Supplement of Atmos. Chem. Phys. Discuss., 15, 28659–28697, 2015
http://www.atmos-chem-phys-discuss.net/15/28659/2015/
doi:10.5194/acpd-15-28659-2015-supplement

Supplement of

Secondary formation of nitrated phenols: insights from observations during the Uintah Basin Winter Ozone Study (UBWOS) 2014

B. Yuan et al.

Correspondence to: B. Yuan (bin.yuan@noaa.gov)

1. Sensitivities of phenols in PTR-TOF

The sensitivities of VOC species X (S_X) in PTR-TOF are calculated as:

$$S_X = S_Y \times \frac{k_X}{k_Y} \qquad (1)$$

Here, S_Y is sensitivity of the surrogate species Y, which has a comparable mass in PTR-ToF as the species X. k_X and k_Y are the rate coefficients of the proton transfer reaction between the hydronium ion (H_3O^+) and X (or Y), respectively.

Table S1. Determination of sensitivities of phenols from the calibrated aromatic compounds

Target species			Surrogate species		
Name	k^b, 10^{-9} cm^3 molecule^{-1} s^{-1}	Sensitivity, ncps/ppb	Name	k, 10^{-9} cm^3 molecule^{-1} s^{-1}	Sensitivity, ncps/ppb
Phenol	2.18	23.0	Toluene	2.08	21.9
Cresol	2.30	25.7	C8-aromatics	2.26	25.2
DMP[a]	N/A	21.7	C9-aromatics	2.40	21.7

a: DMP indicates dimethylphenols.

b: Proton transfer reaction rate coefficients between the hydronium ion (H_3O^+) and selected VOCs (Cappellin et al., 2012).

2. Gas-particle partitioning

The fraction in particles (F_p) for a species X can be expressed as:

$$F_p = \frac{c_p}{c_g + c_p}$$

where c_g and c_p are concentrations of the species in the gas phase and particle phase, respectively. F_p can be calculated based on equilibrium absorption partitioning theory:

$$F_p = (1 + \frac{C^*}{C_{OA}})^{-1}$$

where C_{OA} is the concentrations of organic aerosol (OA). C^* is the effective saturation mass concentration, which is calculated as:

$$C^* = \frac{M 10^6 \zeta P_V}{760RT}$$

where M (g mol^{-1}) is the molecular weight of the species, P_V is vapor pressure in Torr. ζ is the activity coefficient of the species in the OA mixture (assumed =1). R is the gas constant (8.2×10^{-5} m^3 atm K^{-1} mol^{-1}). T is ambient temperature in K.

The dependence of vapor pressure is accounted for using the Clausius-Clapeyron relationship with reported enthalpies of evaporation (ΔH_{vap}) (Schwarzenbach et al., 1988).

$$P_V = P_{V,0}\exp\left[\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]$$

where P_V (Torr) and $P_{V,0}$ (Torr) is vapor pressure of the species at temperature T (K) and at reference temperature T_0 (K), respectively.

The uptake rate (R_{in}) and volatilization rate (R_{out}) of a gas phase species by particles with radius r are approximated by (Jacob, 2000):

$$R_{in} = \left(\frac{r}{D_g}+\frac{4}{\upsilon\alpha}\right)^{-1} A\times c_g$$

$$R_{out} = \left(\frac{r}{D_g}+\frac{4}{\upsilon\alpha}\right)^{-1} A\times \frac{c_p}{K_{ep}}$$

where D_g is the gas-phase molecular diffusion coefficient (m^2 s^{-1}), υ is the mean molecular speed (m s^{-1}), α is the mass accommodation coefficient, A is the aerosol surface area per unit volume of air (m^2 m^{-3}). K_{ep} is the equilibrium constant, i.e. c_p/c_g, or $(1-F_p)/F_p$. The characteristic time scales of mass transfer are of the order minutes for particles in the troposphere (Bowman et al., 1997;Jacob, 2000). Here, we assume that the equilibrium is maintained at each model step (5 min).

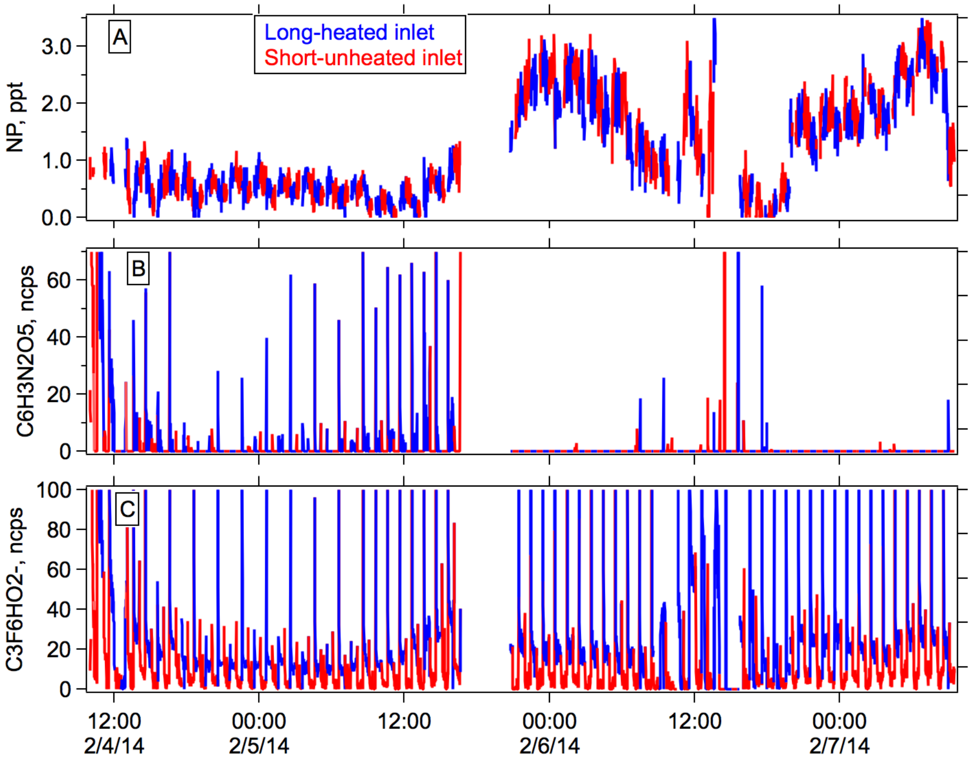

Fig. S1. Comparison of concentrations of NP (A) and the signals of $C_6H_3N_2O_5^-$ (m/z 183.0047, the masses for DNP) (B) and $C_3F_6HO_2^-$ (m/z 182.9886) (C) measured from a long-heated inlet and a short-unheated inlet. The spikes when switching to the other inlet in B and C were also observed for some fluorine ions in the acetate CIMS (e.g. m/z 112.9856 $C_2F_3O_2^-$, m/z 143.9840 $C_3F_4O_2^-$ and m/z 162.9824 $C_3F_5O_2^-$), which were believed to be Teflon impurity (Veres et al., 2010).

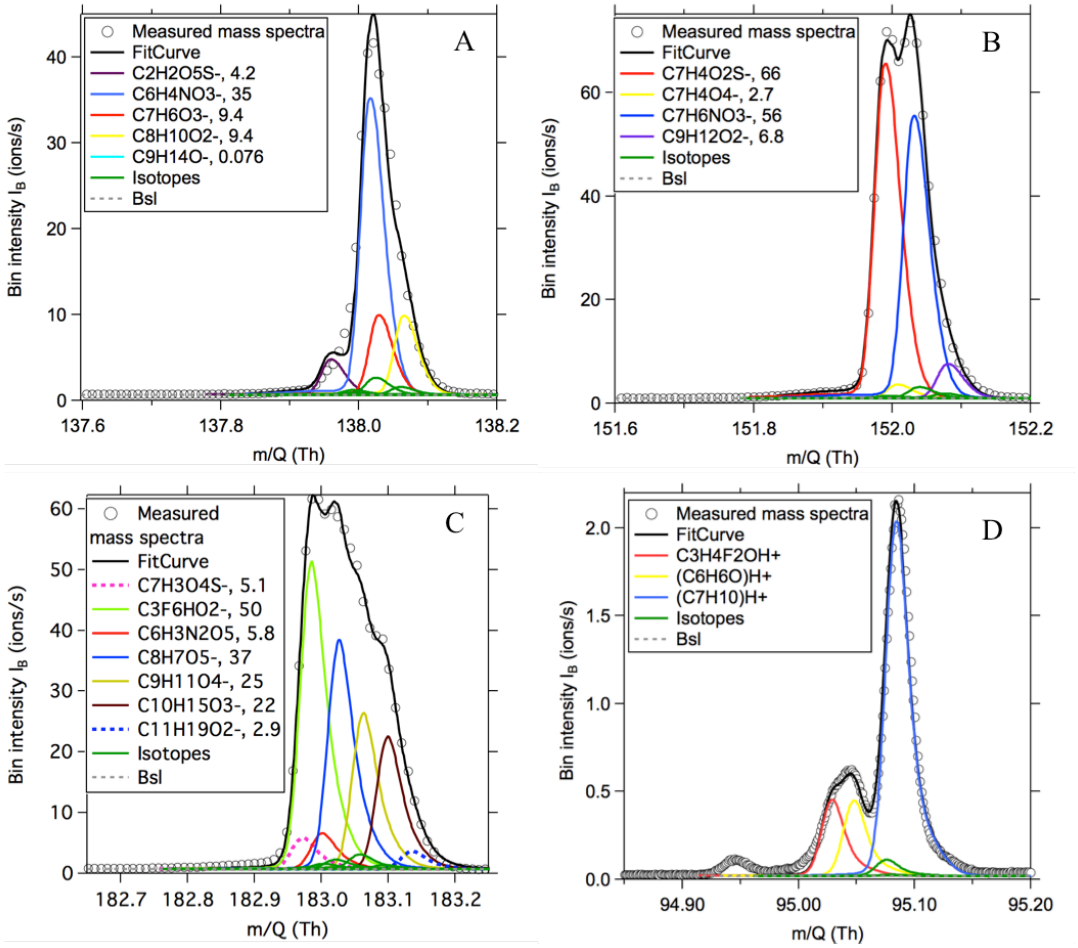

Figure S2. High-resolution peak fitting to the mass spectra of m/z 138 (A), m/z 152 (B) and m/z 183 (C) collected by Acetate CIMS and m/z 95 (D) collected by PTR-TOF on a typical day (January 25, 2014) during UBWOS 2014 campaign.

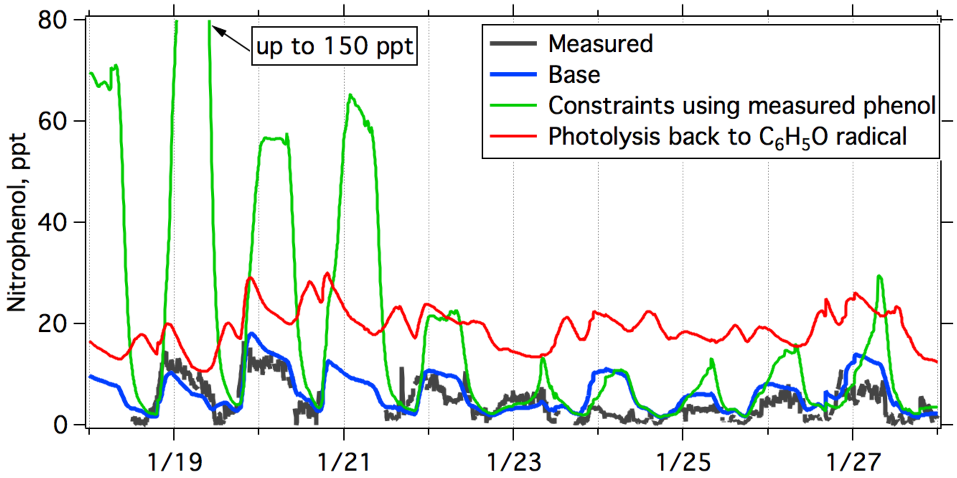

Figure S3. Comparison of measured and modeled time series of NP from the base simulation, a simulation using measured phenol concentrations as constraints, and a simulation assuming photolysis of NP generates C_6H_5O radicals.

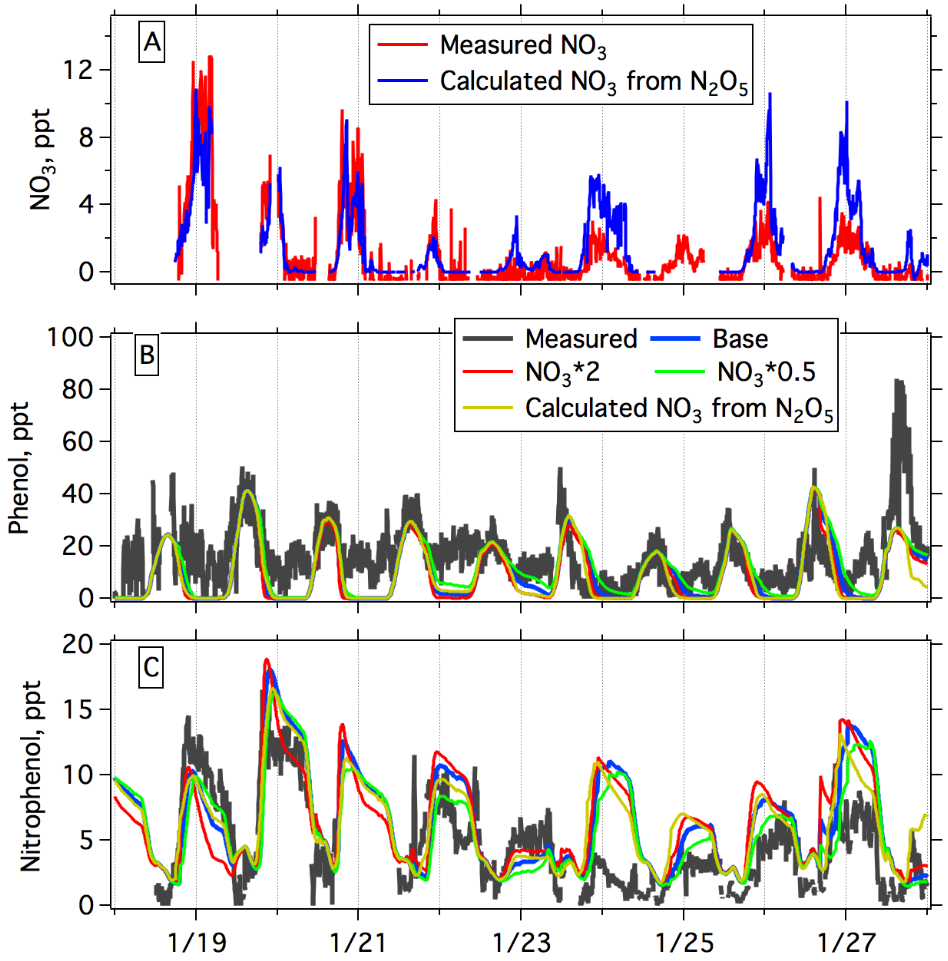

Fig. S4. (A) Time series of measured NO_3 concentrations and NO_3 concentrations calculated from the equilibrium between N_2O_5 and NO_3 (Brown et al., 2003). (B and C) Comparison of measured and modeled time series of phenol (B) and NP (C) from the base simulation, and simulations using constraints by varying measured NO_3 concentrations by a factor of 2 and using predicted NO_3 concentrations from N_2O_5 concentration as constraints.

Reference:

Bowman, F. M., Odum, J. R., Seinfeld, J. H., and Pandis, S. N.: Mathematical model for gas-particle partitioning of secondary organic aerosols, Atmospheric Environment, 31, 3921-3931, http://dx.doi.org/10.1016/S1352-2310(97)00245-8, 1997.

Brown, S. S., Stark, H., and Ravishankara, A. R.: Applicability of the steady state approximation to the interpretation of atmospheric observations of NO3 and N2O5, J. Geophys. Res., 108, doi: 10.1029/2003jd003407, 10.1029/2003jd003407, 2003.

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Mark, T. D., Gasperi, F., and Biasioli, F.: On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry, Environ Sci Technol, 46, 2283-2290, 10.1021/es203985t, 2012.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmospheric Environment, 34, 2131-2159, http://dx.doi.org/10.1016/S1352-2310(99)00462-8, 2000.

Schwarzenbach, R. P., Stierli, R., Folsom, B. R., and Zeyer, J.: Compound properties relevant for assessing the environmental partitioning of nitrophenols, Environmental Science & Technology, 22, 83-92, 10.1021/es00166a009, 1988.

Veres, P., Roberts, J. M., Burling, I. R., Warneke, C., de Gouw, J., and Yokelson, R. J.: Measurements of gas-phase inorganic and organic acids from biomass fires by negative-ion proton-transfer chemical-ionization mass spectrometry, J. Geophys. Res., 115, doi:10.1029/2010JD014033, 10.1029/2010jd014033, 2010.