Sci. Technol.* **2012**, *46* (14), 7454-7462.

79. Fu, G. Q.; Xu, W. Y.; Yang, R. F.; Li, J. B.; Zhao, C. S., The distribution and trends of fog and haze in the North China Plain over the past 30 years. **2014**, *14* (21), 11949-11958.

80. Quan, J.; Zhang, Q.; He, H.; Liu, J.; Huang, M.; Jin, H., Analysis of the formation of fog and haze in North China Plain (NCP). **2011**, *11* (15), 8205-8214.

81. Li, L.; Duan, Z.; Li, H.; Zhu, C.; Henkelman, G.; Francisco, J. S.; Zeng, X. C., Formation of HONO from the NH₃-promoted hydrolysis of NO₂ dimers in the atmosphere. *Proc. Natl. Acad. Sci. USA* **2018**, *115* (28), 7236-7241.

82. Miller, C. J.; Rose, A. L.; Waite, T. D., Hydroxyl radical production by H₂O₂-mediated oxidation of Fe(II) complexed by Suwannee River fulvic acid under circumneutral freshwater conditions. *Environ. Sci. Technol.* **2013**, *47* (2), 829-835.

83. Lee, Y. P.; Fujii, M.; Kikuchi, T.; Terao, K.; Yoshimura, C., Variation of iron redox kinetics and its relation with molecular composition of standard humic substances at circumneutral pH. *PLoS One* **2017**, *12* (4), e0176484.

84. Miller, C. J.; Rose, A. L.; Waite, T. D., Impact of natural organic matter on H_2O_2 -mediated oxidation of Fe(II) in a simulated freshwater system. *Geochim. Cosmochim. Acta* **2009**, *73* (10), 2758-2768.

85. Fujii, M.; Rose, A. L.; Waite, T. D.; Omura, T., Oxygen and superoxide-mediated redox kinetics of iron complexed by humic substances in coastal seawater. *Environ. Sci. Technol.* **2010**, *44* (24), 9337-9342.

86. Sun, Y.; Pham, A. N.; Waite, T. D., Elucidation of the interplay between Fe(II), Fe(III), and dopamine with relevance to iron solubilization and reactive oxygen species generation by catecholamines. *J. Neurochem.* **2016**, *137* (6), 955-968.

87. Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B., Reactivity of HO₂/O₂⁻ Radicals in Aqueous-Solution. *J. Phys. Chem. Ref. Data* **1985**, *14* (4), 1041-1100.

88. Sun, Y.; Pham, A. N.; Waite, T. D., Effect of release of dopamine on iron transformations and reactive oxygen species (ROS) generation under conditions typical of coastal waters. *Environ. Sci. Process. Impacts* **2018**, *20* (1), 232-244.

89. Sun, L.; Li, R.-B.; Tian, X.-P.; Wei, J., Analysis of the temporal and spatial variation of aerosols in the Beijing-Tianjin-Hebei region with a 1 km AOD product. *Aerosol Air Qual. Res.* **2017**, *17* (3), 923-935.

90. Qi, J.; Zheng, B.; Li, M.; Yu, F.; Chen, C.; Liu, F.; Zhou, X.; Yuan, J.; Zhang, Q.; He, K., A high-resolution air pollutants emission inventory in 2013 for the Beijing-Tianjin-Hebei region, China. *Atmos. Environ.* **2017**, *170*, 156-168.

91. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species. *Atmos. Chem. Phys.* **2004**, *4*, 1461-1738.

92. Crowley, J. N.; Carl, S. A., OH formation in the photoexcitation of NO₂ beyond the dissociation threshold in the presence of water vapor. *J. Phys. Chem. A* **1997**, *101* (23), 4178-4184.

93. Wayne, L. G.; Yost, D. M., Kinetics of the rapid gas phase reaction between NO, NO₂, and H₂O. *J. Chem. Phys.* **1951**, *19* (1), 41-47.

94. England, C.; Corcoran, W. H., The rate and mechanism of the air oxidation of parts-permillion concentrations of nitric oxide in the presence of water vapor. *Ind. Eng. Chem. Fund.* **1975**, *14* (1), 55-63.

95. Kaiser, E. W.; Wu, C. H., A kinetic study of the gas phase formation and decomposition reactions of nitrous acid. *J. Phys. Chem.* **1977**, *81* (18), 1701-1706.

96. Streita, G. E.; Wells, J. S.; Fehsenfeld, F. C.; Howard, C. J., A tunable diode laser study of the reactions of nitric and nitrous acids: HNO₃ + NO and HNO₂ + O₃. *J. Chem. Phys.* **1979**, *70* (7), 3439-3443.

97. Zhu, R. S.; Lai, K. Y.; Lin, M. C., Ab initio chemical kinetics for the hydrolysis of N_2O_4 isomers in the gas phase. *J. Phys. Chem. A* **2012**, *116* (18), 4466-4472.

98. Sander, R., Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.* **2015**, *15* (8), 4399-4981.

99. Fuller, E. N.; Schettle.Pd; Giddings, J. C., A new method for prediction of binary gas-phase diffusion coeffecients. *Ind. Eng. Chem.* **1966**, *58* (5), 19-27.

100. Markovits, G. Y.; Schwartz, S. E.; Newman, L., Hydrolysis equilibrium of dinitrogen trioxide in dilute acid solution. *Inorg. Chem.* **1981**, *20* (2), 445-450.

101. Frenzel, A.; Scheer, V.; Sikorski, R.; George, C.; Behnke, W.; Zetzsch, C., Heterogeneous interconversion reactions of BrNO₂, ClNO₂, Br₂, and Cl₂. *J. Phys. Chem. A* **1998**, *102* (8), 1329-1337.

102. Rayson, M. S.; Mackie, J. C.; Kennedy, E. M.; Dlugogorski, B. Z., Accurate rate constants for decomposition of aqueous nitrous acid. *Inorg. Chem.* 2012, *51* (4), 2178-2185.
103. Oblath, S. B.; Markowitz, S. S.; Novakov, T.; Chang, S. G., Kinetics of the formation of hydroxylamine disulfonate by reaction of nitrite with sulfites. 1981, *85* (8), 1017-1021.

104. Clifton, C. L.; Altstein, N.; Huie, R. E., Rate constant for the reaction of nitrogen dioxide with sulfur(IV) over the pH range 5.3-13. **1988**, *22* (5), 586-9.

105. Kuang, B. Y.; Lin, P.; Huang, X. H. H.; Yu, J. Z., Sources of humic-like substances in the Pearl River Delta, China: positive matrix factorization analysis of PM_{2.5} major components and source markers. **2015**, *15* (4), 1995-2008.

106. Ma, Y.; Cheng, Y.; Qiu, X.; Cao, G.; Fang, Y.; Wang, J.; Zhu, T.; Yu, J.; Hu, D., Sources and oxidative potential of water-soluble humic-like substances (HULISWS) in fine particulate matter (PM_{2.5}) in Beijing. **2018**, *18* (8), 5607-5617.

107. Ye, Z.; Li, Q.; Ma, S.; Zhou, Q.; Gu, Y.; Su, Y.; Chen, Y.; Chen, H.; Wang, J.; Ge, X., Summertime day-night differences of PM_{2.5} components (inorganic ions, OC, EC, WSOC, WSON, HULIS, and PAHs) in Changzhou, China. **2017**, *8* (10), 189.

108. Zhao, M.; Qiao, T.; Li, Y.; Tang, X.; Xiu, G.; Yu, J. Z., Temporal variations and source apportionment of Hulis-C in PM2.5 in urban Shanghai. **2016**, *571*, 18-26.

109. Lin, P.; Engling, G.; Yu, J. Z., Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China. **2010**, *10* (14), 6487-6500.

110. Park, S.; Son, S.-C., Size distribution and sources of humic-like substances in particulate matter at an urban site during winter. *Environ. Sci. Process Impacts* **2016**, *18* (1), 32-41.

111. Krivácsy, Z.; Gelencsér, A.; Kiss, G.; Mészáros, E.; Molnár, Á.; Hoffer, A.; Mészáros, T.; Sárvári, Z.; Temesi, D.; Varga, B.; Baltensperger, U.; Nyeki, S.; Weingartner, E. J. J. o. A. C., Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch. **2001**, *39* (3), 235-259.

112. Krivácsy, Z.; Hoffer, A.; Sárvári, Z.; Temesi, D.; Baltensperger, U.; Nyeki, S.; Weingartner, E.; Kleefeld, S.; Jennings, S. G., Role of organic and black carbon in the chemical composition of atmospheric aerosol at European background sites. *Atmos. Environ.* **2001**, *35* (36), 6231-6244.

113. Kiss, G.; Varga, B.; Galambos, I.; Ganszky, I., Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. **2002**, *107* (D21), ICC 1-1-ICC 1-8.

114. Feczko, T.; Puxbaum, H.; Kasper-Giebl, A.; Handler, M.; Limbeck, A.; Gelencsér, A.; Pio, C.; Preunkert, S.; Legrand, M., Determination of water and alkaline extractable atmospheric humic-like substances with the TU Vienna HULIS analyzer in samples from six background sites in Europe. **2007**, *112* (D23).

115. Pio, C. A.; Legrand, M.; Oliveira, T.; Afonso, J.; Santos, C.; Caseiro, A.; Fialho, P.; Barata, F.; Puxbaum, H.; Sanchez-Ochoa, A.; Kasper-Giebl, A.; Gelencsér, A.; Preunkert, S.; Schock, M., Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a west-east transect across Europe. **2007**, *112* (D23).

116. Salma, I.; Mészáros, T.; Maenhaut, W.; Vass, E.; Majer, Z., Chirality and the origin of atmospheric humic-like substances. **2010**, *10* (3), 1315-1327.

117. Baduel, C.; Voisin, D.; Jaffrezo, J. L., Seasonal variations of concentrations and optical properties of water soluble HULIS collected in urban environments. **2010**, *10* (9), 4085-4095.

118. Cavalli, F.; Facchini, M. C.; Decesari, S.; Mircea, M.; Emblico, L.; Fuzzi, S.; Ceburnis, D.; Yoon, Y. J.; O'Dowd, C. D.; Putaud, J.-P.; Dell'Acqua, A., Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic. *J. Geophys. Res.-Atmos.* **2004**, *109* (D24).

119. Salma, I.; Ocskay, R.; Láng, G. G., Properties of atmospheric humic-like substances – water system. **2008**, *8* (8), 2243-2254.

120. Lukács, H.; Gelencsér, A.; Hammer, S.; Puxbaum, H.; Pio, C.; Legrand, M.; Kasper-Giebl, A.; Handler, M.; Limbeck, A.; Simpson, D.; Preunkert, S., Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe. **2007**, *112* (D23).

121. Mayol-Bracero, O. L.; Guyon, P.; Graham, B.; Roberts, G.; Andreae, M. O.; Decesari, S.; Facchini, M. C.; Fuzzi, S.; Artaxo, P., Water-soluble organic compounds in biomass burning aerosols over Amazonia 2. Apportionment of the chemical composition and importance of the polyacidic fraction. **2002**, *107* (D20), LBA 59-1-LBA 59-15.

122. Decesari, S.; Fuzzi, S.; Facchini, M. C.; Mircea, M.; Emblico, L.; Cavalli, F.; Maenhaut, W.; Chi, X.; Schkolnik, G.; Falkovich, A.; Rudich, Y.; Claeys, M.; Pashynska, V.; Vas, G.; Kourtchev, I.; Vermeylen, R.; Hoffer, A.; Andreae, M. O.; Tagliavini, E.; Moretti, F.; Artaxo, P., Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds. **2006**, *6* (2), 375-402.