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Strong anthropogenic control of secondary organic aerosol formation from isoprene in Beijing

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Abstract: Isoprene-derived secondary organic aerosol (iSOA) is a significant contributor to organic carbon (OC) in some forested regions, such as tropical rainforests and the Southeast US. However, its contribution to organic aerosol in urban areas, with high levels of anthropogenic pollutants, is poorly understood. In this study we examined the formation of anthropogenic-influenced iSOA during summer in Beijing, China. Local isoprene emissions and high levels of anthropogenic pollutants, in particular NO_x and particulate SO₄²⁻, led to the formation of iSOA under both high- and low-NO oxidation conditions, with significant heterogeneous transformations of isoprene-derived oxidation products to particulate organosulfates (OSs) and nitrooxy-organosulfates (NOSs). Ultra-pressure liquid chromatography coupled to high-resolution mass spectrometry was combined with a rapid automated data processing technique to quantify 31 proposed iSOA tracers in offline PM_{2.5} filter extracts. The co-elution of the inorganic ions in the extracts caused matrix effects that impacted two authentic standards differently. The average concentration of iSOA OSs and NOSs was 82.5 ng m⁻³, around three times higher than the observed concentrations of their oxygenated precursors (2-methyltetrols and 2-methylglyceric acid). OS formation was dependant on both photochemistry and sulfate available for reactive uptake as shown by a strong correlation with the product of ozone (O₃) and particulate sulfate (SO₄²⁻). A greater proportion of high-NO OS products were observed in Beijing compared to previous studies in less polluted environments. The iSOA derived OSs and NOSs represented on average 0.62 %

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50 of the oxidised organic aerosol measured by aerosol mass spectrometry, but this increased to ~3 % on
certain days. These results indicate for the first time that iSOA formation in urban Beijing is strongly
controlled by anthropogenic emissions and results in extensive conversion to heterogeneous OS products.

1 Introduction

55 Rapidly developing countries such as China often experience very poor air quality. Beijing regularly
experiences periods of very high particle pollution, with annual and 24-hourly levels well above World
Health Organisation guidelines (Chan et al., 2008; Hu et al., 2014). Premature mortality, as a result of
respiratory illness, cardiovascular disease and cancer, has been associated with exposure to poor air
quality (Dockery et al., 1993; Pope et al., 2000, 2006; Jerrett et al., 2009; Beelen et al., 2014; Laurent et
60 al., 2014; Ostro et al., 2015). Lelieveld et al. (2015) estimated that 1.36 million premature deaths in
China in 2010 were a result of exposure to outdoor air pollution. By far the most dangerous pollutant to
health in China are particles less than 2.5 microns in diameter, known as PM_{2.5}, with a recent study
suggesting that a 50 % reduction in excess mortality requires a 62 % reduction in PM_{2.5} in the Beijing-
Tianjin-Hebei (BTH) region (Hu et al., 2017a).

65 Previous measurements using aerosol mass spectrometry (AMS) indicate that PM₁ in Beijing is mainly
composed of sulfate, nitrate, ammonium and organics (Hu et al., 2016; Zhang et al., 2013). Positive
Matrix Factorisation of AMS measurements indicate that oxidised or secondary organic aerosol (SOA)
can make up a substantial fraction of the PM₁ mass (> 25 %), even in urban areas, but the sources of this
70 material are still poorly understood (Zhang et al., 2011; Sun et al., 2018). Hu et al. (2017a) estimated that
exposure to SOA was responsible for 0.14 million deaths in China in 2013 based on mass contribution
alone, ranging from < 1 % to 23 % source contributions to PM_{2.5} depending on location. Zhang et al.
(2017) used ¹⁴C measurements to determine that non-fossil emissions are generally a dominant
contributor of secondary organic carbon (SOC) in Beijing, with a larger contribution in summer as a
75 result of increased biogenic volatile organic compounds (VOCs) emissions.

Hu et al. (2017b) updated the Community Multi-scale Air Quality (CMAQ) model with updated SOA
yields and a more detailed description of SOA formation from isoprene oxidation. Removing all
anthropogenic pollutants from the model resulted in a huge drop in isoprene SOA concentrations,
80 indicating that controlling anthropogenic emissions would result in reduction of both anthropogenic and
biogenic SOA. The predicted SOA was dominated by isoprene in summer across China and in four cities
(Beijing, Guangzhou, Shanghai, Chengdu) with concentrations up to 30 µg m⁻³ in Beijing. However,
there is currently very little observational evidence to support such high SOA mass concentrations from
isoprene oxidation in these Chinese cities. The widely used SOA tracer method (Kleindienst et al., 2007)
85 has been used extensively to estimate the fraction of isoprene-derived SOA (iSOA) across China. Ding
et al. (2014) studied SOA at 14 Chinese sites and found that iSOA dominated the apportioned SOA mass
(46 ± 14 %), with it contributing between 0.4 – 2.17 µg m⁻³ and an average of 1.59 µg m⁻³ in Beijing.
However, only a very limited subset of VOC precursors was included, and this method fails to account
for heterogeneous formation processes. To overcome some of these limitations, Wang et al. (2017) used



90 tracer-based source apportionment of PM_{2.5} with positive matrix factorisation in the Pearl River Delta region during summer. They identified an iSOA factor that contributed up to 4 µg m⁻³ in Guangzhou, and up to 11 % of the total SOC.

95 A multitude of studies have examined iSOA formation (Pandis et al., 1991; Edney et al., 2005; Kroll et al., 2006; Dommen et al., 2006; Kleindienst et al., 2006; Ng et al., 2006; Surratt et al., 2007a, 2007b, 2008, 2010; Ng et al., 2008; Paulot et al., 2009; Chan et al., 2010; Chhabra et al., 2010; Nguyen et al., 2011, 2014, 2015; Zhang et al., 2011, 2012; Lin et al., 2013; Xu et al., 2014; Krechmer et al., 2015; Clark et al., 2016; Riva et al., 2016a, 2016b); however, the magnitude of iSOA formed can be vastly different from study to study (Carlton et al., 2009). Furthermore, there have been limited field measurements to
100 establish if these estimates are representative of urban environments (Wang et al., 2018; Li et al., 2018; Glasius et al., 2018; Le Breton et al., 2018; Hettiyadura et al., 2018,2019; Rattanavaraha et al., 2016; Budisulistiorini et al., 2013).

105 iSOA formation during the daytime is dominated by reaction with hydroxyl radicals (OH), with the concentrations of NO having a strong influence on the reaction products (Wennberg et al., 2018 and references therein). Under low-NO conditions the isoprene peroxyradicals (RO₂) can react with hydroperoxy radicals (HO₂) to form isoprene hydroxyhydroperoxides (ISOPOOH). The ISOPOOH isomers can react further with OH to form isoprene epoxydiol isomers (β- or δ-IEPOX) (Paulot et al., 2009), which can undergo uptake into acidified sulfate particles to form 2-methyltetrol organosulfates (2-MT-OS) (Surratt et al., 2010; Lin et al., 2012). Under high-NO conditions, isoprene RO₂ can react
110 with NO to form alkoxy radicals (RO) producing methacrolein (MACR) and methyl vinyl ketone (MVK) as the main reaction products. The reaction of MACR with OH, and subsequent addition of NO₂, leads to the methylacryloylperoxynitrate (MPAN), which reacts with OH to produce hydroxymethylmethyl-α-lactone (HMML) (Nguyen et al., 2015) or methacrylic epoxide (MAE) (Lin et al., 2013). HMML is
115 thought to be the more abundant product compared to MAE (Nguyen et al., 2015). Subsequent uptake of HMML into wet sulfate aerosols is proposed to lead to either 2-methylglyceric acid (2-MG) or its organosulfate derivative (2-MG-OS), as well as their dimers and higher order oligomers (Surratt et al., 2006; Surratt et al., 2010; Lin et al., 2013; Nguyen et al., 2015). Recently Schwantes et al. (2019) showed that under ambient conditions the formation of SOA from low-volatility nitrates and dinitrates, formed
120 via reactions of isoprene derived RO₂ with NO, is also important. Chamber-derived SOA yields for OH chemistry are variable depending on the experimental conditions, but are generally low (<10 %). The addition of acidified sulfate aerosol, accounting for wall losses and using more atmospherically relevant radical lifetimes can lead to significantly higher SOA yields in chamber studies (Surratt et al., 2010; Lin et al. 2012; Gaston et al., 2014). However, recent work has revealed that isoprene SOA formation can be
125 suppressed when viscous organic coatings are present on acidified sulfate aerosol, impeding the multiphase chemistry of IEPOX yielding additional SOA (Riva et al., 2016b; Zhang et al., 2018; Riva et al., 2019).



130 Observations using aerosol mass spectrometry (AMS) indicate that IEPOX-derived SOA can make up a
significant fraction of organic aerosol in isoprene-rich environments, such as Borneo (23 %; Robinson
et al., 2011), the Amazon (34 %; Chen et al., 2015) and the South East US (33-40 %; Budisulistiorini
et al., 2013; Budisulistiorini et al., 2016; Rattanvaraha et al., 2017). Hu et al. (2015) compared previous
AMS studies and found a magnitude lower average IEPOX-SOA signal in urban studies ($f_{C_{5H_{6O}}} = 0.17$
%) compared to those in isoprene-rich regions ($f_{C_{5H_{6O}}} = 2.2$ %). The average IEPOX-SOA concentration
135 measured in Nanjing, a polluted city in Eastern China, in August 2013 was $0.33 \mu\text{g m}^{-3}$ (Zhang et al.,
2017). This represented only 3.8 % of the total OA, indicating there is limited formation of IEPOX under
high- NO_x conditions (average $\text{NO}_x = 21$ ppb). He et al. (2018) found higher concentrations of the low-
NO isoprene SOA tracers (average = 121 ng m^{-3}) than the high-NO iSOA tracers (average = 9 ng m^{-3}) at
a regional background site (Wanqingsha) situated within the heavily polluted Pearl River Delta Region.
140 Only two high-NO iSOA tracers were measured (2-MG and 2-MG-OS), which could lead to a significant
underestimate of the strength of the high NO_x pathway. Wang et al. (2018) measured a range of OSs
at a regional site 38 km north east of Beijing during May-June 2016. Isoprene-derived OSs ranged from
 $0.9\text{-}20 \text{ ng m}^{-3}$, with a mean isoprene-derived OS concentration of 14.8 ng m^{-3} . In both these studies, the
ratio of the average concentration of the commonly used OS tracers from the low NO versus the high
145 NO pathways was close to 1.5 (2-MT-OS:2-MG-OS; Beijing = 1.47, Wanqingsha = 1.57) indicating that
even in polluted environments low-NO oxidation chemistry can play a significant role in iSOA
formation.

150 The lack of molecular-level measurements of iSOA in highly polluted urban areas makes it difficult to
determine the role of isoprene in summer haze episodes in Beijing. To investigate the formation of iSOA
in Beijing, offline $\text{PM}_{2.5}$ filter samples were collected during summer 2017 as part of the Atmospheric
Pollution and Human Health program (Shi et al., 2019). The filters were extracted and then screened
using a sensitive and selective high throughput method based on ultra performance liquid
155 chromatography coupled to ultra-high resolution mass spectrometry equipped with electrospray
ionization (UPLC/ESI-HR-MS). High-time resolution filter sampling allowed the formation and
evolution of iSOA to be studied, with observed concentrations strongly controlled by levels of
anthropogenic pollutants.

2 Experimental

160 2.1 $\text{PM}_{2.5}$ filter sampling and extraction

Aerosol samples were collected between the 18th May and 24th June 2017 at the Institute of Atmospheric
Physics (IAP) in Beijing, China. This sampling was part of the Sources and Emissions of Air Pollutants
in Beijing (AIRPOLL-Beijing) project, as part of the wider Atmospheric Pollution and Human Health in
a Chinese Megacity (APHH-Beijing) programme (Shi et al., 2019). $\text{PM}_{2.5}$ filter samples were collected
165 using an ECOTECH HiVol 3000 (Ecotech, Australia) high-volume air sampler with a selective $\text{PM}_{2.5}$
inlet, with a flow rate of $1.33 \text{ m}^3 \text{ min}^{-1}$. Filters were baked at $500 \text{ }^\circ\text{C}$ for five hours before use. After
collection, samples were wrapped in foil, and then stored at $-20 \text{ }^\circ\text{C}$ and shipped to the laboratory for
offline analysis. Samples were collected at a height of 8 m, on top of a building in the IAP complex.



170 Samples were collected every 3 hours during the day, approximately between 08:30 and 17:30 and then
one sample was collected overnight between 17:30 and 08:30. Hourly samples were also taken on certain
days towards the end of the sampling period on high pollution days. 24-hour samples were also collected
using a Digital high volume PM_{2.5} sampler at the same location.

175 The extraction of the organic aerosol from the filter samples was based on the method in Hamilton et al.,
(2008). Initially, an 8th of the filter was cut up into roughly 1 cm² pieces and stored in a vial. 4 ml of LC-
MS grade H₂O was then added to the sample and left for two hours. The samples were then sonicated for
30 minutes. Using a 2 ml syringe, the water extract is then pushed through a 0.22 μm filter (Millipore)
into another sample vial. An additional 1 mL of water was added to the filter sample, then extracted
180 through the filter, to give a combined aqueous extract. This extract was then reduced to dryness using a
vacuum solvent evaporator (Biotage, Sweden). The dry sample was then reconstituted in 1 mL 50:50
MeOH:H₂O solution for offline chemical analysis.

2.2 Ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS²)

185 The extracted filter samples and standards were analysed using UPLC-MS², using an Ultimate 3000
UPLC (Thermo Scientific, USA) coupled to a Q-Exactive Orbitrap MS (Thermo Fisher Scientific, USA)
with a heated electrospray ionisation (HESI). The UPLC method uses a reverse phase 5 μm, 4.6 x
100mm, Accucore column (Thermo Scientific, UK) held at 40 °C. The mobile phase consists of LC-MS
grade water and 100 % MeOH (Fisher Chemical, USA). The water was acidified using 0.1 % formic acid
to improve peak resolution. The injection volume was 2 μL. The solvent gradient was held for a minute
190 at 90:10 H₂O:MeOH, then changed linearly to 10:90 H₂O:MeOH over 9 minutes, then held for 2 minutes
at this gradient before returning to 90:10 H₂O:MeOH over 2 minutes and then held at 90:10 for the
remaining 2 minutes, with a flow rate of 300 μL min⁻¹. The mass spectrometer was operated in negative
mode using full scan MS². The scan range was set between 50 - 750 m/z. The ESI voltage was 4 kV,
with capillary and auxiliary gas temperatures of 320 °C. The samples were run in batches of 70, in a
195 repeating sequence of 5 samples followed by one blank. The calibrations were run separately after the
samples were finished, in the following sequence; (3 X same concentration) X number of standards in
calibration curve from the lowest concentration to the highest followed by 2 blanks. The quantification
method will be discussed in the results section.

200 2.3 Construction of accurate mass library

A mass spectral library was built using the compound database function in TraceFinder 4.1 General Quan
software (Thermo Fisher Scientific, USA). Each compound was input into the compound library in the
generic form: C_cH_hO_oN_nS_s (where c, h, o, n, and s represent the number of carbon, hydrogen, oxygen,
nitrogen and sulfur atoms respectively). From literature, species were identified, searched for in the
205 ambient samples according to their accurate mass, and then the retention time (RT) of each isomer was
obtained. The accurate masses, RT and literature references for iSOA tracers are shown in Table 1.

2.4 Automated method for SOA tracer analysis



210 The UPLC/ESI-HR-MS data for each ambient sample and standard was analysed using TraceFinder™.
The mass tolerance of the method was set to 2 ppm and the retention time window was set to 30 s,
although for species with multiple isomers present, the integration was checked to make sure the same
peaks were not being integrated twice, and the window changed accordingly. The peak tailing factor was
set to 2.0 to reduce the integration of the peak tails. The minimum signal to noise (S/N) for a positive
identification was set to 3.0. Using the output from TraceFinder, an *in-house* R code script was
215 developed to combine the identified species and peak areas with the correct filter sampling date/time
midpoint and volume of air sampled. Calibration curves from the standards were then obtained, and the
intercept and gradient inputted to quantify the iSOA tracer concentrations in the extract. These quantified
values were then converted to the mass on the whole filter and divided by the volume of air sampled for
that filter sampling period and converted to units of ng m⁻³. Higher time resolution data were averaged
220 to the filter sampling times.

2.5 Hydrophilic Liquid Interaction Chromatography (HILIC).

A subset of filters (n=15) were also analysed at the University of North Carolina (UNC) using a newly
developed HILIC method interfaced to high-resolution quadrupole time-of-flight mass spectrometry
225 equipped with ESI (i.e., HILIC/ESI-HR-QTOFMS) (Cui et al., 2018). Briefly, filters were extracted with
22 mL of LC/MS-grade methanol by 45 min of sonication; the samples were first extracted for 23 min,
the water bath replaced with cool water, and then extracted again for 22 min. This was done to make
sure the water bath contained within the sonicator did not reach above 30 C. Extracts were filtered
through polypropylene membrane syringe filters in order to remove insoluble filter fibres and soot
230 particles. The extracts were dried under a gentle stream of nitrogen gas. Dried methanol extracts were
reconstituted with 150 µL of 95:5 (v/v) LC/MS-grade acetonitrile/Milli-Q water. Operating details of the
HILIC/ESI-HR-QTOFMS used for these samples is also summarized by Cui et al. (2018).

2.6 Gas Chromatography – Mass Spectrometer

235 Details of the measurement procedure used can be found elsewhere (Fu et al., 2010). Briefly, filter
samples were extracted with dichloromethane/methanol (2:1 v/v), filtered through quartz wool packed
in a Pasteur pipette, concentrated using a rotary evaporator under vacuum, and blown down to dryness
with pure nitrogen gas. The extracts were derivatized and diluted with n-hexane containing the internal
standard prior to GC-MS analysis. Separation was performed on a fused silica capillary column (DB-
240 5MS: 30 m × 0.25 mm × 0.25 µm). The MS detection was conducted in electron ionization (EI) mode at
70 eV, scanning from 50 to 650 Da. Individual compounds were identified by comparison of mass spectra
with those of authentic standards or literature data. 2-methylglyceric acid, C₅-alkene triols (the sum of
cis-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-
trihydroxy-1-butene), and 2-methyltetrols (the sum of 2-methylthreitol and 2-methylerythritol) were
245 quantified using the response factor of *meso*-erythritol. Field blank filters were treated as the real samples
for quality assurance. Target compounds were not detected in the blanks.

2.7 High-Resolution Aerosol Mass Spectrometry measurements



250 The size-resolved non-refractory submicron aerosol species at the same site were measured by an
Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) at a time resolution
of 5 min. The elemental ratios of hydrogen-to-carbon (H:C) and oxygen-to-carbon (O:C) of OA were
determined, and the sources of OA were analysed with positive matrix factorisation. Six OA factors were
identified in summer including two primary factors; hydrocarbon like OA (HOA), cooking OA (COA),
and three oxidised OA factors with increasing degrees of oxidation, OOA1 (O:C = 0.53), OOA2 (O:C =
255 0.74), OOA3 (O:C = 1.18).

2.8 Iodide CIMS

260 A time of flight chemical ionisation mass spectrometer (ToF-CIMS) (Lee et al. 2014; Priestley et al.
2018) using an iodide ionisation system coupled with a filter inlet for gases and aerosols (FIGAERO)
was deployed here to make near simultaneous, real-time measurements of both the gas- and particle-
phase chemical composition. The instrument was originally developed by Lopez-Hilfiker et al. (2014)
and is described and characterised in more detail by Bannan et al., (2019). The experimental set up
employed by the University of Manchester ToF-CIMS is described in Zhou et al., (2019). Only gas phase
data is presented herein.

265 Field calibrations were regularly carried out using known concentration of formic acid in gas mixtures
made in a custom-made gas phase manifold. A range of other species were calibrated for after the
campaign, and relative calibration factors were derived using the measured formic acid sensitivity during
the in-situ calibrations (Bannan et al. 2015). Offline calibrations after the field work campaign were
270 performed specific to the isoprene oxidation species observed here. IEPOX ($C_5H_{10}O_3$) synthesized by
the University of North Carolina, Department of Environmental Sciences & Engineering was specifically
calibrated for. Known concentrations were deposited on the FIGAERO filter in various amounts and
thermally desorbed using a known continuous flow of nitrogen over the filter. For the isoprene nitrate;
 $C_5H_9NO_4$ there was no direct calibration source available and concentrations using the calibration factor
275 of $C_5H_{10}O_3$ are presented here.

2.9 Gas-phase measurements

280 Additional gas-phase measurements were collected at the site from an elevated inlet at 8 m. Data included
Nitrogen oxide, NO, measured by chemiluminescence with a Thermo Scientific Model 42i NO_x analyser
and Nitrogen dioxide, NO₂, was measured using a Teledyne Model T500U Cavity Attenuated Phase Shift
(CAPS) spectrometer. The sum of the NO_y species was measured using a Thermo Scientific Model 42C
NO_x analyser and a heated molybdenum converter at the sample inlet. The molybdenum converter
reduces NO_y compounds to NO allowing measurement by chemiluminescence. Ozone, O₃, was measured
285 using a Thermo Scientific Model 49i UV photometric analyser. All instruments were calibrated
throughout the measurement period, with a 'zero' or 'background' calibration using a Sofnofil/charcoal
trap. Span (high concentration) calibrations were carried out using gas standards. Both the Thermo
Scientific 42i and 42C instrument calibrations are traceable to the National Physical Laboratories (NPL)



290 NO scale. The meteorological variables of wind speed, wind direction, relative humidity (RH), and temperature were measured at 102 m on the IAP 325 m meteorological tower.

295 Observations of VOCs were made using a dual-channel GC with flame ionisation detectors (DC-GC-FID). Air was sampled at 30 L min⁻¹ at a height of 5m, through a stainless-steel manifold (½" internal diameter). 500 mL subsamples were taken, dried using a glass condensation finger held at -40°C and then pre-concentrated using a Markes Unity2 pre-concentrator on a multi-bed Ozone Precursor adsorbent trap (Markes International Ltd). These samples were then transferred to the GC over for analysis following methods described by Hopkins et al. (2011).

300 Further details of the following additional gas phase instrumentation can be found in the SI and Shi et al., 2019. Isoprene was also measured at a height of ~102 m using a Voice200 Selected ion flow tube mass spectrometer (SIFT-MS, Syft Technologies, Christchurch, New Zealand). OH, HO₂ and RO₂ concentrations were measured using Fluorescence Assay by Gas Expansion (FAGE) and NO₃ concentrations were measured using Broadband cavity enhanced absorption spectrometry (Zhou et al., 2018).

305

3 Results and discussion

310 The field campaign was conducted at the Institute of Physics, Beijing, situated between the third and fourth ring roads (Shi et al., 2019). The site is typical of central Beijing, surrounded by residential and commercial properties and is near several busy roads. It is also close to several green spaces including a tree-lined canal to the south and the Olympic forest park to the north-east, providing sources for local isoprene emissions.

3.1 Isoprene gas phase concentrations and loss processes

315 Isoprene was measured hourly using the DC-GC-FID between 18/05/2017 – 20/06/2017 and the observed concentrations are shown in Figure 1, alongside NO, NO₂ and ozone. The mean mixing ratio of isoprene was 0.53 ppb, with a maximum of 2.9 ppb on the 16/06/2017. The ambient temperature ranged from 16 to 38 °C. Day-time isoprene mixing ratios increased with temperature, with all isoprene mixing ratios above 1 ppb occurring when the temperature was > 25 °C. The average diurnal profile of isoprene in Figure 2a shows low values overnight (< 50 ppt), with a rapid increase at 6 am reaching a maximum of around 1 ppb by the afternoon. The mixing ratio rapidly decreased after 18:00 and returned to very low values by around 22:00. There was strong a correlation between the isoprene mixing ratio measured at 8 m by the DC-GC and at 102 m using the SIFT-MS ($R^2 = 0.77$). The SIFT-MS measurements were therefore used to investigate the correlation with iSOA tracers when no DC-GC data was available.

325

Using the average observed diurnal profiles of the main atmospheric oxidants, OH, ozone and NO₃ (shown in SI Figure S1), and isoprene (Figure 2a), the isoprene loss rate was calculated (rate of loss = $k_{ox}[\text{Oxidant}][\text{Isoprene}]$) and is shown in Figure 3a. The percentage contribution of each oxidant to the



330 average diurnal isoprene loss rate is shown in Figure 3b. During the day, OH is responsible for over 90
% of isoprene loss, with NO₃ becoming relatively more important from 18:00 until around 03:00,
although the amount of isoprene available to react rapidly decreased during this time period. OH
chemistry is still an important loss route at night (>30 %) owing to night-time OH sources, such as the
ozonolysis of alkenes. Loss of isoprene via ozonolysis however is a minor route, contributing <15 %.
335 During the daytime (10:00-15:00), the lifetime of isoprene was on average around 20 minutes, increasing
to a maximum of around 6 hours at 03:00. While the high levels of oxidants lead to a short isoprene
lifetime during the day, the ambient concentrations of isoprene are still maintained at the ppb level. This
indicates that there are significant local emissions of isoprene impacting the measurement site and
therefore a high potential for the formation of iSOA in this urban environment.

340 3.2 Isoprene SOA in Beijing

Using the high throughput screening method described, the peak areas of 31 potential isoprene-derived
OSs and NOSs, which are known iSOA tracers, were measured in 132 PM_{2.5} filter extracts. The full list
of iSOA tracers, along with their measured *m/z* and molecular formula is shown in Table 1, ordered by
descending average concentration (weighted by filter sampling time and reported in ng m⁻³) during the
345 campaign.

3.3 Quantification of isoprene OS tracers

Initially, two synthesised isoprene-derived OS standards (2-MT-OS and 2-MG-OS, Cui et al., 2018;
Rattanavaraha et al., 2016) were used to produce calibration curves. Both standards gave strong linear
350 calibration curves ($R^2 = 0.980$ and 0.996 respectively) across an appropriate range of concentrations for
the peak areas in the samples. The gradient obtained for the 2-MT-OS standard was ~4 times higher than
that of the 2-MG-OS, as shown in Figure S2 To investigate the potential for matrix effects from the large
amounts of inorganic sulfate, nitrate and other particulate components that co-elute due to the poor
retention of OS in reverse phase UPLC, standard addition calibrations were used. Five-point standard
355 addition calibrations were run on 6 different filter extracts, covering both day and nighttime samples. 50
μL of filter sample extract and 50 μL of the calibrant solution were combined, giving a dilution factor of
2. The five-point calibration range of standard added to each sample was between 0-3 ppm for 2-MGOS
and 0-1 ppm for 2-MT-OS. Two examples of the standard addition calibrations are shown in SI Figures
S3 (2-MG-OS) and S4 (2-MT-OS), with good linear fits observed ($R^2 = 0.997$ and 0.997 respectively).
360 A strong matrix effect was observed for the 2-MT-OS, with the concentration measured by standard
addition calibration 8.6 to 10 times higher than when using the external calibration carried out on the
same day. In contrast, the 2-MG-OS showed a much lower matrix effect, with the concentrations only
1.1-1.5 times higher when using the standard addition calibration. A further comparison using
camphorsulfonate, which has a longer retention time (3.74 min) and so does not experience high
365 inorganic ion concentrations in the source, showed no matrix effects when using standard addition. SI
Tables 1 and 2 shows a comparison of the concentrations calculated from the standard additions and the
two external calibrations.



370 It is not realistic to carry out standard addition calibrations for all samples and all SOA tracers. When
the 2-MG-OS external calibration was used to predict the 2-MT-OS concentrations during the standard
addition experiments, the concentrations were within a factor of 1.5-2.5. Therefore, the 2-MG-OS
external calibration was used as a proxy for all isoprene SOA tracers, with scaling factors applied to
account for matrix effects (1.33 for 2-MG-OS, 2.33 for 2-MT-OS, and an average of 1.83 used for all
other OSs). Therefore, we estimate an uncertainty on our measured concentrations of 60%. The dinitrate
375 and trinitrate NOS species eluted after the sulfate peak ($R_t > 1.6$ min). In the absence of authentic
standards for these species, camphorsulfonate was used as a proxy for calibration. This work highlights
an additional difficulty of calibration when using ESI-MS to study OSs and indicates that future studies
using reversed phase LC (RPLC) should consider the impacts of matrix effects.

380 3.4 Organosulfates

3.4.1 2-methyltetrol OS (2-MT-OS)

The 2-MT-OS ($C_5H_{12}SO_7$) formed from the uptake of IEPOX into the particle phase is often used as a
marker of low-NO isoprene photochemistry (Wennberg et al., 2018). The time series of 2-MT-OS is
shown in Figure 4a. The particle concentration ranged from 0.7 ng m^{-3} to a maximum of 111 ng m^{-3} , with
385 a mean concentration of 11.8 ng m^{-3} . The mean concentrations of 2-MT-OS and 2-MG-OS are compared
to observations in previous studies in Table 2. The mean concentration observed in Beijing was much
lower than those observed in the Amazon (Riva et al., 2019) and the SE US (Budisulistiorini et al., 2015;
Hettiyadura et al., 2019) but are higher than summer time observations at polluted regional background
sites in China (Wang et al., 2018; He et al., 2018). The lower amounts of IEPOX-derived SOA results
390 in an average AMS f_{CSH6O} in Beijing during the APHH project of only 0.2 %, similar to observations in
other urban studies (Hu et al., 2015).

Hourly samples were collected on selected high pollution days and used to obtain information on the
diurnal evolution of the iSOA tracers. The findings on these days are consistent with the three-hourly
395 data. The particulate 2-MT-OS measured by UPLC-MS, on the 11th - 12th June 2017, had a strong diurnal
profile (Figure 2b), peaking in the late afternoon, between 15:30 and 18:30, with a minimum over-night.
This is consistent with the average diurnal profile of the gas phase precursors IEPOX+ISOPOOH
($C_5H_{12}O_3$) measured using the I-CIMS (SI Figure S5). High levels of ozone were observed in the
afternoon (up to 180 ppb), leading to relatively low levels of NO observed for a highly polluted
400 environment, in some cases below 500 ppt. Thus, although the mixing ratio of NO_x was high, on most
afternoons less than 2 % was in the form of NO. High levels of peroxy radicals were observed, with mean
afternoon concentrations of HO_2 and RO_2 of around $3 \times 10^8 \text{ molecule cm}^{-3}$ and $1.5 \times 10^9 \text{ molecule cm}^{-3}$,
respectively. Zero-dimensional box modelling indicates on some days up to 35 % of the isoprene-derived
 RO_2 radicals can react with HO_2 in the afternoon (Newland et al., 2019). Thus, the diurnal profile seen
405 in Figure 2b, measured in samples during the measurement period suggests that IEPOX was formed at
this urban location by the reaction of OH with local isoprene emissions, with a fraction of the RO_2
radicals formed reacting with HO_2 rather than NO, and subsequent uptake to aerosol forming 2-MT-OS.
OH + isoprene hydroxynitrate also has a small yield of IEPOX (Jacobs et al., 2014). The average diurnal



410 profile of isoprene hydroxynitrates ($C_5H_9NO_4$) in the gas phase measured using the I-CIMS peaks at
around 11:00-12:00 followed by a reduction during the afternoon into the evening/night (SI Figure S6).
This is likely to be a result of the relatively low levels of NO during the afternoon, which will reduce
isoprene nitrate formation from $RO_2 + NO$ reactions, thus isoprene hydroxynitrates are unlikely to be a
significant source of 2-MT-OS in Beijing.

415 The 2-MT-OS showed a moderate correlation with particulate sulfate ($R^2=0.44$), and a weak anti-
correlation with photochemical age, estimated using the ratio of NO_x/NO_y ($R^2=0.23$). All correlations
between species are shown in SI Figure S7. By taking the product of the concentration of ozone, as a
proxy of photochemistry, with the amount of particulate sulfate measured using AMS, $[O_3][pSO_4]$, a
420 much stronger correlation with 2-MT-OS was observed ($R^2=0.61$) as shown in Figure 5. This observation
highlights the role of both local photochemistry and particulate sulfate mass in the formation of 2-MT-
OS (Figure 5). The correlation of $[O_3][pSO_4]$ with 2-MT-OS is likely to be weaker at longer
photochemical ages when the ozone concentration is not directly related to the photochemical formation
of the OS. Again, this highlights the strong role of local photochemistry in the production of low-NO
425 iSOA (2-MT-OS) in Beijing. Elevated levels of 2-MT-OS were observed at the start and end of the
measurement period which were influenced by strong south-westerly winds. There were also elevated
isoprene concentrations (up to 2.9 ppb) and high particulate SO_4^{2-} levels. Therefore, these spikes in 2-
MT-OS could be a result of either higher 2-MT-OS in regional aerosol transported to the site or a high
isoprene emission source to the south west of the site (i.e. producing IEPOX locally) that then reacts with
increased regional sulfate pollution.

430 Analysis of the 2-MT-OS isomer distribution using HILIC/ESI-HR-QTOFMS, on a subset of 15 samples,
indicates that β -IEPOX is the dominant ambient IEPOX isomer, in line with other recent observations
(Cui et al, 2018; Krechmer et al., 2016) see SI Figure S8). The MT-OS derived exclusively from δ -
IEPOX-OS isomers could not be observed in any of the samples. The 4 IEPOX-OS isomers in SI Figure
435 S8 showed similar temporal trends although small changes in the relative proportions were observed.

3.4.2 2-methyl glyceric acid OS (2-MG-OS)

The most common targeted SOA tracer for high-NO isoprene chemistry is 2-methylglyceric acid (2-MG)
and its derivatives. Two observed SOA tracers related to this chemistry are the OS derivatives of 2-
440 methylglyceric acid (2-MG-OS) and the unresolved C_8 dimers of 2-MG-OS ($C_8H_{14}SO_{10}$) that have been
identified previously in chamber-derived iSOA (Surratt et al., 2006; Surratt et al., 2010). 2-MG-OS had
an average concentration during the campaign of 21.5 ng m^{-3} , ranging from 0.3 to 180.5 ng m^{-3} , with the
time series shown in Figure 4b. These values are within the range of 2-MG-OS measured in other urban
locations (Nguyen et al., 2014; Rattanavaraha et al., 2016; Hettiyadura et al., 2019). However these
445 concentrations are considerably higher than previously observed at two Chinese polluted regional sites
(Wang et al., 2018; He et al., 2018). At these locations, the ratio of the low-NO to high-NO isoprene OS
tracer average concentrations was close to 1.5 (2-MT-OS:2-MG-OS; Beijing = 1.47, Wanqingsha =
1.57). However, in central Beijing, this ratio was considerably lower (2-MT-OS:2-MG-OS = 0.55),



450 reflecting the higher proportion of RO₂ radicals reacting with NO at this location compared to the regional measurements. The ratio of 2-MT-OS:2-MG-OS observed in Beijing is compared to previous studies in Table 2 and is considerably lower than measurements taken in a range of isoprene dominated environments (South East US, 2-MT-OS:2-MG-OS = 17, Budisulistiorini et al., 2015.; Amazon, 2-MT-OS:2-MG-OS = 13-118, Glasius et al., (2018).; Atlanta, 2-MT-OS:2-MG-OS = 33, Hettiyadura et al., (2019)) reflecting the strong impact of urban NO emission on iSOA formation.

455 The mean concentration of the 2-MG-OS dimer (C₈H₁₄SO₁₀) was 0.57 ng m⁻³. A strong linear relationship was observed between the 2-MG-OS monomer and dimer concentrations (R²=0.83) with a dimer:monomer ratio of 0.02. Formation of oligomers from reactions of 2-MG and HMML has been shown to be reduced in chamber experiments under humid conditions (Schwantes et al., 2019; 460 Nestorowicz et al., 2018). The average RH during the afternoon of the campaign was ~40 %, which may account for the relatively low formation of the dimer OS compared to the monomer (see SI Figure 9).

The diurnal profile of the 2-MG-OS as shown in SI Figure 10 was similar to the 2-MT-OS peaking during the early afternoon samples but with an enhanced signal at night. There was also a strong correlation 465 between these two species (R² = 0.92) during the campaign. The 2-MG-OS showed a stronger correlation with particulate sulfate (R²=0.52) than 2-MT-OS (R²=0.44), and there was also a weak anti-correlation with photochemical age (R²=0.28). A strong correlation was also observed for 2-MG-OS with [O₃][pSO₄] (R²=0.69), as shown in Figure 5, highlighting that formation is dependent on both photochemistry and sulfate aerosol availability.

470 3.4.3 Other isoprene-related OSs and NOSs

24 additional OSs species, with molecular formulae consistent with iSOA tracers seen in chamber experiments, were also observed in Beijing as shown in Table 1. For C₅ compounds, the most abundant species were C₅H₁₀SO₆ and C₅H₁₀SO₅, with mean concentrations of 28.7 ng m⁻³ and 26.5 ng m⁻³, 475 respectively. The identity of the OS at *m/z* 182 (C₅H₁₀SO₅) is currently unknown and the product ion MS provides little additional information other than sulfate-related fragment ions at *m/z* 97 and *m/z* 80. The OS at *m/z* 198 (C₅H₁₀SO₆) was identified as an IEPOX-related OS in chamber experiments by Nestorowicz *et al.* (2018), but at relatively low concentrations compared to the 2-MT-OS (1-4 %). This is very different to the observed ratio in Beijing, where the C₅H₁₀SO₆ average concentration was more than double that of 2-MT-OS, as shown in Figure 4c. This compound showed a strong correlation with 480 2-MT-OS (R² = 0.77) but it is currently unclear why this compound is the most abundant C₅ species. The molecular weight of this species is 18 Da (-H₂O) lower than 2-MT-OS, which may indicate it is a dehydration product enhanced under acidic aerosol conditions. In addition, this species may also be enhanced if it is formed from additional VOC precursors.

485 Potential low-NO iSOA tracers, seen in chamber experiments, correlated strongly with the 2-MT-OS including unresolved isomers of cyclic hemiacetals [C₅H₁₀SO₇ (R²=0.92)], and lactones [C₅H₈SO₇ (R²=0.83)] (Spolnik et al., 2018). These compounds were similar in concentration to the 2-MT-OS, with



the lactones at MW 212 having a mean concentration of 14 ng m^{-3} and the cyclic hemiacetals at MW 214
490 a mean of 10.6 ng m^{-3} . These compounds were also observed to be the dominant type of isoprene-derived
OSs in Atlanta, Georgia, although they had concentrations a factor of ~ 15 times lower than the observed
2-MT-OS. (Hettiyadura et al., 2019)

Additional small OS compounds, previously identified during high-NO chamber experiments, were also
495 observed in Beijing, including in order of decreasing concentration, glycolic acid sulfate ($\text{C}_2\text{H}_4\text{SO}_6$, mean
= 38.4 ng m^{-3}), hydroxyacetone sulfate ($\text{C}_3\text{H}_6\text{SO}_5$, mean = 20.5 ng m^{-3}) and lactic acid sulfate ($\text{C}_3\text{H}_6\text{SO}_6$,
mean = 14.5 ng m^{-3}) (Surratt et al., 2007; Surratt et al., 2008). These concentrations are in line with
measurements made in other urban locations (Rattanavaraha et al., 2016; Huang et al., 2018; Hettiyadura
500 et al., 2018). While all three C_2 - C_3 -OS compounds had strong correlations with the other iSOA OS tracers
($R^2 = 0.6$ - 0.94), the relative strength of isoprene versus other VOC precursors, such as aromatics, cannot
be determined. As such, they cannot be definitively assigned as iSOA tracers, and are therefore included
in the potential iSOA portion of Figure 6. The sum of the C_2 and C_3 OSs had an average concentration
of 73 ng m^{-3} , with a range of 2.0 - 831 ng m^{-3} .

505 In addition, 9 NOS species related to isoprene were identified as shown in Table 1 (Ng et al., 2008;
Rollins et al., 2009). Some of the NOS observed peaked in the daytime and some were enhanced at night.
In total they had a mean concentration of 24 ng m^{-3} during the campaign. The sources and formation of
these species will be discussed in a separate publication.

510 3.5 Contribution of Isoprene SOA in Beijing

In order to estimate the total amount of isoprene-derived OSs and NOSs, labelled here as iSOA, 13
species were chosen that could be confidently identified as being predominately from isoprene (2-MT-
OS, 2-MG-OS, $\text{C}_5\text{H}_{10}\text{SO}_7$, $\text{C}_5\text{H}_8\text{SO}_7$, $\text{C}_5\text{H}_{11}\text{NSO}_9$, $\text{C}_5\text{H}_9\text{NSO}_{10}$, $\text{C}_5\text{H}_9\text{N}_2\text{SO}_{11}$, $\text{C}_5\text{H}_8\text{N}_3\text{SO}_{13}$). Although
515 there were a number of other compounds with formula similar to iSOA tracers, their trends compared to
previous studies and potential for alternative sources made a confident assignment of VOC precursor
difficult. Therefore, the estimated contribution of iSOA to the observed total particulate mass determined
here should be taken as a lower limit. Figure 6 shows the time series of the iSOA observed in Beijing.
The average concentration was 82.5 ng m^{-3} during the campaign, ranging from 718 ng m^{-3} on the
19/05/2017 (11:38 – 14:30) to 1.9 ng m^{-3} on the 02/06/2017 (14:36-17:28). The contribution of iSOA to
520 the OOA factors measured by the AMS was obtained by assuming all OSs and NOSs species fragment
in the ion source to lose the sulfate and nitrate groups. Across the whole measurement period, the iSOA
tracers represented only a small fraction of the total OOA measured by AMS (0.62% of $\sum[\text{OOA}1-3]$).
However, towards the end of the measurement period, this increased up to a maximum of 3% on the
17/06/2017 (13:32-14:23).

525 Additional iSOA tracers containing only CHO, including 2-methyltetrols, 2-methylglyceric acid and C_5 -
alkene triols, were measured in separate 24-hour filter samples, with the commonly used derivatization
GC-MS method (Claeys et al., 2004; Wang et al., 2005.). The average ratio of the 2-methyltetrols to its



530 corresponding OS (2-MT:2-MT-OS) was 1.4, indicating extensive heterogeneous conversion of isoprene
oxidation products within the particles. The observed ratio is slightly larger than those measured in the
SE US (~0.37-0.96 as shown in Table 2) but much lower than that measured in the Pearl River Delta
region (~40,) where the 2-methyltetrols dominated. In contrast, the average ratio of the high-NO iSOA
tracer, 2-MG and its corresponding organosulfate (2-MG:2-MG-OS) observed in Beijing was 0.33,
535 indicating more extensive transformation to heterogeneous products. This ratio may also reflect the more
volatile nature of 2-MG compared to 2-MT. Overall, the combined concentrations of these isoprene CHO
compounds were generally low (mean 25 ng m⁻³, max 69 ng m⁻³) in comparison to the heterogeneous
iSOA compounds (i.e., isoprene-derived OSs and NOSs) targeted in this work. In addition, the
concentrations of these CHO species may be overestimated based on recent studies demonstrating that
540 thermal decomposition leads to these products being detected by GC-MS and FIGAERO-CIMS methods
(D'Ambro et al., 2019), and so the conversion to heterogeneous products (i.e., OSs and NOSs) may in
fact be larger (2MT:2MT-OS = 0.5-0.91 using the overestimates of 160-288 % observed in Cui et al.,
(2018)).

545 The study presented here shows for the first time that OS species derived from isoprene oxidation can
make a significant contribution to oxidised organic aerosol in Beijing in summer. There is significant
anthropogenic control, from both NO_x and sulfate aerosols, on the products and concentrations of iSOA
in Beijing. The majority of the OS species showed a strong correlation towards the product of [O₃][pSO₄],
highlighting the role of both photochemistry and the availability of particulate sulfate for heterogeneous
reactions. When the observed concentrations of all the OS and NOS species measured in this study,
550 including the additional 19 compounds not confidently assigned to iSOA, are combined they contribute
on average 2.2 % to the total OOA (Σ[OOA1-3]), increasing to a maximum of 10.5 %, indicating
extensive heterogeneous conversion of VOC oxidation products in Beijing in summer.

Author contributions

555 DB analysed the aerosol samples and quantified iSOA tracers. WD and KP developed the UPLC-MS
method. JRH, RD and MS provided the VOC measurements. FS and JL collected the NO, NO₂ and O₃
data. TB, AM, SW, AB, CJP, HC collected and analysed the CIMS data. LW, DH and ES provided the
OH and HO₂ data and BO provided the NO₃ measurements. TC, JDS and WD carried out the offline
HILIC analysis. DL, ZS and RH provided the GC-MS iSOA data. YS and WX carried out the AMS
560 measurements and PMF analysis. ACL and RH lead the APHH projects. DB, ARR and JFH wrote the
manuscript with input and discussion with all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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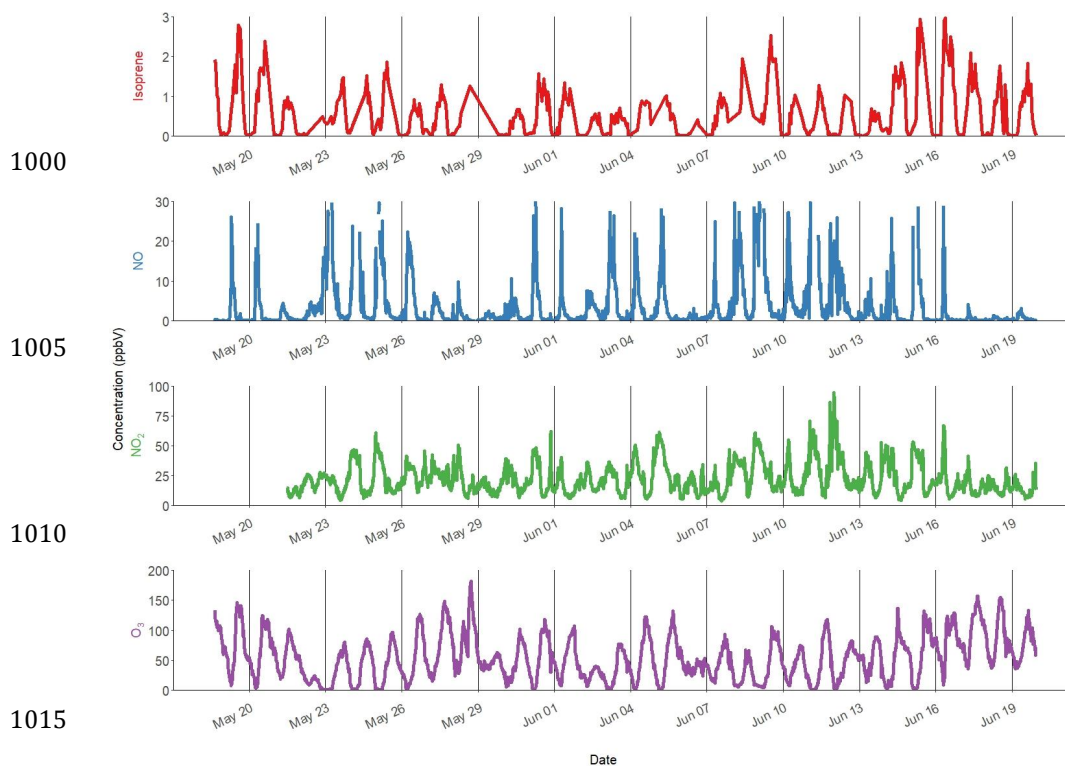
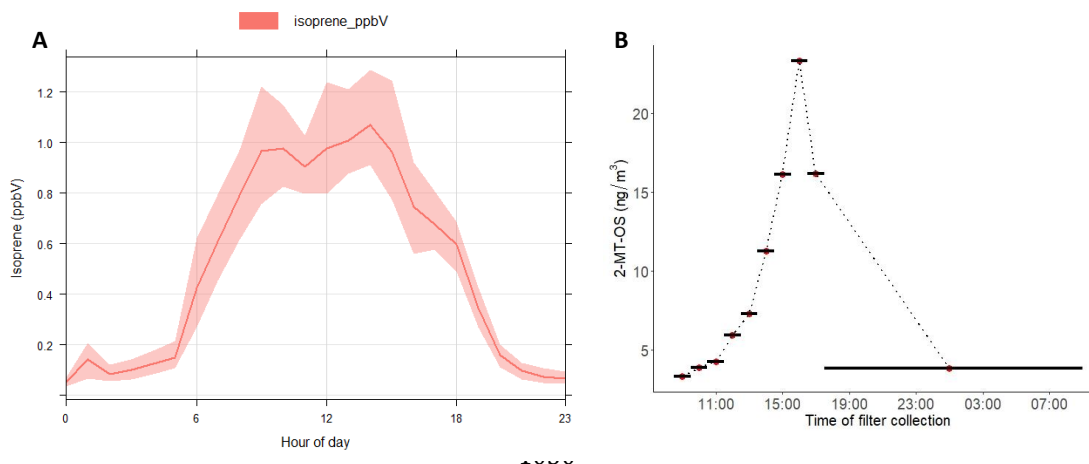


Figure 1. Time series of isoprene, nitric oxide (NO), nitrogen dioxide (NO₂), ozone (O₃).

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1035 **Figure 2.** (A) Average diurnal profile of isoprene mixing ratio measured using DC-GC-FID. (B) Diurnal profile of
1040 2-methyltetrol sulfate (2-MT-OS) in particulate matter (PM_{2.5}) collected on filters hourly over the 11th to 12th June
1045 2017. Black lines indicate length of filter sampling period.

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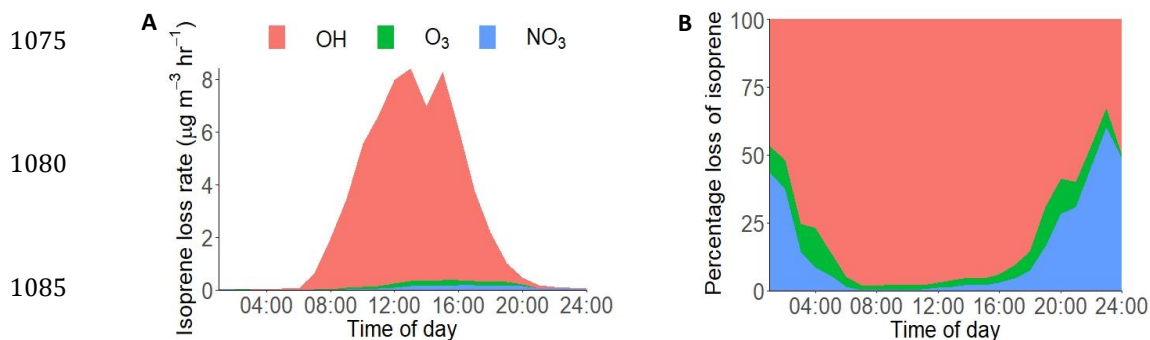
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Figure 3. (A) Diurnal loss rate of isoprene calculated using measured average diurnal profiles of isoprene, OH, NO₃ and ozone. (B) Average diurnal of the percentage loss of isoprene from reactions with OH, O₃ and NO₃ radicals. The IUPAC rate constants used for the calculations are as follows, NO₃: 7×10^{-13} , O₃: 1.27×10^{17} , OH: 1×10^{10} (Atkinson et al., 2006).

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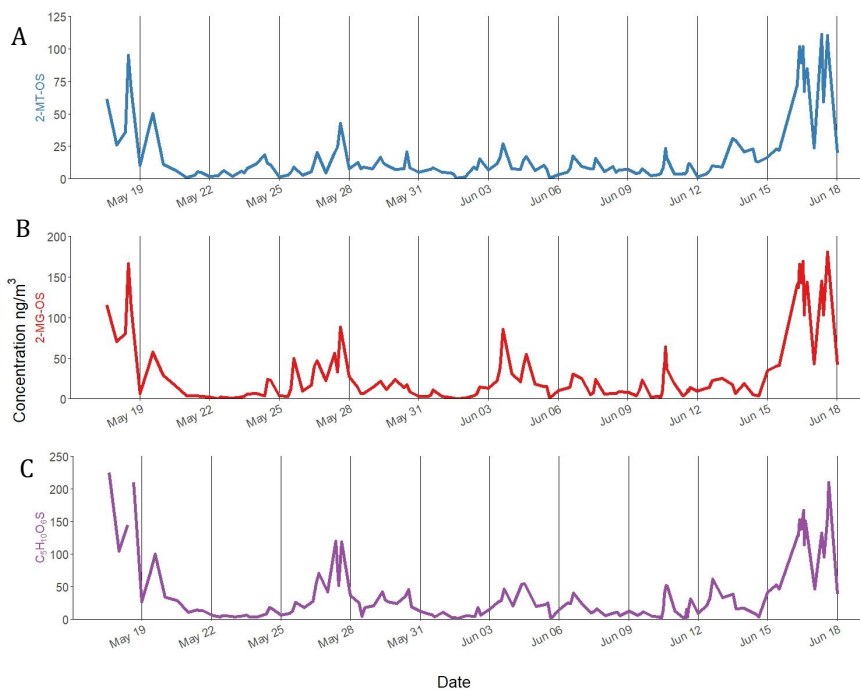
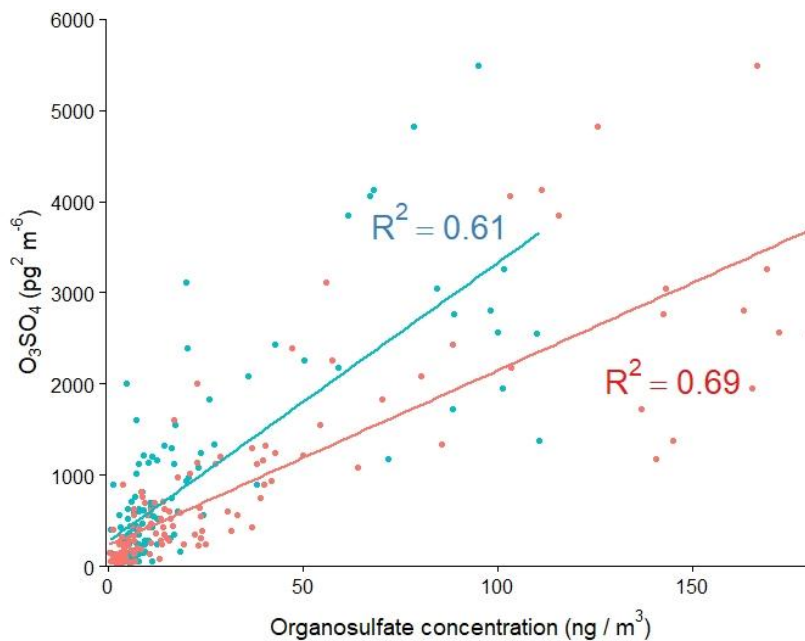


Figure 4. Time series of observed concentrations of iSOA tracers in Beijing during APHH. (A) 2-MT-OS (C₅H₁₂O₇S) (B) 2-MG-OS (C₄H₈O₇S) (C) C₅H₁₀SO₆. For ease of viewing a simple line is used to connect datapoints. It should be noted that the sampling time is not constant and details of the filter collection times are given in SI data. (*doi to be given on acceptance*)

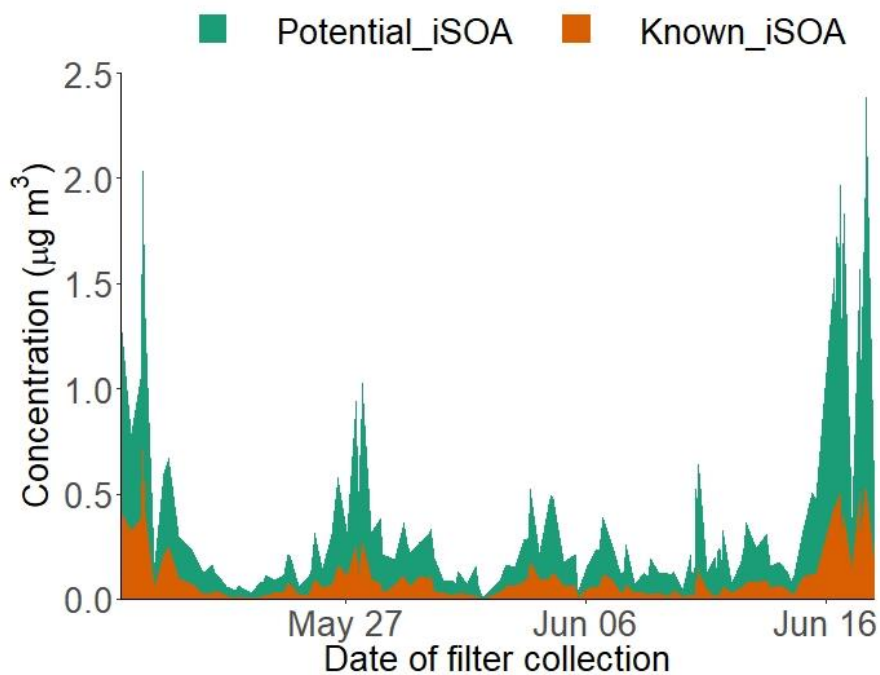


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Figure 5. Plot of 2-MT-OS (C₅H₁₂O₇S, blue) and 2-MG-OS (C₄H₈O₇S, red) concentrations versus [Ozone][SO₄]. The high time resolution data (O₃ and AMS SO₄²⁻) has been averaged to the filter sampling time. The line was calculated using the `stat_smooth` function in the R package `ggplot2`, using the method "lm".



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Figure 6. Time series of the total known isoprene SOA signal (2-MT-OS, 2-MG-OS, $C_5H_{10}SO_7$ (MW 214) $C_5H_8SO_7$ (MW 212) $C_5H_{11}NSO_9$ (MW 261), $C_5H_9NSO_{10}$ (MW 275) $C_5H_{10}O_{11}N_2S$ (MW 306), $C_5H_9O_{13}N_3S$ (MW 351) and the total signal from the other iSOA tracers quantified in this study.

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Table 1. Molecular formulas, negative ion masses, retention times (RT), time weighted means (ng m^{-3}) for the entire sampling period and original reference to where the tracer was found of each proposed iSOA tracer. BD = Below detection

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Isoprene Tracer	[M-H] ⁻¹	RT (min)	Time weighted mean (ng m^{-3})	Maximum (ng m^{-3})	Minimum (ng m^{-3})	Reference
C ₂ H ₄ O ₆ S	154.9656	0.73	38.4	366.1	BD	Surratt et al., 2008
C ₅ H ₁₀ O ₆ S	197.0125	0.79	28.7	336.2	0.25	Surratt et al., 2007
C ₅ H ₁₀ O ₅ S	181.0176	0.93	26.5	448.5	2.91	Nguyen et al., 2010
C ₄ H ₈ O ₆ S	182.9969	0.73	21.7	229.1	0.50	Riva et al., 2016
C ₄ H ₈ O ₇ S	198.9918	0.73	21.5	180.5	0.32	Surratt et al., 2007
C ₃ H ₆ O ₅ S	152.9863	0.73	20.5	327.9	0.98	Surratt et al., 2008
C ₃ H ₆ O ₆ S	168.9812	0.73	14.5	137.7	0.25	Surratt et al., 2008
C ₅ H ₈ O ₇ S	210.9918	0.73	14.0	136.4	0.27	Surratt et al., 2008
C ₅ H ₁₁ O ₉ NS	260.0082	0.86	12.6	154.1	0.10	Surratt et al., 2008
C ₅ H ₁₂ O ₇ S	215.0231	0.71	11.8	110.9	0.77	Surratt et al., 2008
C ₅ H ₁₀ O ₇ S	213.0075	0.73	10.6	104.7	0.38	Surratt et al., 2008
C ₅ H ₉ O ₁₀ NS	273.9874	0.94	9.17	53.8	BD	Nestorowicz et al., 2018
C ₄ H ₈ O ₅ S	167.0019	0.73	9.10	114.5	0.68	Surratt et al., 2007
C ₅ H ₈ O ₅ S	179.0020	0.85	6.59	144.2	0.43	Riva et al., 2016
C ₅ H ₁₀ O ₅ S	181.0176	1.24	4.90	36.3	1.21	Riva et al., 2016
C ₅ H ₁₀ O ₈ S	229.0024	0.75	4.59	40.9	BD	Nestorowicz et al., 2018
C ₅ H ₈ O ₉ S	242.9816	0.64	1.55	13.9	BD	Nestorowicz et al., 2018
C ₅ H ₁₀ O ₁₁ N ₂ S	304.9783	2.18	1.04	8.62	BD	Surratt et al., 2008
C ₁₀ H ₂₀ O ₈ S	299.0806	1.65	1.01	8.38	BD	Riva et al., 2016
C ₅ H ₁₀ O ₁₁ N ₂ S	304.9783	1.89	0.83	7.69	BD	Surratt et al., 2008
C ₈ H ₁₄ O ₁₀ S	301.0235	0.73	0.57	4.16	BD	Surratt et al., 2007
C ₅ H ₁₀ O ₁₁ N ₂ S	304.9783	1.56	0.42	2.90	BD	Surratt et al., 2008
C ₁₀ H ₁₈ O ₇ S	281.0701	1.03	0.33	6.76	BD	Riva et al., 2016
C ₅ H ₁₀ O ₁₁ N ₂ S	304.9783	3.60	0.31	3.32	BD	Surratt et al., 2008
C ₅ H ₉ O ₁₃ N ₃ S	349.9783	5.90	0.19	2.04	BD	Ng et al., 2008
C ₁₀ H ₁₈ O ₈ S	297.0650	0.75	0.14	5.25	BD	Riva et al., 2016
C ₅ H ₁₁ O ₈ NS	244.0133	1.93	0.11	1.46	BD	Nestorowicz et al., 2018
C ₅ H ₉ O ₁₃ N ₃ S	349.9783	5.49	0.02	0.17	BD	Ng et al., 2008
C ₅ H ₉ O ₁₃ N ₃ S	349.9783	5.34	0.008	0.10	BD	Ng et al., 2008
C ₅ H ₁₂ O ₈ S	231.0180	0.75	0.005	0.50	BD	Riva et al., 2016
C ₁₀ H ₂₀ O ₉ S	315.0755	1.46	0.002	0.21	BD	Riva et al., 2016

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Table 2. Comparison of concentrations of ISOA tracer concentrations and ratios in previous studies in the Amazon, SE USA and China. *Selected sample not an average concentration.

Location	Mean Concentration (ng m ⁻³)										Ratio low to high NO		Ratio CHO:CHOS		Reference			
China Urban, Beijing (2017)	17.3	44		91.5		SE US, Atlanta (2015)	861*	163.1										
China Rural, NCP (2013)						SE US, Look Rock (2013)												
China Regional, Beijing (2016)			5.3	2.2	1792	SE US, Look Rock (2013)	2334*	169.5	217	83(wet)/399(dry)	390*							
China Regional, PRD (2008)				7.7		SE US, Look Rock (2013)		7.5										
		19.3				SE US, Centerville (2013)												
			3.6	1.4	53	SE US, Look Rock (2013)		10	10.7	0.7(wet)/30(dry)								
	2.40	2.30		11.9		SE US, Look Rock (2013)		21.7										
	0.55		1.47	1.57	33.8	SE US, Look Rock (2013)		17.0	20.3	118(wet)/13(dry)								
	1.47			41.6		SE US, Look Rock (2013)		0.37	0.96		0.35							
	0.33			5.51		SE US, Look Rock (2013)		0.75										
This work	Li et al., 2018	Wang et al., 2018	He et al., 2018	Hettiyadura et al., 2019	Cui et al., 2018	Budlisulistiiorini et al.,	Riva et al., 2019	Glasius et al., 2018	Cui et al., 2018									