

This manuscript utilized an improved source apportionment approach that has been developed recently, binPMF, to deconvolve nitrate CI-APi-TOF mass spectra from a highly-developed, densely-populated urban region in eastern China. The authors identified factors from different sources and discussed the influence of anthropogenic and biogenic emissions. Overall, the manuscript is well written and scientifically interesting. I recommend publication after the following comments are addressed.

1. All figures have a poor resolution. Formatting issues? Please update.

Response: Thanks for the comment. We have updated all figures in the revised manuscript.

2. Equation 1: Can the authors provide more details about calibration factor determination? Are the inlet configuration and flow rate in the reference the same as these used in this work? Moreover, the reagent ion can have different sensitivities towards different compounds, and the sensitivities also vary for ions from the same species but charged in different ways. Can the authors validate the use of H₂SO₄-based calibration factor for all species and elaborate more about the potential impact on the results?

Response: Thanks for the suggestion.

The deployment of mass spectrometry in atmospheric observations has allowed us to measure thousands of molecules, but has also brought great challenges to instrument calibration. The unknown and diverse molecular structures make it impossible to provide all standard molecules to calibrate and quantify all the molecules. Therefore, we used an empirical method for quantifying OOMs based on the ionization kinetics (pseudo first order reaction approximation) in the reaction tube of the chemical ionization source (Eq. 1) (Heinritzi et al., 2016).

First, we calibrated the sulfuric acid according to the method proposed by Kuerten et al. (2012) during the observation period. Briefly, providing a known concentration of gaseous sulfuric acid by connecting the nitrate CI-APi-TOF to a well-characterized H₂SO₄ generator, and from comparisons of multiple H₂SO₄ concentrations and the signals measured by the nitrate CI-APi-TOF, a value of 4.2e9 molecules cm⁻³ for the H₂SO₄-based calibration factor C, proceeding taking into account the diffusion loss in the sampling line, was obtained. The reaction where nitrate clusters react with H₂SO₄ has proceeded at the collision limit (Viggiano et al., 1997). The uncertainty of C obtained by this method is 33% (Kuerten et al., 2012).

Standards for oxygenated organic molecules (OOMs) measurable by the nitrate CI-APi-TOF are still lacking. Quantum chemistry computations showed that at least two hydrogen bond donor functional groups are needed for an oxygenated organic molecule

to be detected in a nitrate CI-APi-TOF (Hytinen et al., 2015), and when the number of hydrogen bond donating functional groups in the target molecule is greater than or equal to 2, the binding of the target molecule to the reagent ion depends almost linearly on the number of oxygen atoms in the target molecule (Hytinen et al., 2018). Almost all OOMs analyzed in our study have oxygen numbers greater than or equal to 4, which fits the above law. Ehn et al. (2014) employed several methods, both empirical and theoretical, to estimate the sensitivity of the nitrate CI-APi-TOF to highly oxygenated organic molecules (HOMs, with oxygen numbers greater than or equal to 6). They found that the collision frequencies of $(\text{HNO}_3)_x(\text{NO}_3^-)$, $x = 0-1$, with HOMs were comparable to those of nitrate clusters with H_2SO_4 , which means that the sensitivities of nitrate clusters to H_2SO_4 and HOMs can be assumed equal. Finally, they estimated a $\pm 50\%$ uncertainty in reported concentrations of HOMs.

Although one can speculate the assumption that the instrument acquires all molecules with the same ionization efficiency may suffer uncertainties, the calibration procedure for OOMs (H_2SO_4 based calibration factor + mass-dependent transmission efficiency), as a relatively accurate method, is so far the optimized method and has been adopted in many studies (Kirkby et al., 2016a; Trostl et al., 2016; Stolzenburg et al., 2018). And to our best knowledge, there is still no way to calibrate the nitrate chemical ionization source for charging efficiency for a wide range of molecules. The sensitivity of the instrument for some moderately oxygenated organic molecules, not HOMs, are weaker than that of H_2SO_4 . Although we cannot provide an exact uncertainty of these OOMs concentration, some implications can be obtained from previous studies. Ehn et al. (2014) found that the calibration factor of perfluoroheptanoic acid was 3-4 times higher than that of H_2SO_4 in the nitrate CI-APi-TOF, and Massoli et al. (2018) found that the calibration factor of malonic acid was about 4 times higher than that of H_2SO_4 . Similarly, the concentrations of moderately oxygenated organic molecules were presumably underestimated by a factor of 4 to match the observation in the study of Trostl et al. (2016). More efforts are needed to accurately quantify these OOMs.

In summary, our calibrations lead towards a lower limit estimate of OOMs concentrations, but it is the optimized option available to our best knowledge. It should be noted that the accurate quantification of OOMs is not the main result of this study and that errors in the quantification of OOMs do not affect our conclusions.

We've rephrased the sentences about calibration in the manuscript for clarity, **line 158-181**:

Due to the diversity and unknown molecular structures of oxygenated organic compounds, standards for OOMs measurable by the nitrate CI-APi-TOF are still lacking. Like other studies have done (Kirkby et al., 2016b; Trostl et al., 2016; Stolzenburg et al., 2018), an empirical method was used to quantify the

concentrations of OOMs based on the ionization kinetics (pseudo first order reaction approximation) in the reaction tube of CI (Eq. 1) (Heinritzi et al., 2016).

$$[OOM_i] = \ln \left(1 + \frac{\sum_{n=0}^1 [OOM_i \cdot (HNO_3)_n \cdot NO_3^- + (OOM_i-H)^-]}{\sum_{n=0}^2 [(HNO_3)_n \cdot NO_3^-]} \right) \times C \times T_i \quad (1)$$

Here $[OOM_i]$ is the concentration (molecules cm^{-3}) of one OOM. On the right side of the equation, the numerator in the parenthesis is the detected total signals (ions/s) of one OOM charged by nitrate ions in forming-adduct or deprotonated ways, the denominator is the sum of all reagent ion signals (ions/s). First, a H_2SO_4 -based calibration factor C , with a value of 4.2×10^9 molecules cm^{-3} , was obtained from a calibration using H_2SO_4 (Kuerten et al., 2012) proceeding taking into account the diffusion loss in the sampling line by assuming that all detected OOMs have the same ionization efficiency as H_2SO_4 . The collision frequency of HOMs with nitrate clusters is comparable to that of sulfuric acid with nitrate clusters (Ehn et al., 2014; Hyttinen et al., 2015), yet the collision frequency of some moderately oxygenated molecules with nitrate clusters is relatively slower. Therefore, calibration by this method leads to a lower limit estimate of OOMs concentrations (Ehn et al., 2014; Trostl et al., 2016), but the accurate quantification of OOMs is not the main concern of this study and the errors in the quantification of OOMs do not change our conclusions.

3. Equation (2): Can the authors include more details of the equation, i.e. how CS is calculated, k_{OH+SO_2} value (or calculation) and source?

Response: Thanks for the suggestion. We've add these details in the revised manuscript, line 211-223:

$$[OH] = \frac{[H_2SO_4] \cdot CS}{k_{OH+SO_2} \cdot [SO_2]} \quad (2)$$

Where k_{OH+SO_2} is a termolecular reaction constant for the rate-limiting step of the formation pathway of H_2SO_4 in the atmosphere (Finlayson-Pitts and Pitts, 2000), and condensation sink (CS) is the loss rate of H_2SO_4 by condensation to aerosol surface. The value of k_{OH+SO_2} is inferred from the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (<https://iupac-aeris.ipsl.fr/>, last access: 09 August 2021). The value of CS was calculated following Eq. (3) (Kulmala et al., 2012):

$$CS = 2\pi D \sum_i \beta_{m_i} d_{p_i} N_i \quad (3)$$

Where D is the diffusion coefficient of gaseous sulfuric acid, β_m is a transition-regime correction factor dependent on the Knudsen number (Fuchs and Sutugin, 1971), and d_{p_i} and N_i are the diameter and number concentration of particles in size bin i .

4. Line 212: “the raw spectra with were...” Some words seemed missing here.

Response: We’ve re-phased these sentences in the revised manuscript, [line 239](#):

Briefly, the raw spectra were divided into narrow bins with a width of 0.006 Th after mass calibration.

5. Figure 1: Can the authors add the diurnal patterns of all parameters? The NO, temperature, and J(O¹D) diurnals were included in Figure 4 and 12, but it would be good to have a summary plot.

Response: Thanks for the suggestion. We’ve add the suggested plot in the supplement ([Fig. S1](#)).

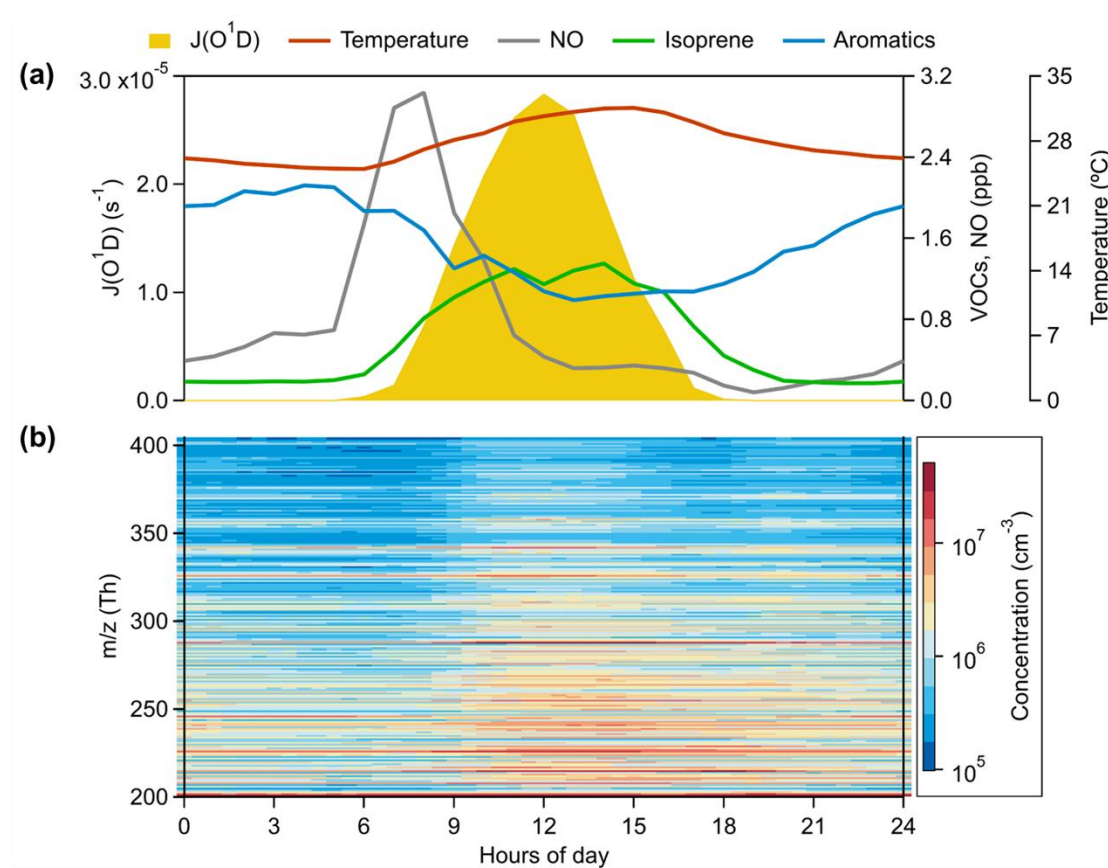


Fig. S1. Median diurnal variations of (a) J(O¹D), Temperature, NO, total aromatics (benzene + toluene + C8 aromatics + C9 aromatics + C10 aromatics + styrene), and isoprene, and (b) mass spectra of nitrate CI-APi-TOF with m/z in the range of 201-404 Th.

6. Table 1: As mentioned before, the authors may need to consider the effects of

assuming a constant ionization efficiency. How credible are the reported concentrations? Can the authors include uncertainties?

Response: As the details provided in the response of second comment, HOMs can be well measured by the nitrate CI-API-TOF with a $\pm 50\%$ uncertainty in quantification (Ehn et al., 2014). For other OOMs (moderately oxygenated organic molecules), an exact uncertainty is not available. We inferred from previous studies that these OOMs may be underestimated by a factor of 3-4 (Ehn et al., 2014; Massoli et al., 2018; Trostl et al., 2016). By the way, we did not intend to emphasize the quantitative concentrations of OOMs in this study. We've rephrased the statement as follows in the revised manuscript, **line 175-181**:

The collision frequency of HOMs with nitrate clusters is comparable to that of sulfuric acid with nitrate clusters (Ehn et al., 2014; Hyttinen et al., 2015), yet the collision frequency of some moderately oxygenated molecules with nitrate clusters is relatively slower. Therefore, calibration by this method leads to a lower limit estimate of OOMs concentrations (Ehn et al., 2014; Trostl et al., 2016), but the accurate quantification of OOMs is not the main concern of this study and the errors in the quantification of OOMs do not change our conclusions.

7. Line 341: The authors used “autoxidation” instead of “auto-oxidation” elsewhere. Please be consistent. Moreover, the diurnal pattern of Aro-OOMs almost followed that of NO, would autoxidation be suppressed?

Response: Thanks for the comment and suggestion.

First, we have uniformly used the word "autoxidation".

Second, NO does suppress autoxidation, but the reactions are supposed to be very complex. As showed in Fig. 4(f), the peak time of Aro-OOMs is later than that of NO, but overlaps with the peak time of the production rates of OH-initiated primary RO₂ from aromatics. Hence, we suggest that Aro-OOMs are mainly controlled by the photo-oxidation of aromatics, i.e., the source of RO₂, while the influence from the sink of RO₂ may be minor, e.g., RO₂ + NO.

8. Figure 8: One obvious difference between the two isoprene oxidation products from this figure is that C₅H₁₀O₈N₂ was mostly attributed to Isop-OOMs and Photo-related factors, while C₅H₉O₁₀N₃ was to Isop-OOMs and O_x & SOA-related factors. As the authors proposed that C₅H₉O₁₀N₃ was more likely to be transported than C₅H₁₀O₈N₂, does this imply that the O_x & SOA-related factor was transported?

Response: Thanks for the comment and suggestion. From the molecular formulas, we can assume that C₅H₉O₁₀N₃ is a bit more ‘aged’ than C₅H₁₀O₈N₂, but the chemical aging

processes and regional transport are not directly correlated. An air mass that stays local can also keep aging. We prefer saying that during the period of August 13 to August 17, 2019 (Fig. 8), $C_5H_9O_{10}N_3$ was almost entirely transported (**mainly from the Isop-OOMs factor**), while $C_5H_{10}O_8N_2$ has strong in situ photochemical generation (from the Photo-related factor), in addition to the source of transport (from the Isop-OOMs factor). As for the O_x & SOA-related factor, its time series (Fig. A2) seems to be composed of background concentrations (having episodes) and photochemical production (having diurnal variation). We speculate that this factor comes from the photo-oxidation process of VOCs, which produces ozone and SOA concurrently and may occur regionally. We need more observations and analysis to confirm the contribution of regional transport to the observed Isop-OOMs.

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