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Supplement of

Measurement report: Online measurement of gas-phase nitrated phenols utilizing a CI-LToF-MS: primary sources and secondary formation

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Figures

**Figure S1.** Chemical structures and high-resolution peak fits of reagent ions and nitrated phenols (NPs) investigated in this study.

**Figure S2.** (a) Background ions and ions detected during the calibration period (calibrated at the end of the campaign, on Jan 26, 2019); (b) Calibration line of ions (y) and the standard gas-phase concentration of nitrophenol (x). The signals were normalized by reagent ions (NO$_3^-$ ($\text{HNO}_3$)$_{0.2}$).

**Figure S3.** The measured concentration of nitrated phenols and their secondary formation simulation by the box model in different model scenarios.

**Figure S4.** Air quality and meteorology conditions during the sampling period in Beijing: time series of (a) wind speed, (b) RH, (c) PM$_{2.5}$, (d) NO$_y$ and (e) CO from Dec 1 to Dec 31, 2018.

**Figure S5.** Consensus maps of brunet, KL, offset, lee, nsNMF and snmf/l algorithms in NMF. The consensus approach was used to estimate the proper method and cluster method of simulation. The color of the consensus map indicated the coefficient and an ideal consensus map was a color-coded heat map in which red blocks along the diagonal on a blue background (Monti et al., 2003; Simpson et al., 2010). KL approach was the optimal one.

**Figure S6.** NMF rank survey of factors 3 to 7. The cophenetic coefficient and RSS curves were used for the judgment of factor numbers. The first decreasing cophenetic value (Brunet et al., 2004) and an inflection point of the RSS curve (Hutchins et al., 2008) was the optimal factor number, that was, four factors in this study.

**Figure S7.** Diurnal profiles of coal combustion (a), biomass burning (b), industry (c) and vehicle exhaust (d) sources. Coal combustion and biomass burning displayed a nighttime peak while the source of vehicle exhaust showed peaks at rush hour which were evidence of the NMF source apportionment.

**Figure S8.** Source profile from the PMF model. (a) Source profile of PMF results. SO$_2$, chloromethane, aromatics and 1,3-butadiene as the markers of coal combustion,
biomass burning, industry and vehicle exhaust sources. (b) Contribution of primary emission (in dark blue borderline) and second formation (in red borderline) of NPs.

Figure S1. Chemical structures and high-resolution peak fits of reagent ions and nitrated phenols (NPs) investigated in this study.
Figure S2. (a) Background ions and ions detected during the calibration period (calibrated at the end of the campaign, on Jan 26, 2019); (b) Calibration line of ions ($y$) and the standard gas-phase concentration of nitrophenol ($x$). The signals were normalized by reagent ions (NO$_3^-$, HNO$_3$). Yuan et al. calibrated nitrophenol (NP), methyl nitrophenol (MNP) and dinitrophenol (DNP) in the previous study utilizing nitrate-CIMS. The sensitivity of NP, MNP and DNP were 13.2, 16.6, 10.3 nps ppt$^{-1}$, respectively (Yuan et al., 2016). The sensitivities of MNP and DNP ranged -26% and 22% from NP. Rebecca H. Schwantes et al. estimated sensitivity factors for CIMS operated in both negative and positive mode using CF$_3$O$^-$ and H$_3$O·(H$_2$O)$^+$. The estimated sensitivities of o-nitrophenol, 3-nitrocatechol, 4-methyl-2-nitrophenol were 1.48, 1.16 and 1.69, respectively. The sensitivities of NC and MNP ranged 22% and -14% from NP (Schwantes et al., 2017). Even though uncertainties remain, the addressed NPs calibrated by NP were correct in concentration levels and magnitudes. Besides, the secondary formation process simulated by the box model is constrained only by precursors of NPs measured by online GC-MS rather than the actual concentrations of NPs. NMF model might be influenced by the uncertainties in the quantification.
However, the high time resolution of CIMS increased sample inputs of the NMF model and reduced the uncertainties for this statistical approach. Even though the actual contrition of sources faces uncertainties, the proportion of source profiles is still reliable in this approach.

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