This paper discussed the measurements of oxygenated organic molecules (OOMs) performed in Nanjing in eastern China. A nitrate-ion-based chemical ionization mass spectrometer was used to perform these ambient measurements, and source apportionment analysis was performed using a recently developed approach positive matrix factorization on binned mass spectra (binPMF). The authors reported several factors related to anthropogenic VOCs daytime chemistry and biogenic VOCs (BVOCs) chemistry, and they discussed the influences of anthropogenic and biogenic emissions on the formation and evolution of these factors. In general, the manuscript was very well-written and the results were presented in a very clear, coherent manner. The topic is of interest to the atmospheric community. I recommend publication after the authors have addressed the following comments:

1. More details need to be provided for the quantification of OOMs (equation 1) especially since OOMs are the focus of this paper. How was equation 1 derived?

Response: Thanks for the comment.

Equation 1 was derived based on the theoretical framework for deriving concentrations of a certain compound from ion count rates for the CI-APi-TOF, and has been described in detail in the study of Heinritzi et al. (2016):

Ionization of a compound X via primary ions $P^{\pm}$ can be described by the following reaction:

$$P^{\pm} + X \xrightarrow{k} X^{\pm} + P$$
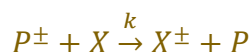
The relation between primary ion concentration $[P^{\pm}]$ and the concentration of the desired compound $[X]$ in the reaction tube of the instrument is given by the following expression, where k is the reaction rate constant for the ionization reaction:

$$\frac{d[P^{\pm}]}{dt} = -k[P^{\pm}][X]$$

Assuming $[X]$ as constant over the reaction time t (pseudo first order reaction approximation) enables a simple integration. The additional assumption that the total amount of charge is constant in the reaction tube leads to the following expression for the concentration of $[X]$:

$$[X] = \frac{1}{kt} \ ln(1 + \frac{[X^{\pm}]}{[P^{\pm}]})$$

The concentration of compound X is proportional to the ratio of concentrations of product ions $[X^{\pm}]$ and primary ions $[P^{\pm}]$. However, the mass spectrometer does not

measure the ion concentrations in the reaction chamber directly, but only ion count rates at the location of the detector of the instrument. Therefore replacing the concentrations [X$^{\pm}$] and [P$^{\pm}$] by ion count rates i(X$^{\pm}$) and i(P$^{\pm}$) is only justified if we account for the relative mass discrimination of the two ion species inside the mass spectrometer:

$$[X] = \frac{1}{kt} \; ln(1 + \; \frac{i(X^{\pm})}{i(P^{\pm})}) \cdot \frac{1}{T_X}$$

Here, T_X is the factor that describes the mass discrimination of ions $X^{\pm}$ relative to that of the primary ions $P^{\pm}$. This factor can be strongly dependent on the m/z ratio of the involved ions.

The reaction rate constants (k) for the ionization of each compound X via primary ions is hard to get. We obtain an apparent factor for $\frac{1}{kt}$ by calibrating, i.e., C.

Since this is a common quantification method for the CI-APi-TOF (Kirkby et al., 2016b; Stolzenburg et al., 2018; Trostl et al., 2016), we only summarize the main points of Eq. (1) in the manuscript and give references for the reader's further inquiry, **line 160-183**:

Like other studies have done (Kirkby et al., 2016b; Stolzenburg et al., 2018; Trostl et al., 2016), 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).

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

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$_2$SO$_4$-based calibration factor C, with a value of 4.2×10^9 molecules cm^{-3}, was obtained from a calibration using H$_2$SO$_4$ (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$_2$SO$_4$. 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. Second, a mass

2. Why did the authors assume that the detected OOMs have the same ionization efficiencies as sulfuric acid? Have they tested their assumption? What are the uncertainties that arise from using this assumption?

Response: Thanks for the comment.

The reaction of nitrate clusters with H_2SO_4 has been found to proceed at the collision limit (Viggiano et al., 1997).

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 (Hyttinen 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 (Hyttinen 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 $(HNO_3)x(NO_3^-)$, 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 ±50% uncertainty in reported concentrations of HOMs.

The sensitivity of the instrument for some **moderately** oxygenated organic molecules, not HOMs, are weaker than that of H_2SO_4. Although we cannot give an 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 was presumably underestimated by a factor of 4 to match the observation in the study of Trostl et al. (2016).

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; Stolzenburg et al., 2018; Trostl et al., 2016). 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. 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 stated this 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.

3. The authors stated that VOCs were measured using a PTR-MS. Was the data used in this paper? It was not clear to me whether and/or how the data was used to support results discussed in this paper.
Response: Thanks for the comment. We calculated the rates of RO_2 production from some VOCs (Fig. 4), and correlated the VOCs and OOMs data to explore the characterization process of OOMs (Fig. 5).

4. More details need to be provided for equation 2. How was CS calculated?
Response: Thanks for the comment, we've added these details in the revised manuscript, **line 211-223**:

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

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):

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

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.

5. Were calibrations performed during the field campaign? If no, how confident are the authors that the ionization efficiencies for their nitrate-ion-based CIMS source were constant throughout the entire sampling period?
Response: Thanks for the comment.

And we have calibrated this instrument for this observations period:

First, we calibrated the instrument for this observation according to the method proposed by Kuerten et al. (2012) during the observation period. 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 proceeding taking into account the diffusion loss in the sampling line.

Second, a mass dependent transmission efficiency Ti of APi-TOF was inferred in a separate experiment by depleting the reagent ions with several perfluorinated acids, following the method of Heinritzi et al. (2016).

6. Higher resolution figures are needed.
Response: Thanks for the comment. We have updated all figures in the revised manuscript.

Reference

Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476-479, 2014.
Finlayson-Pitts, B. J. and Pitts, J. N.: CHAPTER 8 - Acid Deposition: Formation and Fates of Inorganic and Organic Acids in the Troposphere. In: Chemistry of the Upper and Lower Atmosphere, Finlayson-Pitts, B. J. and Pitts, J. N. (Eds.), Academic Press,

San Diego, 2000.

Fuchs, N. A. and Sutugin, A. G.: High-Dispersed Aerosols. In: Topics in Current Aerosol Research, Hidy, G. M. and Brock, J. R. (Eds.), Pergamon, 1971.

Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kuerten, A., Hansel, A., and Curtius, J.: Characterization of the mass-dependent transmission efficiency of a CIMS, Atmospheric Measurement Techniques, 9, 1449-1460, 2016.

Hyttinen, N., Kupiainen-Määttä, O., Rissanen, M. P., Muuronen, M., Ehn, M., and Kurtén, T.: Modeling the Charging of Highly Oxidized Cyclohexene Ozonolysis Products Using Nitrate-Based Chemical Ionization, The Journal of Physical Chemistry A, 119, 6339-6345, 2015.

Hyttinen, N., Otkjaer, R. V., Iyer, S., Kjaergaard, H. G., Rissanen, M. P., Wennberg, P. O., and Kurten, T.: Computational Comparison of Different Reagent Ions in the Chemical Ionization of Oxidized Multifunctional Compounds, J. Phys. Chem. A, 122, 269-279, 2018.

Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, Nature, 533, 521-526, 2016a.

Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Trostl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X. M., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kurten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Perakyla, O., Piel, F., Petaja, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipila, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tome, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P. L., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, Nature, 533, 521-+, 2016b.

Kuerten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, J. Phys. Chem. A, 116,

6375-6386, 2012.

Kulmala, M., Petaja, T., Nieminen, T., Sipila, M., Manninen, H. E., Lehtipalo, K., Dal Maso, M., Aalto, P. P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K. E., Laaksonen, A., and Kerminen, V. M.: Measurement of the nucleation of atmospheric aerosol particles, Nat Protoc, 7, 1651-1667, 2012.

Massoli, P., Stark, H., Canagaratna, M. R., Krechmer, J. E., Xu, L., Ng, N. L., Mauldin, R. L., Yan, C., Kimmel, J., Misztal, P. K., Jimenez, J. L., Jayne, J. T., and Worsnop, D. R.: Ambient measurements of highly oxidized gas-Phase molecules during the Southern Oxidant and Aerosol Study (SOAS) 2013, ACS Earth and Space Chemistry, 2, 653-672, 2018.

Stolzenburg, D., Fischer, L., Vogel, A. L., Heinritzi, M., Schervish, M., Simon, M., Wagner, A. C., Dada, L., Ahonen, L. R., Amorim, A., Baccarini, A., Bauer, P. S., Baumgartner, B., Bergen, A., Bianchi, F., Breitenlechner, M., Brilke, S., Mazon, S. B., Chen, D., Dias, A., Draper, D. C., Duplissy, J., El Haddad, I., Finkenzeller, H., Frege, C., Fuchs, C., Garmash, O., Gordon, H., He, X., Helm, J., Hofbauer, V., Hoyle, C. R., Kim, C., Kirkby, J., Kontkanen, J., Kuerten, A., Lampilahti, J., Lawler, M., Lehtipalo, K., Leiminger, M., Mai, H., Mathot, S., Mentler, B., Molteni, U., Nie, W., Nieminen, T., Nowak, J. B., Ojdanic, A., Onnela, A., Passananti, M., Petaja, T., Quelever, L. L. J., Rissanen, M. P., Sarnela, N., Schallhart, S., Tauber, C., Tome, A., Wagner, R., Wang, M., Weitz, L., Wimmer, D., Xiao, M., Yan, C., Ye, P., Zha, Q., Baltensperger, U., Curtius, J., Dommen, J., Flagan, R. C., Kulmala, M., Smith, J. N., Worsnop, D. R., Hansel, A., Donahue, N. M., and Winkler, P. M.: Rapid growth of organic aerosol nanoparticles over a wide tropospheric temperature range, Proc. Natl. Acad. Sci. U. S. A., 115, 9122-9127, 2018.

Trostl, J., Chuang, W. K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L., Frege, C., Bianchi, F., Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven, J. S., Duplissy, J., Adamov, A., Almeida, J., Bernhammer, A. K., Breitenlechner, M., Brilke, S., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Gysel, M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H., Kim, J., Krapf, M., Kurten, A., Laaksonen, A., Lawler, M., Leiminger, M., Mathot, S., Mohler, O., Nieminen, T., Onnela, A., Petaja, T., Piel, F. M., Miettinen, P., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Sipila, M., Smith, J. N., Steiner, G., Tome, A., Virtanen, A., Wagner, A. C., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Carslaw, K. S., Curtius, J., Dommen, J., Kirkby, J., Kulmala, M., Riipinen, I., Worsnop, D. R., Donahue, N. M., and Baltensperger, U.: The role of low-volatility organic compounds in initial particle growth in the atmosphere, Nature, 533, 527-531, 2016.

Viggiano, A. A., Seeley, J. V., Mundis, P. L., Williamson, J. S., and Morris, R. A.: Rate Constants for the Reactions of XO3-(H2O)n (X = C, HC, and N) and NO3-(HNO3)n with H2SO4: Implications for Atmospheric Detection of H2SO4, The Journal of Physical Chemistry A, 101, 8275-8278, 1997.