Report #1

The authors characterized organic nitrates at an urban site in south China based on the measurements of aerosol mass spectrometer and volatile organic compounds (VOCs). The ratios of NO+/NO2+ and positive matrix factorization were used to estimate the concentrations of organic nitrates. The authors found that organic nitrates contribute substantial fractions of total nitrate in spring, summer and autumn, and the reactions between biogenic VOCs and NO3 radical were the major formation pathway. This manuscript is generally well written, and I have some comments below.

1. Concerning the PMF results, the authors need to show more diagnostic plots to justify the results. For example, previous study by the same group (He et al., 2011) was able to identify four OA factors in autumn at the same site, while the biomass burning OA was not resolved in this study. The spectrum of LO-OOA in autumn (Figure S1) shows clear m/z 60 and 73 signals, suggesting that more factors are needed. In addition, I would suggest the authors checking the changes in NO+, NO2+ in OA factors across different fpeak values, and give an estimation of uncertainties.

REPLY:

According to the diagnostic plots of the PMF analysis shown in Figure S2 to S4 in the supplementary, the same organic factors were obtained in PMF based on only OA spectra and OA spectra combining with NO_X^+ ions. Although the 3-factor solution for OA seemed to have a “mixed factor” problem (Zhu et al., 2018), such as HOA mixed with COA (clear $C_3H_3O^+$ in m/z 55 for spring, summer and autumn) (Mohr et al., 2012) and BBOA mixed with LO-OOA (clear m/z 60 and 73 signals in LO-OOA for autumn) (Cubison et al., 2011), running PMF with more factors would produce unexplained factors but little influence the apportion between organic nitrate and inorganic nitrate (Table S1). In addition, the uncertainties of NO^+ and NO_2^+ in OA factors across different fpeak values (from –1.0 to 1.0) were very small (Table S2). Thus, the 3-factor solution was finally used for quantifying organic nitrates in spring, summer and autumn. We have added the related description in section 2.3.

Table S1. The correlation coefficients (R) of $NO_{3,org}$ and $NO_{3,inorg}$ in 3- to 5-factors solutions estimated by PMF method with these estimated by NOx method, respectively.

		3-factor solution		**4-factor solution**		**5-factor solution**	
		$NO_{3,org}$ (NOx vs. PMF)	$NO_{3,inorg}$ (NOx vs. PMF)	$NO_{3,org}$ (NOx vs. PMF)	$NO_{3,inorg}$ (NOx vs. PMF)	$NO_{3,org}$ (NOx vs. PMF)	$NO_{3,inorg}$ (NOx vs. PMF)
Spring	R	0.82	0.92	0.81	0.90	0.80	0.91
	Slope	1.21	0.76	1.15	0.78	1.20	0.82
Summer	R	0.82	0.87	0.82	0.88	0.81	0.90
	Slope	1.53	0.70	1.50	0.65	1.45	0.64
Autumn	R	0.77	0.86	0.75	0.85	0.76	0.83
	Slope	0.81	0.85	0.76	0.82	0.75	0.78

Table S2. The mass fraction of NO^+ and NO_2^+ in OA factors when fpeak is 0 and the uncertainties of NO^+ and NO_2^+ in OA factors across different fpeak values (from –1.0 to 1.0)

			HOA	**LO-OOA**	**MO-OOA**
Spring	NO^+	fpeak=0	$1.3*10^{-2}$	$1.4*10^{-2}$	$9.8*10^{-3}$
		uncertainty	3.4%	1.4%	6.8%
	NO_2^+	fpeak=0	$1.2*10^{-2}$	$1.5*10^{-4}$	$3.0*10^{-8}$
		uncertainty	8.5%	3.8%	4.3%
Summer	NO^+	fpeak=0	$1.5*10^{-2}$	$1.0*10^{-2}$	$1.2*10^{-2}$
		uncertainty	1.5%	5.1%	3.0%
	NO_2^+	fpeak=0	$1.47*10^{-6}$	$6.7*10^{-4}$	$1.8*10^{-3}$
		uncertainty	4.8%	6.9%	4.0%
Autumn	NO^+	fpeak=0	$1.1*10^{-2}$	$3.1*10^{-2}$	$1.0*10^{-2}$
		uncertainty	4.5%	0.5%	1.2%
	NO_2^+	fpeak=0	$7.0*10^{-8}$	$9.8*10^{-8}$	$2.8*10^{-7}$
		uncertainty	0.6%	1.9%	1.2%

2. High NO+ signal and NO+/NO2+ ratio were also observed in HOA spectrum, are they organic nitrates from direct emissions or some other sources. Please calculate the mass fractions of organic nitrates in three OA factors. A major fraction would be expected in LO-OOA, and not surprisingly, organic nitrates were well correlated with LO-OOA.

REPLY:

The mass fraction of organic nitrates in HOA, LO-OOA and MO-OOA was 31%, 49% and 20%, respectively, in spring; 28%, 52% and 20%, respectively, in summer; 30%, 46% and 24% in HOA, LO-OOA and MO-OOA, respectively, in autumn. We have added this statement in section 3.1.

3. The authors calibrated AMS every two weeks, could the authors show the NO+/NO2+ ratio for each calibration to check the stability of the instrument.

REPLY:

In this study, R_{NH4NO3} was determined by IE calibration using pure NH_4NO_3 on every two weeks for each campaigns and the results show stable values: In spring, the average R_{NH4NO3} was 2.66 for the first IE calibration and 2.94 for the second IE calibration; in summer, the average R_{NH4NO} was 3.05 and 3.34 for the first and second IE calibration, respectively; in autumn, the average R_{NH4NO3} was 3.33 and 3.31 for the first and second IE calibration, respectively; in winter, the average R_{NH4NO3} was 3.45 and 3.51 for the first and second IE calibration, respectively. We have added this in section 2.3.

4. In the abstract and conclusions, the authors highlight the importance of organic nitrates using its

contribution in total nitrates. I would suggest the authors using the mass fractions of organic nitrates in total OA. In addition, could the authors compare the mass concentrations of organic nitrates with previous studies in Pearl River Delta?

REPLY:

We have amended the description in the abstract and conclusions according to this comment. According to the best of our knowledge, no literature has reported the mass concentrations of organic nitrates in Pearl River Delta region, but we have added section 3.5 to compare the organic nitrates in this study to other similar studies across the world.

5. I suggest the authors adding the time series of non-refractory aerosol species during three seasons in supplementary. This is good for readers to evaluate the sources of organic nitrates. For example, the time series of organic nitrates in spring in Figure 2(a) showed clear plumes, which were very likely from regional transport. Without showing other aerosol species, it is hard to tell.

REPLY:

We have added the time series of non-refractory aerosol species in Figure S1 in the supplementary.

6. A more detailed description of VOC measurements is needed in experimental methods.

REPLY:

We have added the related description in section 2.2.2. “In the spring campaign, ambient VOC concentrations were also measured using an on-line VOC monitoring system (TH-300B, Tianhong Corp.), including an ultralow-temperature preconcentration cold trap and an automated in-situ gas chromatograph (Agilent 7820A) equipped with a mass spectrometer (Agilent 5977E). The system had both a flame ionization detector (FID) gas channel for C2–C5 hydrocarbons and a mass spectrometer (MS) gas channel for C5–C12 hydrocarbons, halohydrocarbons and oxygenated VOCs. A complete working cycle of the system was one hour and included five steps: sample collection, freeze-trapping, thermal desorption, GC-FID/MS analysis, heating and anti-blowing purification. The sample collection time was 5 min, the sampling flow was 60 ml min-1, and the anti-blowing flow was 200 ml min-1. The calibration of over 100 VOCs was performed using mixed standard gas before and after the campaign. Detection limits for most compounds were near 5pptv. More description of this instrument can be found in Wang et al. (2014).”

7. Spell out “VOCs” in the abstract, and show slopes in Figure 2(b).

REPLY:

We have amended it and the slopes were given in Table S1.

References

Wang, M.; Zeng, L.; Lu, S.; Shao, M.; Liu, X.; Yu, X.; Chen, W.; Yuan, B.; Zhang, Q.; Hu, M.; Zhang, Z.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, 6, (23), 9424-9434. Analytical Methods, https://doi.10.1039/C4AY01855A, 2014.