Response to Reviewers' Comments

We thank both reviewers for their careful reading of the manuscript and for their useful insights. Below, the comments from the reviewers are shown in black. The responses to the comments are shown in blue and the changes to the manuscript are shown in bold blue.

Anonymous Referee #1

In this work, the authors used a new analytical technique that allows for high time resolution and sensitive measurements of nitrated phenols in the gas phase. The measurement technique is based on time of flight chemical ionization mass spectrometry (ToF-CIMS) with acetate as the reagent ion. The sampling was conducted in winter of 2014 at the Horse Pool site in the Uintah Basin. The authors combined the measured diurnal profile of nitrophenols with box model simulations to provide insight into the generation and removal pathways of the nitrophenols. Overall, this is a nice manuscript that demonstrates the ability of the techniques to measure low level of nitrated VOCs and improve our understanding of their evolution in the atmosphere. The manuscript is recommended for publication. More detailed comments follow below:

Reply: We would like to thank the reviewer for these valuable comments.

1. P15, L2 Different vapor pressures for 2,4-dinitrophenol and 4-nitrophenol were reported in the literature (Mackay et al., 2006) with values ca. 2 orders of magnitude lower than in Schwarzenbach et al. (1988), this might explain the difference in the calculated fraction of nitrophenols in the particle phase in this work and the experimental data for 4-NP (Cecinato et al., 2005) and DNP (Morville et al., 2006).

Reply: We checked all of the vapor pressure values for 4-nitrophenol and 2,4-dinitrophenol compiled from various literatures sources in Mackay et al. (2006). The differences among the values listed in Mackay et al. (2006) are partially due to the different vapor pressures for solid and sub-cooled liquid at the same temperature. For the ideal gas-particle absorption partitioning theory, vapor pressure of sub-cooled liquid should be used (Yatavelli et al., 2014). The solid vapor pressure $p_s(T)$ and sub-cooled liquid vapor pressure $p_L(T)$ at temperature T are related as (Cappa et al., 2008):

$$ln\frac{p_L(T)}{p_s(T)} = \frac{\Delta S_{fus}}{R}(\frac{T_m}{T} - 1)$$

where, ΔS_{fus} is the entropy of fusion (60.1 J/mol*K for 4-nitrophenol and 62.3 J/mol*K for 2,4-dinitrophenol from the NIST Chemistry WebBook), T_m is the melting temperature (385 K for 4-nitrophenol and 388 K for 2,4-dinitrophenol from the NIST Chemistry WebBook), and R is the gas constant. At 298 K, $\frac{p_L(T)}{p_s(T)}$ for 4-nitrophenol and 2,4-dinitrophenol are 8.25 and 9.61, respectively. After correcting all of the solid vapor pressures to sub-cooled liquid vapor pressures in Mackay et al. (2006) and considering the different vapor pressures at different temperatures (e.g. 20 °C vs. 25 °C), the values agree with each other within a factor of 5 for the two compounds.

Moreover, we found that most of the values listed in Mackay et al. (2006) are cited from previous estimates or compilations in various handbooks or databases. Schwarzenbach et al. (1988) provides the only direct measurement for 4-nitrphenol. In addition to Schwarzenbach et al. (1988), the other measurement result for 2,4-dinitrophenol was from Hoyer and Peperle (1958). This early measurement (Hoyer and Peperle, 1958) was published in German and we have no clue on the robustness of the reported solid vapor pressure due to the language barrier. Schwarzenbach et al. (1988) reported the direct measurements of the sub-cooled vapor pressures of 4-nitrophenol, 2,4-dinitropenol and other nitrated phenols at different temperatures. Thus, Schwarzenbach et al. (1988) provides the most comprehensive results for the vapor pressures of nitrated phenols and is preferred to be used in this study. We agree with the reviewer that the measurements in Schwarzenbach et al. (1988) may need additional validation from other independent measurements. We added the information in the revised manuscript.

Although vapor pressures from Schwarzenbach et al. (1988) might have significant uncertainties, Schwarzenbach et al. (1988) provided the only comprehensive measurements of sub-cooled liquid vapor pressures of nitrated phenols reported in the literature.

2. P11 L25 Which hydrocarbons were measured and used for the simulation. It would be nice to show a table in the supplement with characteristic concentrations.

Reply: We added a table in the supplement (Table S2) to show the averages and standard deviations of measured concentrations of VOCs, NOx and ozone, which were used for constraints in the box model simulations in Jan. 18-Jan. 27 during UBWOS 2014 campaign.

3. P12L10. What was the assumption with respect to an emission rate of benzene?

Reply: Benzene was mainly emitted from oil and gas activities during the UBWOS campaigns. The variations of emission rates of benzene, CH_4 and other VOCs at different time of the day are expected to be small (Koss et al., 2015). Thus, the lower concentrations of benzene and CH_4 in the afternoon indicate a higher physical loss rate (i.e. dilution) at this time of day, in accordance with previous modeling studies for the UBWOS campaigns (Edwards et al., 2014;Yuan et al., 2015).

4. P13 L25 Vinylfuran was detected in biomass burning (Stockwell et al., 2015), but very low BB influence was claimed in this study. What is the source of vinylfuran and why is it not present in the daytime?

Reply: Vinylfuran has the same molecular formula as phenol. We suspect vinylfuran might be an interference for phenol measurements and it may account for the difference between measured and modeled phenol concentrations. However, we have no information from the measurements for the source of this potential interference.

5. **(A)** Perhaps the online GC-MS used in this study can give some insight on the interference at mass 138.

Reply: The comment #5 is a long comment. We have divided the comment into six small comments (A-F) (see below) and we will deal with them one by one.

(A) We would like to clarify that there is no evidence for an interference to the NP measurement at mass 138 of the acetate ToF-CIMS during UBWOS 2014.

(B) The C3H4F2OH+ ion that overlaps with the phenol peak (Fig. 2d) looks a little unusual. Does it come from the heated Teflon inlet? It would be useful to show the zero air signal with this ion to demonstrate this.

Reply: We checked the instrument background signals of $C_3H_4F_2OH^+$ ion in PTR-TOF. The background signals decreased gradually during the measurements period. The

ambient signals of $C_3H_4F_2OH^+$ were not significantly larger than the instrument background. Taken together, we believe $C_3H_4F_2OH^+$ signals were the result of continuous fluxes from instrument walls. As no inlet switching was performed for PTR-TOF during UBWOS 2014, it is not possible to determine whether it is solely from sampling inlet.

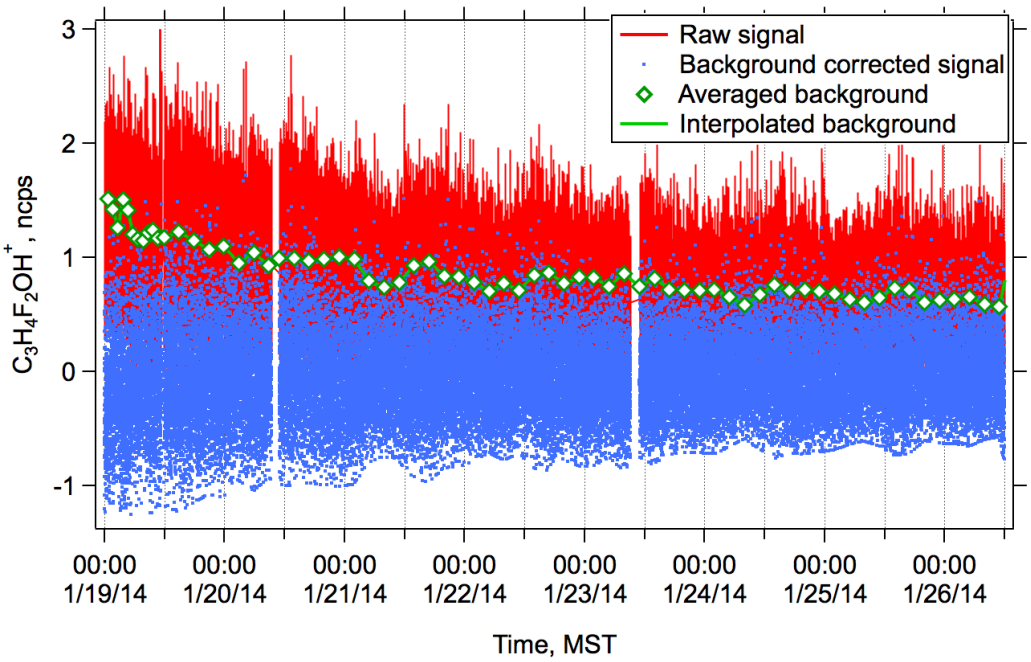

Figure R1. Time series of the raw signals, averaged background signals, interpolated background signals and background-corrected signals for the $C_3H_4F_2OH^+$ ion in PTR-TOF during UBWOS 2014. The background-corrected signal is symmetrically scattered around zero, indicating no measurable signal in ambient air.

(C) Figure S2a, b, c show a large number of radical species measured. Since the acetate ionization technique is a soft method, some explanation is necessary about the source of these radicals. Is it because of the strong voltage used in the declustering region?

Reply: The ions observed in acetate CIMS are mainly from the proton abstraction of the targeted acids. Ions without deprotonation were also observed at low intensities in acetate TOF-CIMS. Examples for this are the ions with only C, H and O in the formula (e.g. $C_8H_{10}O_2^-$ at m/z 138) at even masses. These ions without deprotonation are believed to be from electron transfer reactions and/or fragmentation (Stark et al., 2015). We do not expect that atmospheric radicals contributed significantly to the signals of the ions without deprotonation.

(D) It would be useful to show the peaks at m/z 137 along with the peaks at m/z 138 in figure 2a in order to show that the peaks at 138 are not the C13 isotopes.

Reply: The isotopes from lower masses were always taken into account in the high-resolution peak fitting to the mass spectra in UBWOS 2014. The isotope signals from lower masses are shown as dark green curves in Figure 2 in the revised manuscript (also in Figure R2 below). These isotope signals were subtracted from the measured signals at each m/z, and then peak fitting to the mass was performed (Stark et al., 2015). Based on Figure 2 in the revised manuscript, isotope signals from lower masses only accounted for minor fractions of the measured signals at m/z 138 and other m/z in revised Figure 2.

(E) According to P8 L26 the error in peak fitting was 0-10%, according to figure S2 the DNP peak area account for about 3% of the whole peak area at m/z 183 (DNP peak height 10% from the total peak height and peak width about 1/3 of the total peak width), therefore the area of the DNP peak is below the accuracy of the peak fitting. Some additional explanation about the accuracy of the peak fitting is needed.

Reply: The mass spectrum of m/z 183 shown in Figure 2 (C) of the revised manuscript (also Figure R2 C) are the average from January 25, 2015, when the interference of DNP from $C_3F_6HO_2^-$ ions was significant. The averaged mass spectrum of m/z 183 from Jan. 18, when the interference from $C_3F_6HO_2^-$ ions was small, is shown in Figure R2 (D). The errors of ion signals from HR peak fitting are dependent on the ratios of ion signals relative to its neighboring peaks (Cubison and Jimenez, 2015). It is clear that the ratios of the DNP signal ($C_6H_3N_2O_5^-$) to $C_3F_6HO_2^-$ signal on Jan. 18 was much larger than those in Jan. 25. Thus, only DNP measurements in Jan. 18-22 were used for the analysis in this study.

The precision and accuracy of peak fitting are affected by the ratios between the targeted peaks and their neighboring peaks. Smaller ratios of the signals between the targeted peak and its neighboring peaks have been shown to deteriorate the precision of fitted signals for the targeted peak (Cubison and Jimenez, 2015;Müller et al., 2011;Corbin et al., 2015). Based on the reviewers' comments, a more detailed discussion on peak-fitting uncertainties is added to the revised manuscript (see revisions after the response to

comment 5F).

(F) Figure 7 shows that the measured DNP concentration sometimes has a negative value, is it an artifact from the peak fitting procedure or background subtraction? Does the DNP peak area correlate with the area of the C8H7O5- peak?

Reply: Negative values of DNP concentration in Figure 8 in the revised manuscript (Figure 7 in ACPD version) are due to background subtraction. The peak fitting by definition only returns positive values for different product ion signals. Averaging over a longer time would reduce the variations of concentrations at low levels.

Based on the collective reviewers' comments, we have expanded the discussion of peak-fitting in Section 2, including mass calibration and its error, interpretation of the mass spectra, discussions on the uncertainty of the fitted signals. The inlet issue for DNP presented in Section 3.3 is also moved to this part. A graph showing the sensitivity of fitted ion intensities to mass calibration errors is also included in the supplement (Figure S2). The added or modified paragraphs are:

Post-measurement mass calibrations were performed using nine isolated ions, including m/z 31.9904 (O_2^-), m/z 34.9694 (Cl^-), m/z 44.9982 (CHO_2^-), m/z 59.0139 ($C_2H_3O_2^-$), m/z 61.9884 (NO_3^-), m/z 143.9840 ($C_3F_4O_2^-$), m/z 162.9824 ($C_3F_5O_2^-$), m/z 193.9808 ($C_4F_6O_2^-$) and m/z 243.9776 ($C_5F_8O_2^-$). The four fluorine-containing ions in the list were released from Teflon inlet during UBWOS 2014 and their persistent presence was used for mass calibration. The accuracy of mass calibration was 4.7±1.9 ppm for the whole campaign and the errors of mass calibration for individual ions were usually within 10 ppm (average+3σ).

High-resolution (HR) peak fitting to m/z 138, m/z 152 and m/z 183 in the averaged mass spectra of ToF-CIMS on a typical day (January 25, 2014) are shown as examples in Figure 2. Isotope signals from lower masses (dark green lines) accounted for small fractions of the m/z signals. Multiple overlapping ion peaks were identified in the m/z channels. In addition to nitrated phenols, several ions without deprotonation were also present in the even m/z (e.g. $C_8H_{10}O_2^-$ at m/z 138), possibly due to electron transfer reactions and/or fragmentation in the quadrupole

ion guides (Stark et al., 2015). The signals of NP and MNP were either the largest or significant larger than their neighboring peaks at their respective m/z, whereas the signal of DNP was much smaller than its neighboring peaks on January 25, 2014. Smaller ratios of the signals between the targeted peak and its neighboring peaks have been shown to deteriorate the precision of fitted signals for the targeted peak (Cubison and Jimenez, 2015;Müller et al., 2011;Corbin et al., 2015). Based on the provided equations in Cubison and Jimenez (2015), the imprecision arising from mass calibration (not including counting error) for the signals of NP, MNP and DNP are 3.2%, 1.8% and 47% based on the mass spectra of January 25, respectively. Imperfect mass calibration can also affect fitted magnitudes of ion signals. Figure S2 shows the sensitivity of the fitted signals of various masses as a function of the errors in mass calibration. The signal changes at a 10 ppm (average+3σ) error of mass calibration relative to perfect mass calibration (error=0 ppm) for NP, MNP and DNP signals are as high as 14%, 5% and 81%, respectively. The results from both precision calculation and sensitivity of fitted magnitudes indicate that the peak signals of NP and MNP can be fitted well with low uncertainties. The peak fitting at m/z 166 for DMNP shows similar results as m/z 138 for NP and m/z 152 for MNP. However, large uncertainties are associated with the peak signals of DNP on January 25, 2014, which is mainly affected by the $C_3F_6HO_2^-$ ions (m/z 182.9886) as indicated by the opposite behaviors of the DNP ion and $C_3F_6HO_2^-$ ion in Figure S2C.

The $C_3F_6HO_2^-$ ion (m/z 182.9886) was released from the heated Teflon inlet along with other fluorine-containing ions that were used for mass calibration. The release of $C_3F_6HO_2^-$ ion was supported by much higher signals from the long-heated inlet compared to the short-unheated inlet, when inlet-switching experiments were conducted in February 2-5 (Figure S1). Long-heated inlets were used for most of the time during UBWOS 2014 (January 23- February 13), except during January 18-22, when a short-unheated inlet was used. The averaged mass spectra of m/z 183 measured on January 18 is shown in Figure 2D. Compared to the mass spectra on January 25, $C_3F_6HO_2^-$ signals on January 18 were lower and the signals of DNP were larger than of $C_3F_6HO_2^-$ ions. As a result, the uncertainty from peak fitting for the DNP ion was much lower on January 18 (Figure S2D). Thus, we will only use

measured DNP data in the beginning of the campaign (January 18-22), when the long heated inlet was not connected to the acetate CIMS and no inlet switching was performed.

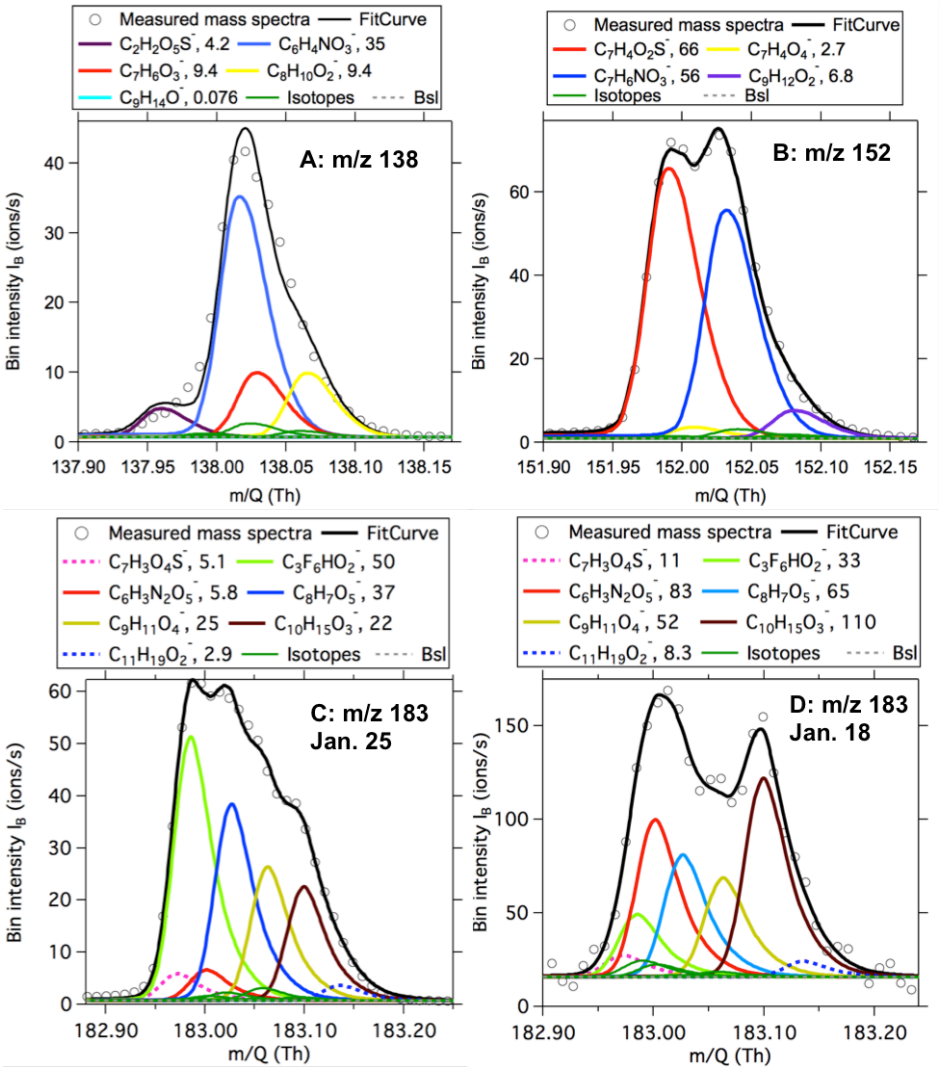

Figure R2 (Figure 2 in the revised manuscript). High-resolution peak fitting to the averaged mass spectra of acetate ToF-CIMS for m/z 138 (A), m/z 152 (B) and m/z 183 (C) on January 25, 2014 and m/z 183 (D) on Jan. 18, 2014 during UBWOS 2014. The dark green lines indicate the calculated isotope signals from lower masses.

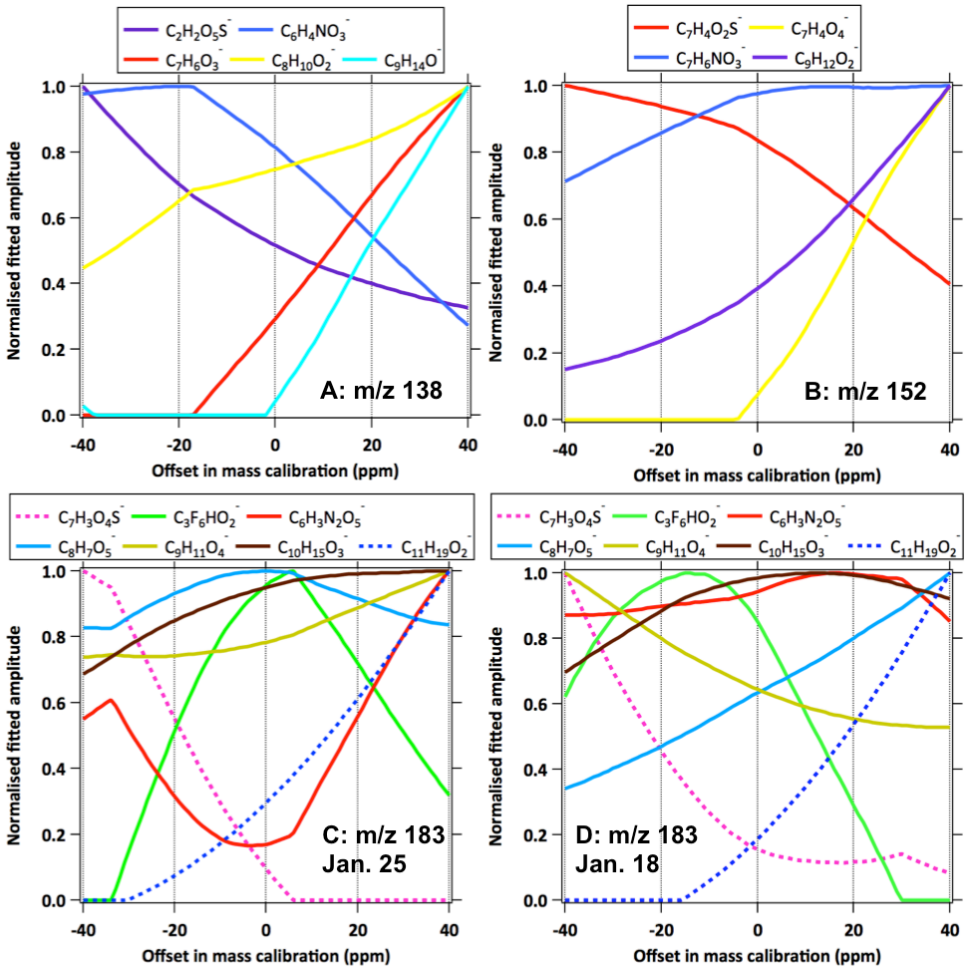

Figure R3 (Figure S2 in the revised manuscript). Sensitivity of the fitted ion intensities to mass calibration errors for ions at m/z 138 (A), m/z 152 (B) and m/z 183 (C) based on the averaged mass spectra on January 25, 2014 and m/z 183 (D) based on the averaged mass spectra on January 18, 2014 (see mass spectra in Figure 2). The results in the plots were obtained by (1) shifting the measured mass spectra by varying amount (from -40 ppm to 40 ppm) and (2) conducting peak fitting to the shifted mass spectra using the same ion locations calculated from their formula (Stark et al., 2015). The fitted signals relative to the maximum signals obtained between -40 ppm and 40 ppm are shown for each individual ion. The accuracy of mass calibration was 4.7±1.9 ppm for the whole campaign and the errors of mass calibration for individual ions were usually within 10 ppm (average+3σ).

P7 L6 What was the length of the short inlet?

Reply: The length of the short inlet used during February 1-5 was around 2 meters. We added this information in the revised manuscript.

Technical: P36 fig 5 What is the line for the G/P partitioning using 4-NP?

Reply: The legend of Figure 5 in ACPD version is updated in the revised manuscript to better convey the information. The green solid line is the modeled gas-phase concentration from the G/P partitioning using 4-NP. The updated graph is shown below.

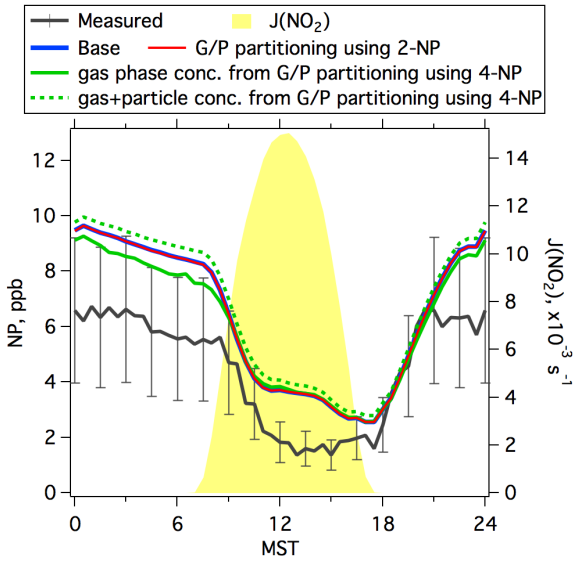

Figure R4. Diurnal profiles of measured and modeled concentrations of NP from the base simulation and the simulations considering gas/particle partitioning. Photolysis frequencies of NO_2 are shown for reference. Error bars indicate the accuracies of concentrations of NP (40%).

Anonymous Referee #2

This manuscript describes some novel measurements of nitrated phenols made in the Uintah Basin late January into early February, 2014. The measurements themselves are novel and indicate a high sensitivity and reasonable specificity for the target species. The measurements are complemented by a fairly simple modeling exercise, which shows that the data can be fitted by a chemical model accompanied by deposition and dilution terms without too much tweaking. Overall, this is a valuable study, which can be published without too many changes. The measurements are fairly novel, and perhaps would benefit from a little more discussion.

Reply: We would like to thank the reviewer for these valuable comments.

The figures showing mass spectral peak-fitting are central to understanding the quality of the data, but are relegated to Supplemental Material. I would like to see them featured more prominently, and with some further discussion. For example, how variable are the other signals shown in Figures S2 (A-D)? What are the proposed identities of some of the other peaks, and do they show similar diurnal profiles? For that matter, when were the shown spectra taken (date, time of day)? A little more information along these lines would help others to assess the reliability and generality of the technique.

On the other hand, quite a lot of space is devoted to the model, which does not really bring a whole lot of insight to the chemistry. Admittedly, it is shown that the modeled diurnal profiles match the measurements quite well, but it is after all "only" a box model, and transport and dilution are treated simplistically. However, the interpretation of the model does not overstep its limits, and the exercise is useful, if only in showing that the measured diurnal profiles are reasonable.

Reply: We agree with the reviewer that high-resolution peak fitting to the mass spectra is essential for the quality of the results presented in this study. The uncertainties due to high-resolution peak fitting have been discussed in several recent papers (Corbin et al., 2015;Cubison and Jimenez, 2015;Müller et al., 2011). We moved the mass spectra plots from the supplemental information to the main text in the revised manuscript. The mass spectra in the plots (Figure 2 in the revised manuscript) were averaged from the mass spectra measured on January 25 (and also January 18 in the Figure 2D). As shown in

Figure 5 in the revised manuscript, January 25 was a typical measurement day during the UBWOS campaign, with similar concentrations of nitrated phenols as the campaign averages shown in Figure 3. Thus, they are representative for the peak-fitting issues encountered during UBWOS 2014. Based on the reviewer's comments and also comments from reviewer #1, we have expanded the discussions of peak fitting in Section 2, including mass calibration and its error, interpretation of the mass spectra, discussions on the uncertainty of the fitted signals. The inlet issue for DNP presented in Section 3.3 is also moved to this part. A graph showing the sensitivity of fitted ion intensities to mass calibration errors is also included in the supplement (Figure S2). The added and modified paragraphs are (same revision as described in our response to Reviewer 1):

Post-measurement mass calibrations were performed using nine isolated ions, including m/z 31.9904 (O_2^-), m/z 34.9694 (Cl^-), m/z 44.9982 (CHO_2^-), m/z 59.0139 ($C_2H_3O_2^-$), m/z 61.9884 (NO_3^-), m/z 143.9840 ($C_3F_4O_2^-$), m/z 162.9824 ($C_3F_5O_2^-$), m/z 193.9808 ($C_4F_6O_2^-$) and m/z 243.9776 ($C_5F_8O_2^-$). The four fluorine-containing ions in the list were released from Teflon inlet during UBWOS 2014 and their persistent presence was used for mass calibration. The accuracy of mass calibration was 4.7±1.9 ppm for the whole campaign and the errors of mass calibration for individual ions were usually within 10 ppm (average+3σ).

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provided equations in Cubison and Jimenez (2015), the imprecision arising from mass calibration (not including counting error) for the signals of NP, MNP and DNP are 3.2%, 1.8% and 47% based on the mass spectra of January 25, respectively. Imperfect mass calibration can also affect fitted magnitudes of ion signals. Figure S2 shows the sensitivity of the fitted signals of various masses as a function of the errors in mass calibration. The signal changes at a 10 ppm (average+3σ) error of mass calibration relative to perfect mass calibration (error=0 ppm) for NP, MNP and DNP signals are as high as 14%, 5% and 81%, respectively. The results from both precision calculation and sensitivity of fitted magnitudes indicate that the peak signals of NP and MNP can be fitted well with low uncertainties. The peak fitting at m/z 166 for DMNP shows similar results as m/z 138 for NP and m/z 152 for MNP. However, large uncertainties are associated with the peak signals of DNP on January 25, 2014, which is mainly affected by the $C_3F_6HO_2^-$ ions (m/z 182.9886) as indicated by the opposite behaviors of the DNP ion and $C_3F_6HO_2^-$ ion in Figure S2C.

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1. Specific comments: There are a few spots in the manuscript where the grammar needs tightening up. E.g., P28662, line 16. “oxidation… with nitration process…” P28666, lines 7-20. Repeats discussion of acetic anhydride. Also, it wasn’t totally clear whether you

were talking about your own IMR, or comparing to others. P28670, line 10. "inertial" should be "inert" ?

Reply: P28662 line 16: the sentence is changed to: **Further oxidation of nitrated phenols by obtaining another nitro- group produces dinitrophenols (DNP).**

P28666 line 7-20: "The different sensitivity ratios of 4-NP/2-NP between our instrument and that in Mohr et al. (2013) can be caused by many different instrumental conditions" is changed to "**The different sensitivity ratios of 4-NP/2-NP can be caused by many different instrumental conditions between our instrument and that in Mohr et al. (2013)**".

P28670 line 10: Changed.

2. P28670, model tests in Fig S3. Was the photolysis to give phenoxy + NO2 the only channel included? Since this channel reforms NP, you can't really rule out its occurrence concurrently with HONO production, since as you say it would be a null channel. Since the overall quantum yield is only about 1E-3, there is a lot of room for parallel channels occurring. Admittedly, though, Bejan et al. (2006) point out that photolysis of 2.5 ppm 3-methyl-2-nitrophenol led to <0.14 ppb NO2, so the channel is probably only small.

Reply: We are thankful for the reviewer's comments. The model tests presented in Figure S3 in the ACPD version (Figure S4 in the revised manuscript) assumes the photolysis only gives phenoxy + NO_2. From our simulation test, we concluded this photolysis pathway is not an effective loss for NP.

We agree with the reviewer that this pathway may still occur concurrently with the pathway forming HONO + 2-phenoxy biradicals. As the photolysis rate of NP in Bardini (2006) was derived from the change of NP concentrations in a chamber associated with OH scavenger, the photolysis rate determined in Bardini (2006) may not include this pathway even though it may be happening. We added this discussion in the revised manuscript.

The simulation test in Figure S3 indicates that the pathway forming C_6H_5O radicals and NO_2 is an ineffective sink for NP, since C_6H_5O radical will re-form NP by reacting with NO_2. However, we cannot exclude this pathway to occur along with

that producing 2-phenoxy biradicals and HONO. The photolysis frequency determined in Bardini (2006) from concentration changes of 2-nitrophenol in a chamber may not include this pathway as well. As a result, attributing the photolysis rates determined in Bardini (2006) to other pathways other than Route2 is reasonable.

3. P28671, lines 17-22. What is the rationale for assuming that the interference is only present during the night? How would alternative assumptions affect the conclusions from the model?

Reply: The modeled phenol concentrations agreed reasonably well with measurements during the daytime, but significant disagreement was observed at night. One possible explanation is a chemical interference of phenol that is only present. We cannot rule out that such an interference was also present in the daytime. If similar magnitudes of interferences also occurred in the daytime, modeled phenol concentrations would be higher than measurements in the daytime, but still in the combined uncertainty of measurement and the model in this period.

4. P28675. Presumably the reaction of OH with phenol is such a small contributor to NP production because the OH mostly adds to the ring? Maybe a comment would help to clarify this. It is interesting that so many sources of C6H5O2 (and consequently, C6H5O) exist. Of the flux through C6H5O2 + NO, only about a third makes NP. Is this because phenoxy radicals cycle back to RO2 through the O3 reaction? How does the inclusion of the phenoxy + NO reaction affect the phenoxy and NP budgets around midday? Interpretation of these figures might be a little easier if the NO2 and O3 levels were given somewhere.

Reply: The reaction of OH with phenol mainly happens through OH addition, ultimately forming catechol (yield=80% in MCM). The yield of NP from the reaction of OH with phenol is only 6% in MCM. We added this information in the revised manuscript.

The reaction of phenol with OH radicals only accounts for a small fraction of the production of C_6H_5O radicals (2% for 24-hour average), due to the small yield of NP (6%) from the reaction of OH with phenol in the MCM.

Most of the phenoxy radicals formed from the $C_6H_5O_2$+NO reaction recycle back to $C_6H_5O_2$ radicals through its reaction with O_3. Based on Figure 7 (B and C) in the revised manuscript, only about of a third of C_6H_5O radicals form NP. The production of C_6H_5O radicals is not affected by the inclusion of the C_6H_5O+NO reaction. The inclusion of the C_6H_5O+NO reaction reduces formation rates of NP in the noontime, as the loss of C_6H_5O is higher and the steady-state concentration of C_6H_5O is lower in the midday. The average concentrations of NO, NO_2 and O_3 in Jan. 18-Jan.27 during UBWOS 2014 are shown in a table (Table S2) in the supplement in the revised manuscript. The discussions on the effects of C_6H_5O + NO reaction to NP budget are added in the revised manuscript.

The inclusion of the reaction of phenoxy radicals (C_6H_5O) with NO discussed in section 3.2.2 would mainly affect NP budget in the noontime, with smaller production and loss in this period.

5. P28676, line 17. Just to clarify; you mean 100% of nitrated phenols that are actually lost by photolysis (since the overall quantum yield is <1E-3).

Reply: Here, we mean that each molecule of nitrated phenols lost by photolysis (the rate is 1.4%*J(NO_2)) yields one HONO molecule. We changed the sentence slightly in the revised manuscript to make it clearer.

"If we assume photolysis of nitrated phenols at rates of 1.4%×J(NO_2) yields HONO at a 100% yield (upper limit),…"

6. Figure 5, caption. Delete "in (b) and (d)".

Reply: Done.

References:

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

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Abstract

We describe the results from online measurements of nitrated phenols using a time of flight chemical ionization mass spectrometer (ToF-CIMS) with acetate as reagent ion in an oil and gas production region in January and February of 2014. Strong diurnal profiles were observed for nitrated phenols, with concentration maxima at night. Based on known markers (CH_4, NO_x, CO_2), primary emissions of nitrated phenols were not important in this study. A box model was used to simulate secondary formation of phenol, nitrophenol (NP) and dinitrophenols (DNP). The box model results indicate that oxidation of aromatics in the gas phase can explain the observed concentrations of NP and DNP in this study. Photolysis was the most efficient loss pathway for NP in the gas phase. We show that aqueous-phase reactions and heterogeneous reactions were minor sources of nitrated phenols in our study. This study demonstrates that the emergence of new ToF-CIMS (including PTR-TOF) techniques allows for the measurement of intermediate oxygenates at low levels and these measurements improve our understanding of the evolution of primary VOCs in the atmosphere.

1. Introduction

Nitrated phenols are a family of aromatic compounds with both nitro (-NO_2) and hydroxyl groups (-OH) connected to a benzene ring. Nitrated phenols have been detected in the gas phase, aerosol, cloud water and rainwater (Harrison et al., 2005a). Many studies have shown that nitrated phenols are one of the important components of brown carbon in aerosol (Desyaterik et al., 2013;Mohr et al., 2013;Zhang et al., 2013;Lin et al., 2015), as they absorb light in the atmosphere (Bejan et al., 2007). Photolysis of some nitrated phenols was reported to produce nitrous acid (HONO) (Bejan et al., 2006) and hydroxyl (OH) radicals (Cheng et al., 2009), while the oxidation and photolysis of them contribute to secondary organic aerosol (SOA) formation, especially in biomass burning plumes (Mohr et al., 2013;Kitanovski et al., 2012;Lauraguais et al., 2014). There is also evidence that nitrated phenols are phytotoxic and contribute to forest decline (Rippen et al., 1987;Natangelo et al., 1999). Some nitrated phenols are known to be mutagenic and are of concern to human health (Fernandez et al., 1992).

Sources of nitrated phenols in the atmosphere include emissions from vehicle exhaust (Inomata et al., 2013;Tremp et al., 1993;Sekimoto et al., 2013) and biomass burning (Mohr et al., 2013). Nitrated phenols are also produced from photooxidation of aromatic hydrocarbons in the atmosphere: for example benzene oxidizes to 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP), and toluene oxidizes to methylnitrophenols (MNP) (Harrison et al., 2005a). Figure 1 shows the reactions leading to secondary formation of NP and dinitrophenols (DNP) in the atmosphere (Jenkin et al., 2003). Oxidation of benzene by OH radicals forms phenol and further reactions of phenol with either OH or NO_3 radicals yield phenoxy (C_6H_5O) radicals, which react further with NO_2 to generate NP. In addition to benzene oxidation, C_6H_5O radical is also generated from the reaction of NO with phenyl peroxy ($C_6H_5O_2$) radicals, a product from reactions of some other aromatic precursors, e.g. benzaldehyde (Caralp et al., 1999). Further oxidation of nitrated phenols by obtaining another nitro- group produces dinitrophenols (DNP). The yields of NP from phenol oxidation by OH radicals (Atkinson et al., 1992;Olariu et al., 2002;Berndt and Boge, 2003) and NO_3 radicals (Atkinson et al., 1992;Bolzacchini et al., 2001) have been reported. Berndt and Boge (2003) also showed that the NP yield from

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66 OH oxidation of phenol increases at higher NO_2 concentrations. In addition to gas phase
67 reactions, nitrated phenols are formed from aqueous-phase reactions in aerosol or cloud
68 water (Vione et al., 2001, 2005). The importance of the aqueous reactions compared to
69 gas-phase reactions is highly dependent on liquid water content in the atmosphere
70 (Harrison et al., 2005b).

71 The sinks of nitrated phenols in the gas phase include reactions with OH radicals
72 (Atkinson et al., 1992;Bejan et al., 2007), with NO_3 radicals (Atkinson et al., 1992), with
73 chlorine atoms (Bejan et al., 2015) and photolysis (Bejan et al., 2007;Chen et al., 2011).
74 It has been proposed that photolysis is the dominant gas phase atmospheric loss for
75 nitrated phenols (Bejan et al., 2007). Despite the importance of photolysis of nitrated
76 phenols, the photolysis frequency of nitrated phenols under ambient conditions was only
77 reported in a single non-peer reviewed publication (1.4% of photolysis frequency of NO_2)
78 (Bardini, 2006). The chemical products from photolysis of nitrated phenols were
79 proposed, but the proposed products were not fully evaluated against experimental results
80 (Bejan et al., 2006). Nitrated phenols are also removed by various processes in the
81 aqueous phase, including reactions with OH, NO_3 and photolysis (Vione et al., 2009).

82 Measurements of nitrated phenols have been mainly conducted using offline
83 methods (Harrison et al., 2005a). Air samples are usually collected on filters or cartridges
84 and then analyzed by liquid chromatography (LC) methods (Rubio et al., 2012;Harrison
85 et al., 2005a;Delhomme et al., 2010). These detection methods are time-consuming and
86 measurements as a function of the time of day are not usually possible (Delhomme et al.,
87 2010). The lack of fast-response online measurements has prevented, at least partially, a
88 thorough investigation of sources and sinks of nitrated phenols. Recently, Mohr et al.
89 (2013) deployed a chemical ionization mass spectrometer (CIMS) using acetate as the
90 reagent ion to measure nitrated phenols online in the particle phase in winter in London
91 and based on their measurements the authors concluded that nitrated phenols were mainly
92 from wood burning in this region of the atmosphere.

93 In this study, we conducted high time resolution measurements of nitrated phenols
94 in the gas phase at a site in an oil and gas production region in winter. High
95 concentrations of ozone and secondary products (Edwards et al., 2014) were observed at

this site, as the result of photochemical degradation of large amounts of alkanes and aromatics emitted from oil and gas production in this region (Warneke et al., 2014). Using the present dataset, we investigate diurnal variations, sources and sinks of nitrated phenols. We use a box model to analyze the budget of nitrated phenols in the atmosphere, and provide insights into the formation mechanism of nitrated phenols.

2. Measurements

The Uintah Basin Winter Ozone Study (UBWOS 2014) was conducted in January and February of 2014 at the Horse Pool site in the Uintah Basin, where over 10,000 active oil and gas wells are located.

2.1 Acetate ToF-CIMS

2.1.1 Instrument operation

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An Aerodyne time-of-flight (ToF) CIMS (Lee et al., 2014) that uses acetate ($CH_3C(O)O^-$) as the reagent ion was deployed at the Horse Pool site during the UBWOS 2014 to measure organic acids, inorganic acids and nitrated phenols. These compounds are ionized in the ion-molecule reaction region (IMR, 61.8±0.3 mbar) via proton abstraction (Veres et al., 2008) or by a sequence of clustering-declustering/deprotonation reactions (Brophy and Farmer, 2015) in the reaction with acetate ions. Acetate ions were produced by introducing saturated acetic anhydride/N_2 mixture (5 mL/min) mixed with another flow of N_2 (2.5 L/min) into a polonium-210 (^{210}Po) radioactive source. The instrument was operated at strong de-clustering conditions by applying voltages in the first quadruple ion guide (i.e. SSQ, 2.50±0.01 mbar) during UBWOS 2014, with the ratio of acetate cluster ($CH_3C(O)O^-•CH_3C(O)OH$)/acetate ($CH_3C(O)O^-$) at 0.4%±0.1%. Under such de-clustering conditions, the conjugate anions were usually observed as the product ions, with little contribution from cluster ions. The reagent ions and product ions are analyzed using a high-resolution time of flight mass spectrometer (TOFWERK, Switzerland). The signal of acetate ion was approximately 1-2×10^6 count per second (cps) during the campaign (ToF extraction frequency=25 kHz). The mass resolution for the ToF during UBWOS 2014 was approximately 3200 for ions of m/z >200.

Background signals associated with the instrument were measured every 2 hours for 15 min by passing ambient air through three stages of zero air generation: a platinum catalytic converter heated to 350 °C, nylon wool coated with sodium bicarbonate ($NaHCO_3$), and activated charcoal, which were used in series to remove acidic gases from the sample air and determine instrument backgrounds. During the UBWOS 2014 study, two CIMS inlets constructed from Teflon heated to ~40 °C with similar lengths (~10 m) placed at heights of 1 m and 18.5 m above ground were switched automatically every 30 min during the period of January 24- February 1, to measure the vertical concentration gradient of nitrated phenols and other acidic gases. Inlet switching between a long-heated and a short-unheated inlet was also conducted during February 1-5, to explore possible inlet interferences to CIMS measurements of nitrated phenols from the long-heated inlet. We did not observe differences in signals between the long and short inlets for nitrated phenols except DNP (Figure S1), indicating that potential loss in sampling line was minimal for the reported single nitrated phenols in this study. The inlet issues for DNP will be discussed in Section 2.1.2.

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2.1.2 Data processing

The ToF-CIMS data was processed using the TOFware software package (www.tofwerk.com/tofware) written in Igor Pro (Wavemetrics Inc., USA). The detailed data processing procedures are presented in recent studies (Yatavelli et al., 2014;Stark et al., 2015). Post-measurement mass calibrations were performed using nine isolated ions, including m/z 31.9904 (O_2^-), m/z 34.9694 (Cl^-), m/z 44.9982 (CHO_2^-), m/z 59.0139 ($C_2H_3O_2^-$), m/z 61.9884 (NO_3^-), m/z 143.9840 ($C_3F_4O_2^-$), m/z 162.9824 ($C_3F_5O_2^-$), m/z 193.9808 ($C_4F_6O_2^-$) and m/z 243.9776 ($C_5F_8O_2^-$). The four fluorine-containing ions in the list were released from Teflon inlet during UBWOS 2014 and their persistent presence was used for mass calibration. The accuracy of mass calibration was 4.7±1.9 ppm for the whole campaign and the errors of mass calibration for individual ions were usually within 10 ppm (average+3σ). The fitted raw signals for the targeted compounds were normalized using an acetate signal at the level of 1×10^6 cps.

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The fitted m/z used for quantification of concentrations of nitrated phenols in the acetate CIMS are m/z 138.0197 ($C_6H_4NO_3^-$) for NP, m/z 152.0353 ($C_7H_6NO_3^-$) for MNP,

m/z 166.0510 ($C_8H_8NO_3^-$) for dimethylnitrophenol+ ethylnitrophenol (DMNP) and m/z 183.0047 ($C_6H_3N_2O_5^-$) for DNP. Compounds with same molecular formulas as nitrated phenols include phenyl nitrates/benzyl nitrates, methoxynitrobenzenes, nitrobenzyl alcohols and hydroxycarboxylic acids derived from pyridine. The first three groups of compounds have lower acidities than acetic acid (Bartmess, 2015) and hence they are unlikely to be observed in acetate CIMS, while hydroxycarboxylic acids derived from pyridine are expected to be small in the atmosphere.

High-resolution (HR) peak fitting to m/z 138, m/z 152 and m/z 183 in the averaged mass spectra of ToF-CIMS on a typical day (January 25, 2014) are shown as examples in Figure 2. Isotope signals from lower masses (dark green lines) accounted for small fractions of the m/z signals. Multiple overlapping ion peaks were identified in the m/z channels. In addition to nitrated phenols, several ions without deprotonation were also present in the even m/z (e.g. $C_8H_{10}O_2^-$ at m/z 138), possibly due to electron transfer reactions and/or fragmentation in the quadrupole ion guides (Stark et al., 2015). The signals of NP and MNP were either the largest or significant larger than their neighboring peaks at their respective m/z, whereas the signal of DNP was much smaller than its neighboring peaks on January 25, 2014. Smaller ratios of the signals between the targeted peak and its neighboring peaks have been shown to deteriorate the precision of fitted signals for the targeted peak (Cubison and Jimenez, 2015;Müller et al., 2011;Corbin et al., 2015). Based on the provided equations in Cubison and Jimenez (2015), the imprecision arising from mass calibration (not including counting error) for the signals of NP, MNP and DNP are 3.2%, 1.8% and 47% based on the mass spectra of January 25, respectively. Imperfect mass calibration can also affect fitted magnitudes of ion signals. Figure S2 shows the sensitivity of the fitted signals of various masses as a function of the errors in mass calibration. The signal changes at a 10 ppm (average+3σ) error of mass calibration relative to perfect mass calibration (error=0 ppm) for NP, MNP and DNP signals are as high as 14%, 5% and 81%, respectively. The results from both precision calculation and sensitivity of fitted magnitudes indicate that the peak signals of NP and MNP can be fitted well with low uncertainties. The peak fitting at m/z 166 for DMNP shows similar results as m/z 138 for NP and m/z 152 for MNP. However, large uncertainties are associated with the peak signals of DNP on January 25, 2014, which is mainly affected

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by the $C_3F_6HO_2^-$ ions (m/z 182.9886) as indicated by the opposite behaviors of the DNP ion and $C_3F_6HO_2^-$ ion in Figure S2C.

The $C_3F_6HO_2^-$ ion (m/z 182.9886) was released from the heated Teflon inlet along with other fluorine-containing ions that were used for mass calibration. The release of $C_3F_6HO_2^-$ ion was supported by much higher signals from the long-heated inlet compared to the short-unheated inlet, when inlet-switching experiments were conducted in February 2-5 (Figure S1). Long-heated inlets were used for most of the time during UBWOS 2014 (January 23- February 13), except during January 18-22, when a short-unheated inlet was used. The averaged mass spectra of m/z 183 measured on January 18 is shown in Figure 2D. Compared to the mass spectra on January 25, $C_3F_6HO_2^-$ signals on January 18 were lower and the signals of DNP were larger than of $C_3F_6HO_2^-$ ions. As a result, the uncertainty from peak fitting for the DNP ion was much lower on January 18 (Figure S2D). Thus, we will only use measured DNP data in the beginning of the campaign (January 18-22), when the long heated inlet was not connected to the acetate CIMS and no inlet switching was performed.

The response of the CIMS instrument for nitrated phenols, including 2-NP, 4-NP, 2-methyl-4-nitrophenol and 2,5-dinitrophenol, was calibrated using a Liquid Calibration Unit (LCU, IONICON Analytik). In the LCU, a water solution with known concentrations of the targeted compounds is nebulized and diluted by another gas stream at different flow rates to produce a gas standard at various concentrations (Kaser et al., 2013). The results of the calibrations to various nitrated phenols are shown in Table 1. The sensitivity of 4-NP in our instrument was determined to be higher than that of 2-NP by a factor of 2.1. A higher sensitivity of 4-NP in acetate CIMS was reported in Mohr et al. (2013), but in that study the difference was significantly larger at three orders of magnitude (Mohr et al., 2013). The different sensitivity ratios of 4-NP/2-NP can be caused by many different instrumental conditions between our instrument and that in Mohr et al. (2013), such as the amount of acetic anhydride introduced into instrument, IMR and SSQ pressures, and de-clustering settings in the quadrupole ion guides, all of which affect sensitivities of acetate CIMS significantly (Stark et al., 2012). The main reagent ions in IMR were shown to be acetic acid-acetate clusters rather than acetate (Bertram et al., 2011) and the cluster distributions in IMR may depend on operated

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pressure in IMR and the amount of acetic anhydride into the ion source. While de-clustering in SSQ helps the interpretation of recorded mass spectra, de-clustering also obscures a precise understanding of cluster distributions in IMR and hence accurately prediction of sensitivities in acetate CIMS. This result also emphasizes the importance of instrument calibrations in deriving concentration from acetate CIMS. We note that 3-nitrophenol (3-NP) is not usually present in the atmosphere (Harrison et al., 2005a). Thus, the average of the sensitivities of 2-NP and 4-NP was used for calculating concentrations of NP. DMNP was not calibrated in this study and we assumed the same sensitivity as determined for MNP.

The accuracies of nitrated phenols measurements by the CIMS are conservatively estimated to be around 40% for NP and 50% for other nitrated phenols, mainly arising from uncertainties in the concentrations output of the LCU (~10%), uncertainties associated with calibration procedures (~5%), errors in high-resolution (HR) peak fittings to mass spectra (see above and Figure S2), and the representativeness of the calibrated species to other isomers (0-30% for NP and 0-40% for other nitrated phenols). Assuming random errors in the observed ion counts follow a Poisson distribution, detection limits of nitrated phenols, i.e. concentrations with a signal to noise ratio (S/N) of 3, are calculated to be 0.1-0.3 ppt for 1-min average data (Table 1). Following the discussions in Bertram et al. (2011), the measured background ion counts in ToF-CIMS drift over time and thus detection limits are more appropriately calculated as the concentrations at three times of the standard deviation of the measurement background counts. The determined detection limits of nitrated phenols increase to the range of 0.3-0.5 ppt based on this approach (Bertram et al., 2011) (Table 1).

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2.2 Other measurements

Volatile organic compounds (VOCs), including hydrocarbons and oxygenates, were measured using an online gas chromatography-mass spectrometer (GC-MS) (Gilman et al., 2013). A commercial proton transfer reaction time of flight mass spectrometer (PTR-TOF) (IONICON Analytik, Austria) was also deployed at the Horse Pool site to measure various VOC species (Warneke et al., 2015). Measurements of phenol, cresols and dimethylphenols+ethylphenols (DMP) were accomplished by the PTR-TOF at m/z

95.0491 ($C_6H_6OH^+$), m/z 109.0648 ($C_7H_8OH^+$) and m/z 123.0804 ($C_8H_{10}OH^+$), respectively. An example of high-resolution peak fitting to m/z 95 in the mass spectra of PTR-TOF is shown in Figure S3. The sensitivities to these phenols are estimated here from the calibrated sensitivities of m/z 93.0699 (toluene), m/z 107.0855 (C8-aromatics) and m/z 121.1012 (C9-aromatics) and the ratio of proton-transfer rate coefficients (k) of the phenols versus the aromatic hydrocarbons (Cappellin et al., 2012) (see details in the SI). Considering the uncertainties in the rate coefficients k, the accuracies of the determined concentrations of phenols can be up to 50% (de Gouw and Warneke, 2007).

Measurements of NO_3 and N_2O_5 were conducted by a cavity ring-down spectroscopy instrument (Dubé et al., 2006). NO_x ($NO+NO_2$), NO_y and O_3 were measured with another cavity ring-down spectroscopy instrument (Wild et al., 2014). Measurements of methane (CH_4) and carbon dioxide (CO_2) were performed with a commercial cavity ring-down spectrometry instrument (Picarro G2301). A pair of commercial spectral radiometers (Metcon Inc.) was used to measure photolysis frequencies of ozone and NO_2.

3. Results and Discussions

3.1 Diurnal variations

Measured diurnal profiles of NP, MNP and DMNP during the UBWOS 2014 are shown in Figure 3. Very strong diurnal variations in concentrations of these nitrated phenols were observed. Concentrations of nitrated phenols were higher at night and lower in the daytime. The ratios between the concentrations in the two hours around midnight (23:00-1:00 MST) and in the two hours around noon (11:00-13:00 MST) are 2.9, 3.9 and 4.7 for NP, MNP and DMNP, respectively. This indicates that the substituted alkyl groups enhance the diurnal variations of nitrated phenols, either through larger source at night or larger sink in the daytime.

Primary emissions of VOCs and NO_x at the Horse Pool site are predominantly due to oil and gas production activities, as the Horse Pool site is surrounded by oil and gas production wells. VOCs and NO_x emitted from nearby oil and gas wells led to periodic concentration spikes during the UBWOS campaigns (Warneke et al., 2014;Yuan et al., 2015). Figure 4 shows two types of episodes encountered during UBWOS 2014. The first

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was associated with high concentrations of methane and benzene, as an example of fugitive emissions from oil and gas wells. No enhancement of nitrated phenols was observed for the first emission episode. The second episode was associated with high concentrations of NO_y, NO_x and CO_2, as an example of either vehicle emissions or other fuel combustion activities related to oil and gas extractions (e.g., compressors, dehydrators and pump jacks). High NO_x/NO_y ratios (0.96±0.01) indicate that a fresh combustion plume was encountered. We observed small enhancement of NP during the second emission episode. The enhancement ratio of NP/NO_y in this plume is determined to be $4.6\pm0.7\times10^{-3}$ ppt/ppb, which is comparable with the reported NP/NO_x emission ratios ($1\text{-}50\times10^{-3}$ ppt/ppb) from gasoline and diesel vehicles (Inomata et al., 2013;Sekimoto et al., 2013). Using the obtained enhancement ratio of NP/NO_y, we determine that primary emissions from combustion sources only account for less than 2% of NP concentrations during UBWOS 2014. In addition to these primary sources, biomass burning was not observed in the UBWOS campaigns, based on the absence of any enhancement of biomass burning markers like acetonitrile. We conclude that primary emissions of nitrated phenols were not significant during UBWOS 2014.

In addition to primary emissions, secondary formation from oxidation of phenols is an important source for nitrated phenols (Harrison et al., 2005a). Phenol exhibited a concentration maximum in the afternoon (Figure 3B). The diurnal profile of phenol is more similar to that of secondary acetaldehyde, than that of primary emitted benzene. It suggests that secondary formation was the most important source of phenol. Substituted phenols (cresols and DMP) also had similar diurnal variations as phenol.

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3.2 Modeling analysis for NP

3.2.1 Box model results

We will focus on NP to understand the budget of nitrated phenols, because NP had higher concentrations than the substituted nitrated phenols (MNP and DMNP) and there is more information on sources and sinks of NP in the literature. A series of zero-dimensional box model simulations on the formation of phenol and NP were conducted using the online AtChem tool (https://atchem.leeds.ac.uk). The MCM v3.2 (Jenkin et al., 2012) was used as the chemical mechanism in the box model. We note that ambient

temperature (-5±5 °C) during UBWOS 2014 was much lower than the temperature (around 25 °C) at which rate constants of many reactions are usually measured. Rate constants as a function of temperature are only available for the reactions of OH radical with benzene and phenol among those shown in Figure 1 and they were already included in MCM v3.2. The model ran in a time-dependent mode and a 48-hour spin-up time was applied in the box model. Measured concentrations of various hydrocarbons, NO_x, O_3, NO_3 and photolysis frequencies (Table S2) were used as constraints in the box model. The simulation period of the model was chosen to be January 18-27, a period associated with several buildup episodes of ozone and other secondary products, with high measured concentrations of NP and without precipitation. Following previous box model studies (Yuan et al., 2015;Edwards et al., 2014), dilution and deposition processes were represented together using a diurnally varying first-order physical loss parameter in the box model. The physical loss rate at night (5.8×10^{-6} s^{-1}) was calculated from the decrease rate of NP concentration between 0:00-6:00 am when the chemical loss was expected to be low (see section 3.3.4). A higher physical loss rate (2.0×10^{-5} s^{-1}) during daytime was used to account for larger turbulent mixing during daytime (Edwards et al., 2014), which results in the decrease of concentrations of inert tracers in the afternoon, e.g. benzene (Figure 3) and methane. Based on sensitivity tests of the box model, increase and decrease of the physical loss rate terms by a factor of two resulted in a -48% and +39% of change in the modeled NP concentrations.

As shown in the introduction, photolysis has been recognized as an important sink for nitrated phenols. However, the photolysis of NP (and other nitrated phenols) is not included in the MCM v3.2. We added the photolysis frequency of NP from Bardini (2006) (1.4% of photolysis frequency of NO_2) into the MCM v3.2 and this model run is referred to as the base simulation. Here, we assume that photolysis of NP produces 2-phenoxy biradicals and HONO, as proposed in Bejan et al. (2006) (Figure 1 Route1). There are other possible chemical routes for photolysis of NP: producing phenoxy radicals (C_6H_5O) by losing NO_2 (Route2 in Figure 1) and producing nitrophenoxy radical by hydrogen abstraction (Route3 in Figure 1). The simulation test in Figure S4 indicates that the pathway forming C_6H_5O radicals and NO_2 is an ineffective sink for NP, since C_6H_5O radical will re-form NP by reacting with NO_2. However, we cannot exclude this

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pathway to occur along with that producing 2-phenoxy biradicals and HONO. The photolysis frequency determined in Bardini (2006) from concentration changes of 2-nitrophenol in a chamber may not include this pathway as well. As a result, attributing the photolysis rates determined in Bardini (2006) to other pathways other than Route2 is reasonable. The route producing nitrophenoxy radical will be discussed in Section 3.3.

The simulated results for phenol and NP from the base case of the box model are shown in Figure 5. The modeled diurnal variations agreed reasonably well with the observation for both NP and phenol in the base simulation, except for the phenol nighttime levels that will be discussed below. Although modeled NP concentrations are higher than the measurements for both daytime and nighttime, the agreement between measurements and model results is still within their combined uncertainties.

The average measured concentrations of phenol at night are higher than 10 ppt, but the modeled phenol concentrations are usually less than 2 ppt. At night, the production of phenol from benzene oxidation halts, and the fast reaction with NO_3 (2.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K) removes phenol quickly (Figure 7 and discussion in section 3.2.3). Measured nighttime NO_3 radicals were quite low during UBWOS 2014 (1.4±2.4 ppt). As a check on the possible uncertainties in measurements of NO_3 at these low levels, simulations by varying NO_3 concentrations by a factor of 2 result in little improvement for the modeled concentrations of phenol (Figure S5). Another simulation using calculated NO_3 concentrations from the equilibrium between NO_3 and N_2O_5 (Figure S5) also indicates that uncertainties in NO_3 measurements cannot account for the discrepancies between measured and modeled phenol at night. The high phenol concentrations measured at night might be a result of primary emissions. Indeed, the measured phenol concentration was slightly enhanced in the plume with high methane concentrations (see Figure 4A). However, a simulation using the measured phenol concentrations as a constraint in the box model, predicted much higher NP concentrations than measurements (Figure S4). Perhaps a more likely explanation for the enhanced phenol concentrations at night is that the measurements of phenol by PTR-TOF suffer from chemical interferences at night. Vinylfuran might be a candidate (Karl et al., 2007;Stockwell et al., 2015). Thus, the modeled concentrations of phenol shown in Figure 5 will be used in the following discussions.

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3.2.2 NO_2 dependence of NP yields

As shown in Figure 1, NP is generated from the reaction of NO_2 with phenoxy radicals ($C_6H_5O\cdot$) (Berndt and Boge, 2003), which is an intermediate from the reactions of OH and NO_3 radicals with phenol and the reaction of phenylperoxy radicals ($C_6H_5O_2$) with NO. In addition to NO_2, $C_6H_5O\cdot$ radicals also react with NO and O_3 (Platz et al., 1998) (see Figure 1), thus the yield of NP has been reported to depend on NO_2 concentrations in the atmosphere (Berndt and Boge, 2003).

In the MCM v3.2, only the reactions of C_6H_5O radical with O_3 and NO_2 are included and here we added the reaction of C_6H_5O with NO (k=1.88×10^{-12} cm^3 molecule^{-1} s^{-1}) for a new simulation. Compared to the base simulation, the modeled concentrations of NP are lower, especially for the period of 11:00-17:00, as the effective yield of NP is reduced (Figure 5). The small enhancement during the period of 11:00-17:00 in NP concentrations from the base simulation is absent in the simulation with the reaction of C_6H_5O with NO. The variations of modeled NP concentrations in the daytime from the new simulation are in better agreement with the measurements (Figure 5). This indicates the reaction of NO and C_6H_5O radical should be considered to account for the NO_2 dependence of NP formation.

Another simulation using fixed NP yields from phenol oxidation reported in Atkinson et al. (1992) (6.7% for OH oxidation and 25.1% for NO_3 oxidation) is also performed. This simulation neglects any dependence of NP yield from phenol oxidation on concentrations of NO_2, O_3 and NO. We observed lower concentrations during both the day and night compared to the base simulation (Figure 5). However, the enhancement of modeled NP in the period of 11:00 -17:00 is distinctly observed with the simulation using the fixed yields in Atkinson et al. (1992), which is in contrast to the lowest concentration in the afternoon from our observations. This, again, indicates there must be a dependence of NP yield from phenol oxidation on NO_2 concentrations in the atmosphere.

3.2.3 Gas-particle partitioning of NP

NP formed in the gas phase can partition into particles (Harrison et al., 2005a). Measurements in several studies demonstrated that 2-NP and MNP were mainly found in the gas phase (Herterich and Herrmann, 1990;Cecinato et al., 2005;Morville et al., 2006).

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However, the reported particle fractions of 4-NP and DNP exhibit a broad range in values: the particle fractions of 4-NP and DNP reported in Herterich and Herrmann (1990) were both lower than 15%, whereas most of the concentrations of 4-NP (>75%) (Cecinato et al., 2005) and DNP (>95%) (Morville et al., 2006) were detected in particles in these other two studies.

The concentrations of NP and other nitrated phenols in particles were not measured in this study. We acknowledge that some fractions of nitrated phenols in particles may evaporate into gas phase in the heated inlets. If it holds true, the measured concentrations of nitrated phenols in this study would fall somewhere between concentrations in gas-phase and the total gas+particle concentrations. Here, the gas-particle partitioning of NP as a function of time was estimated using the equilibrium absorption partitioning theory (Pankow, 1994;Donahue et al., 2006) (see details in the SI), based upon pure compound liquid vapor pressure of 2-NP and 4-NP (Schwarzenbach et al., 1988) (Table 2) and measured organic aerosol (OA) concentrations with an aerosol mass spectrometer (AMS). The dependence with temperature was accounted for using the Clausius-Clapeyron relationship with reported enthalpies of evaporation (H_{vap}) (Schwarzenbach et al., 1988). Although vapor pressures from Schwarzenbach et al. (1988) might have significant uncertainties, Schwarzenbach et al. (1988) provided the only comprehensive measurements of sub-cooled liquid vapor pressures of nitrated phenols reported in the literature.

The calculated fractions in particle (F_p) for 2-NP were generally very low (campaign average: $1.1\pm0.9\times10^{-4}$, max: 7.3×10^{-4}), whereas F_p for 4-NP were higher (average: 0.053 ± 0.048, max: 0.38). The variability of the determined F_p values is the result of variations of both OA concentrations (12.5 ± 8.7 μg/m^3, min: <1 μg/m^3, max; 42.6 μg/m^3) and ambient temperature (-5±5 °C, min: -17 °C, max: 10 °C) during the campaign. The higher F_p for 4-NP is expected, as 4-NP (1.4×10^{-3} Torr at 298 K) has much lower vapor pressure than 2-NP (0.20 Torr at 298 K) (Table 2). In addition to absorption, partitioning of NP into aqueous phase of particles is another possible pathway affecting F_p. This mechanism is estimated using Henry's law constants (Sander, 2015) and determined liquid water content (LWC) (8.4 ± 7.5 μg/m^3) in aerosol using the ISORROPIA model (Fountoukis and Nenes, 2007). The estimated F_p values based on aqueous phase

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partitioning for 2-NP (1.3×10^{-7}) and 4-NP (3.0×10^{-5}) are both much lower than F_p estimated from the equilibrium absorption partitioning theory, indicating partitioning of NP into particle aqueous phase was not important during UBWOS 2014.

The gas-particle partitioning of 2-NP and 4-NP determined above was incorporated into the box model by constraining the estimated F_p in the determination of gas-particle mass transport rates. The mass transport rates (R_{in} and R_{out}) of a species into and out of particles with radius r are approximated by (Jacob, 2000):

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

$$R_{out} = \left(\frac{r}{D_g} + \frac{4}{\upsilon\alpha}\right)^{-1} A \times \frac{c_p}{K_{ep}} = \frac{1}{\tau} \times \frac{c_p}{K_{ep}} \qquad (2)$$

where c_g and c_p are concentrations of the species in the gas and particle phase. 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 $F_p/(1-F_p)$. The characteristic time scale of mass transfer (τ) is estimated to be on the order of minutes for particles in the troposphere (Bowman et al., 1997;Jacob, 2000). Thus, rather than determining the characteristic time scale explicitly, we assume that the equilibrium is maintained at each model step (τ=5 min). After entering into particles, no further reaction of NP was prescribed in the model. The modeled diurnal profiles of NP associated with the inclusion of gas-particle partitioning are shown in Figure 6. Compared to the base simulation, the modeled NP concentrations in the gas phase using the estimated F_p from 4-NP are lower (4-8%) for most of the day and slightly higher (2-3%) in the morning when NP concentrations decreased quickly. Since the predicted F_p from 2-NP is very small, the modeled NP concentrations in the gas phase using the estimates from 2-NP were almost identical to the base simulation. In contrast with the modeled concentrations of NP in the gas phase, the modeled total concentrations of NP in gas and particle phase are consistently higher than the base simulation that do not consider gas-particle partitioning. In summary, we observe relatively small changes of the modeled gaseous NP concentrations after the inclusion of gas-particle partitioning in the box model.

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Further measurements of the gas/particle partitioning of nitrated phenols are needed to explain the variety of F_p values observed in different studies and/or the potential differences between measurements and prediction from the equilibrium absorption partitioning model.

3.2.4 Budget analysis of phenol and nitrophenol

Diurnal profiles of formation and loss rates derived from the base simulation of the box model for both phenol and NP are shown in Figure 7. Production of phenol only occurs in the daytime from OH oxidation of benzene. The magnitudes of losses of phenol due to OH oxidation (21 ppt/day) and NO_3 oxidation (19 ppt/day) are comparable on a daily basis. From morning to afternoon (8:00-15:00), production of phenol is larger than the losses, resulting in continuous growth of phenol concentrations in this period. After 15:00 pm, the losses start to surpass the production and phenol concentrations decrease quickly. With fast reduction of phenol concentrations in the evening, phenol loss from the reaction with NO_3 is mainly occurred before midnight.

As shown in Figure 7, NP is produced during both daytime and night, with more production in the daytime. As mentioned earlier, the only formation pathway of NP is from the reaction of phenoxy radicals (C_6H_5O) with NO_2, so the contribution from different pathways to NP formation can be derived from source analysis of C_6H_5O radicals (Figure 7C). The production of C_6H_5O radicals is dominated by the reaction of $C_6H_5O_2$ radicals with NO during daytime (71% for 24-hour average) and the reaction of phenol with NO_3 radicals at night (27% for 24-hour average). There are several sources contributing to the formation of $C_6H_5O_2$ radicals in the MCM, including photolysis of benzaldehyde and peroxybenzoic acid, OH oxidation of benzoic acid and phenyl hydroperoxide, and degradations of other radicals (e.g., phenylperoxyacyl radical $C_6H_5CO_3$), suggesting a wide range of aromatic compounds as the precursors of NP in the daytime. The reaction of phenol with OH radicals only accounts for a small fraction of the production of C_6H_5O radicals (2% for 24-hour average), due to the small yield of NP (6%) from the reaction of OH with phenol in the MCM. It indicates phenol is not an important precursor for NP during daytime. The destruction of NP is mainly due to photolysis (17 ppt/day), with some contributions from NO_3 reaction (1.7 ppt/day). The

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reaction with OH radicals is not important for the losses of NP in the UBWOS 2014. Dilution/deposition processes account for 20% of the total loss of NP in the box model. Our results are consistent with previous proposal on photolysis as the dominant chemical loss pathway for nitrated phenols (Bejan et al., 2007). Based on the conditions at the Horse Pool site, the lifetime of NP due to photolysis at noontime is calculated to be ~80 min. As the result of the short lifetime of NP during daytime, the production (23.6 ppt/day) and loss rates (23.1 ppt/day) of NP maintain a balanced budget of NP on a daily basis. The inclusion of the reaction of phenoxy radicals (C_6H_5O) with NO discussed in section 3.2.2 would mainly affect NP budget in the noontime, with smaller production and loss in this period.

The different diurnal variations of production and loss rates of NP explain the measured diurnal profile of NP concentrations shown in Figure 3. The increase of loss rates from photolysis result in the quick decline of NP concentrations in the morning. The formation of NP from NO_3 oxidation of phenol in the evening exceeds the destruction of NP, which accounts for the enhancement of NP in this period. The formation and loss rates of NP are comparable in the afternoon and relatively constant concentrations of NP were observed.

A previous study showed that photolysis of nitrated phenols contributes to HONO formation (Bejan et al., 2006). If we assume photolysis of nitrated phenols at rates of 1.4%×J(NO_2) yields HONO at a 100% yield (upper limit), photolysis of NP, MNP and DMNP together accounted for a formation rate of HONO of 1.5±1.9 ppt/hour around noontime (9:00-15:00) during UBWOS 2014. This photolysis source would increase the steady state concentrations of HONO by 0.5 ppt in early morning (7:00-8:30) and 0.2 ppt during the noontime period (9:00-15:00), which are only small fractions of measured HONO concentrations (50-100 ppt) during UBWOS 2014 (Edwards et al., 2014).

3.3 Dinitrophenol

Further oxidation of NP in the presence of NO_x produces DNP. The measured time series of DNP in January 18-22 is shown in Figure 8. A similar diurnal profile was observed for DNP as other nitrated phenols, associated with higher concentrations at night and lower in the daytime. We also notice that the peak time of DNP concentrations

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at night was somewhat later than NP, consistent with further oxidation of NP as the source of DNP.

In the MCM v3.2, reactions of NP with OH or NO_3 radicals generate nitrophenoxy radicals ($NO_2C_6H_5O\cdot$), which react further with NO_2 to form DNP. Here, we assume DNP has the same photolysis rate as NP (1.4% of photolysis frequency of NO_2) (Bardini, 2006) and we added the photolysis into the MCM v3.2. The simulated concentrations of DNP from the box model are also displayed in Figure 8. The agreement between measurements and simulation is quite good from the base simulation. DNP has also been observed in the particle phase at significant fractions (Morville et al., 2006). Using the equilibrium absorption partitioning theory described in section 3.3.3 and vapor pressures of two different DNP isomers (2,4-DNP and 2,5-DNP) (Table 2), we incorporated the calculated particle fractions of DNP (Table 2) into the box model as a sensitivity simulation. The predicted DNP concentrations from this simulation are around 5% lower than the base simulation at night. Considering the limited information on DNP formation, the agreement between measured and modeled concentrations of DNP from both simulations is encouraging. This degree of agreement implies that DNP concentrations measured in UBWOS 2014 is explainable by known chemical reactions in the gas phase.

As described in Section 3.2, photolysis is the dominant sink for NP and box model results indicate that photolysis of NP may not generate phenoxy radical (by losing NO_2). The other possible product from photolysis of NP is nitrophenoxy radical (Figure 1 Route 3), which would act as a secondary source of DNP. This assumption is evaluated as a new simulation. The simulation predicted concentration peaks of DNP in the morning (the orange line in Figure 8), which are not observed in our measurements. Thus, we exclude nitrophenoxy radical as the main products of photolysis of NP. However, the products and exact chemical mechanisms for photolysis of NP remain unclear and thus the photolysis of NP warrants further detailed studies.

3.4 Non-gas phase reactions

The box model only considers gas phase reactions that produce nitrated phenols. In addition to gas phase reactions, aqueous reactions in particles and heterogeneous reactions are other potential sources of nitrated phenols (Harrison et al., 2005a). As

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shown in section 3.3.3, using chemical compositions of aerosol at the Horse Pool site and the ISORROPIA model (Fountoukis and Nenes, 2007), the liquid water content (LWC) in aerosol during UBWOS 2014 was estimated to be 8.4±7.5 μg/m^3 (whole campaign average), or 8.4±7.5×10^{-12} expressed as the volume fraction. Based on the box modeling results in Harrison et al. (2005b), aqueous reactions contribute less than 2% of NP production at 3×10^{-9} volume fraction LWC. Thus, aqueous reactions in UBWOS 2014 should not be a significant source for nitrated phenols compared to gas phase reactions.

The Uintah Basin was covered by snow during UBWOS 2014. The importance of heterogeneous reactions on snow surface to formation of nitrated phenols is evaluated using measurements of the vertical gradients of these species. Here, the concentration gradient is defined as the concentrations measured at 18.5 m subtracted from those measured at 1 m. As shown in Figure 9, we observed negative concentration gradients for nitrated phenols at night, indicating that deposition was playing a role and consequently ground snow was a net sink for nitrated phenols at night. A previous study suggested heterogeneous reaction of N_2O_5 with phenol in the aqueous phase produces NP (Heal et al., 2007). Strong deposition of N_2O_5 to the snow surface was observed at night during UBWOS 2014, but as discussed no production of nitrated phenols near the snow surface was detected at night (Figure 9). The vertical gradients for nitrated phenols in the daytime fluctuated around zero with large variations, which might be a result of their low concentrations during daytime. The analysis of vertical gradients implies that heterogeneous reactions on snow surface may not be important for formation of nitrated phenols in the atmosphere during UBWOS 2014.

4. Conclusions

In this study, nitrated phenols in the gas phase were measured using an online acetate ToF-CIMS in an oil and gas production region during winter. Strong diurnal profiles were observed for nitrated phenols, with concentration maxima at night. As the dominant sink for nitrated phenols, photolysis accounted for lower concentrations of nitrated phenols during daytime. We determined that the photolysis of nitrated phenols was not an important source of HONO during UBWOS 2014. Based on box model results, NP was mainly formed in the daytime (73%) from a wide range of precursors,

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with significant contribution from the reaction of phenol with NO_3 radicals at night (27%). Box model results also indicated that gas phase oxidation of aromatics was able to explain the measured concentrations of NP and DNP. We demonstrated that box model results provided valuable information on the detailed chemical mechanisms in the formation and destruction of NP, e.g., the NO_2 dependence of NP yields from phenol oxidations and chemical products of NP photolysis. We determined that aqueous-phase reactions and heterogeneous reactions were minor sources of nitrated phenols in this study. Although the dataset of nitrated phenols was collected in an oil and gas production region, the chemistry in secondary formation of nitrated phenols and the dynamics of the budget of nitrated phenols in other regions, e.g., urban areas, should behave similarly to those shown in this study.

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Biomass burning activity did not affect the UBWOS 2014 measurements, and the concentrations of phenols and nitrated phenols were mainly from oxidations of aromatics in the atmosphere. The measurements during UBWOS 2014 provided a great opportunity to study secondary formation of nitrated phenols in the absence of other confounding sources. The UBWOS 2014 campaign also represented the first coincident and high time-resolution measurements of aromatic hydrocarbons, phenols and nitrated phenols in ambient air. The measurements of phenol and nitrated phenols provided a better understanding of their sources, budgets and roles in atmospheric chemistry and for the evaluation of the oxidation mechanisms of aromatics. This is achieved by the emergence of the new ToF-CIMS and PTR-TOF techniques. We envision that these techniques will provide the ability to detect many other intermediate compounds in the atmosphere and that the measurements will advance the understanding of atmospheric oxidation processes.

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Figures

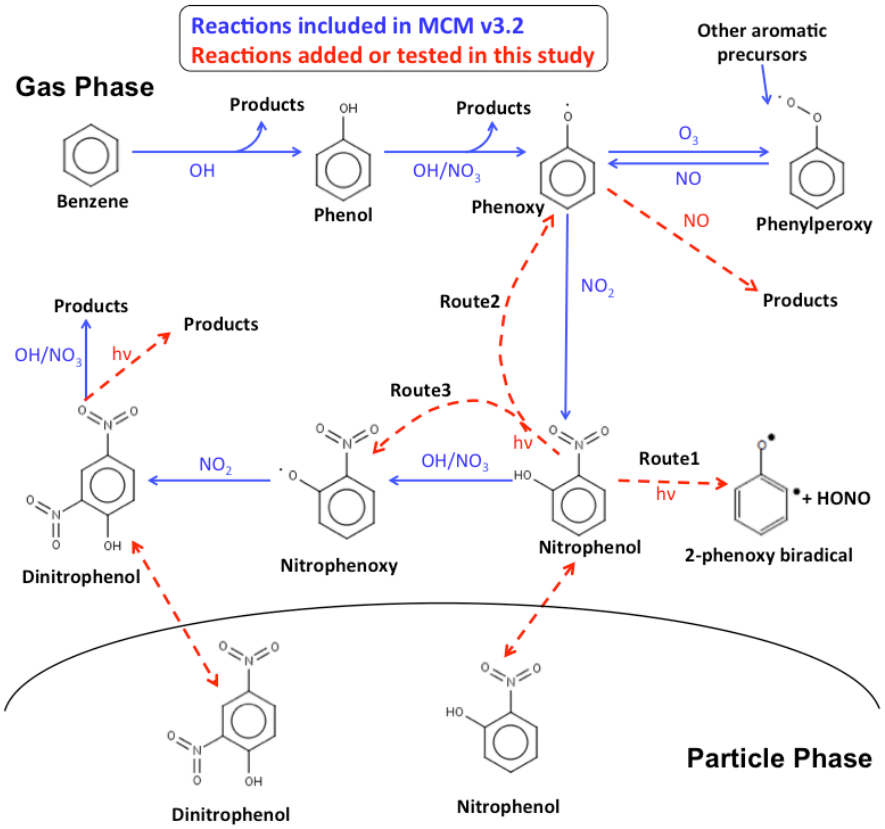


Figure 1. Formation of phenol, nitrophenol (NP) and dinitrophenol (DNP) from the photo-oxidation of benzene in the atmosphere (Jenkin et al., 2003). Reactions in blue are included in the MCM v3.2, whereas reactions in red are added or evaluated in this study. For NP, DNP and the intermediate radicals, other isomers are expected but not shown for the sake of clarity.

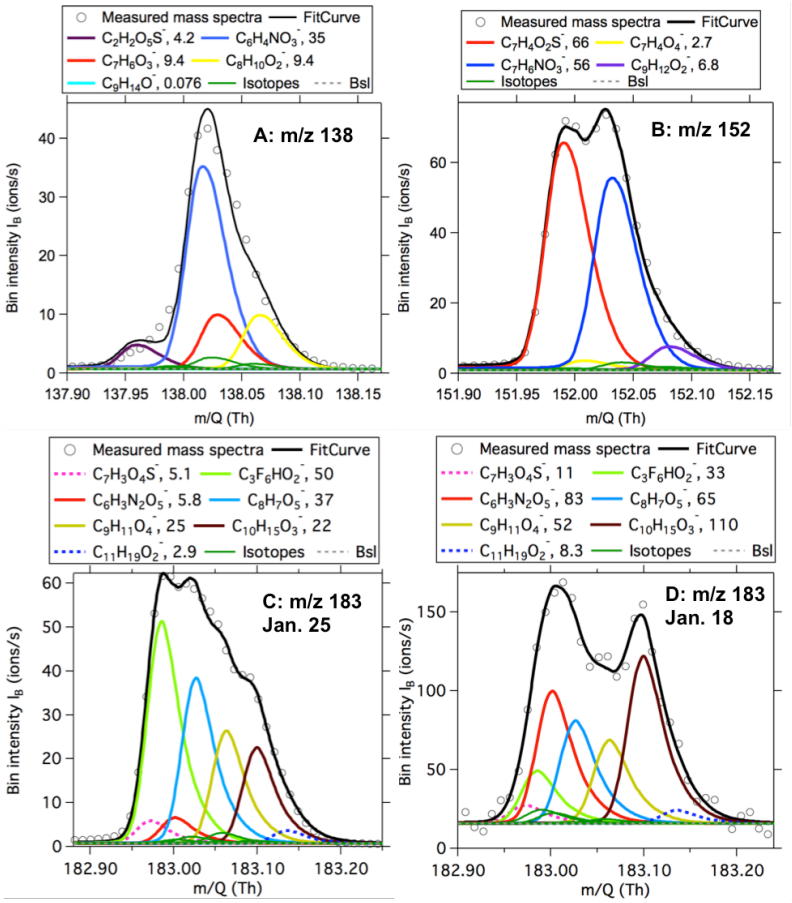
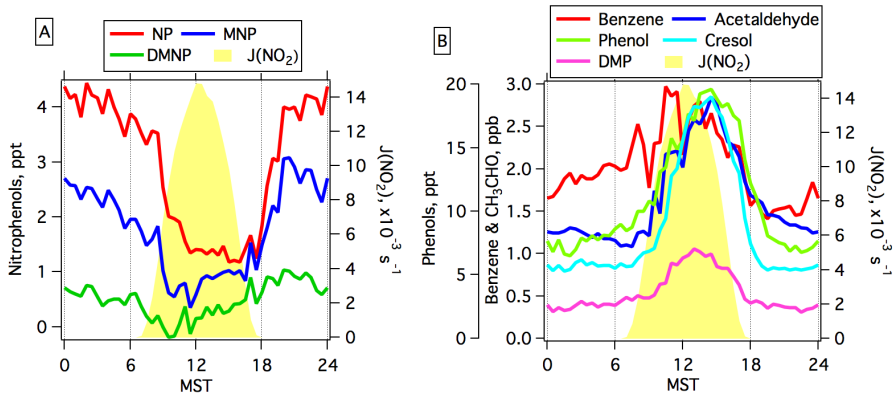


Figure 2. High-resolution peak fitting to the averaged mass spectra of acetate ToF-CIMS for m/z 138 (A), m/z 152 (B) and m/z 183 (C) on January 25, 2014 and m/z 183 (D) on Jan. 18, 2014 during UBWOS 2014. The dark green lines indicate the calculated isotope signals from lower masses.



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974 Figure 3. (A) Diurnal profiles of measured NP, MNP, DMNP. (B) Diurnal profiles of

975 benzene, acetaldehyde, phenol, cresol and DMP. Photolysis frequencies of NO_2 are

976 shown in both A and B for reference.

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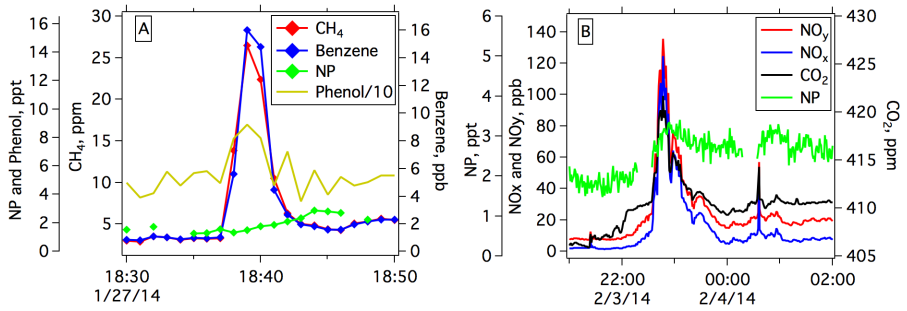

Figure 4. (A) An episode with high concentrations of methane and benzene on January 27, 2014 during UBWOS 2014. The source for this episode was fugitive emissions from oil and gas activities. (B) An episode with high concentrations of NO_y and CO_2 on February 3, 2014 during UBWOS 2014. The source for this episode was fuel combustion (e.g., vehicle exhaust and/or other combustion sources for oil and gas extraction).

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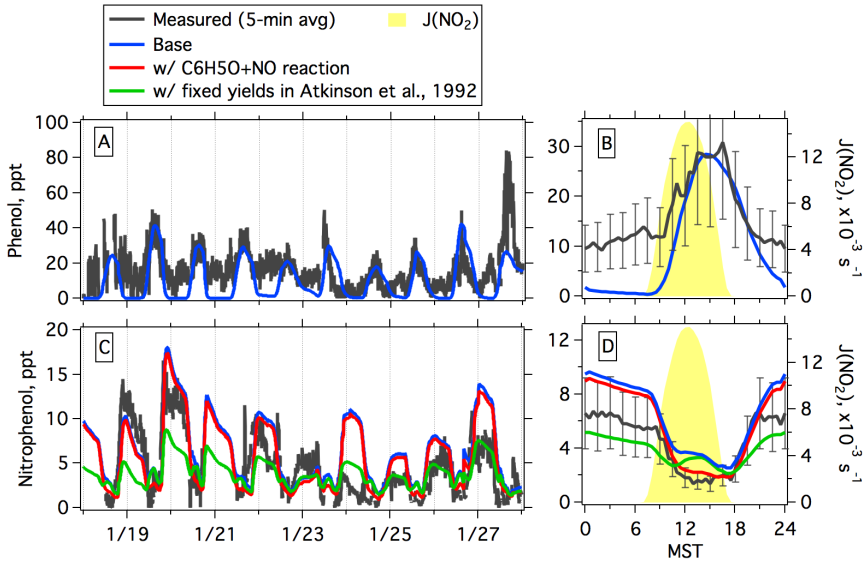

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987 Figure 5. (A and C) Comparison of measured and modeled time series of phenol (A) and
988 NP (C). (B and D) Diurnal profiles of measured and modeled concentrations of phenol
989 (B) and NP (D). Photolysis frequencies of NO_2 are shown in B and D for reference. Error
990 bars in (B) and (D) indicate the accuracies of concentrations of phenol (50%) and NP
991 (40%), respectively.
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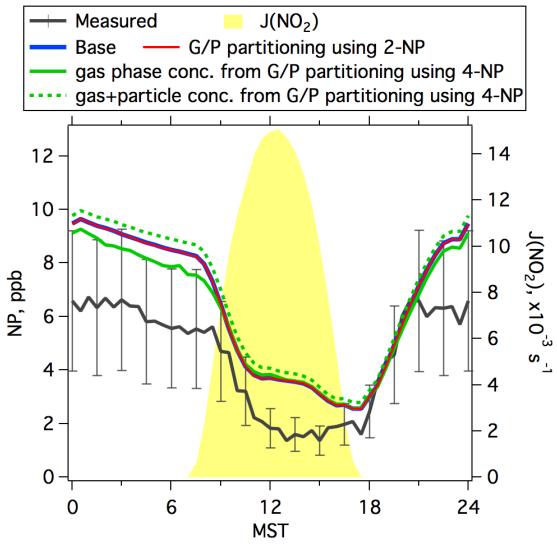

Figure 6. Diurnal profiles of measured and modeled concentrations of NP from the base simulation and the simulations considering gas/particle partitioning. Photolysis frequencies of NO_2 are shown for reference. Error bars indicate the accuracies of concentrations of NP (40%).

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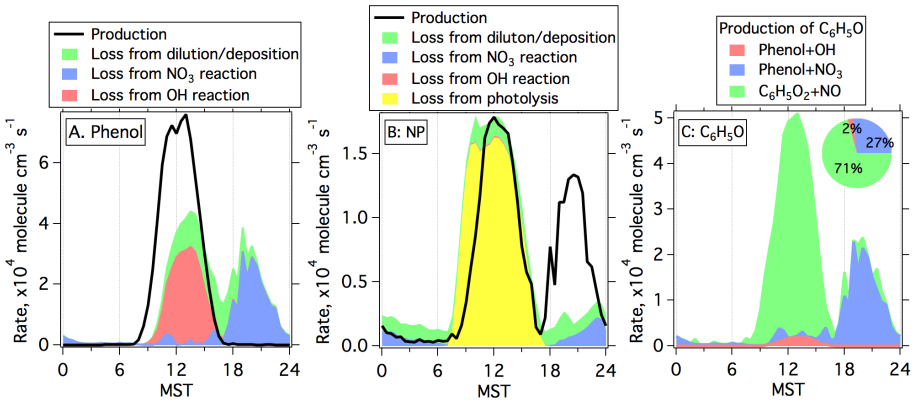

Figure 7. Diurnal profiles of production and loss rates from different pathways for phenol (A) and NP (B) derived from the base simulation of the box model. (C) Diurnal profiles of production rates from different pathways for C_6H_5O radicals. The inserted pie in C shows contributions from three different pathways to the formation of C_6H_5O radicals on a daily basis.

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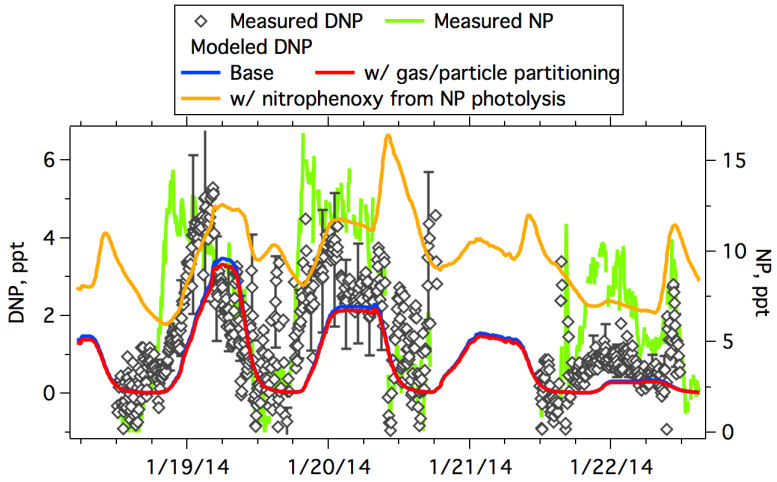

Figure 8. Comparison of measured and modeled time series of DNP. Measured time series of NP is also shown for comparison. Error bars indicate the accuracies of DNP concentrations (50%).

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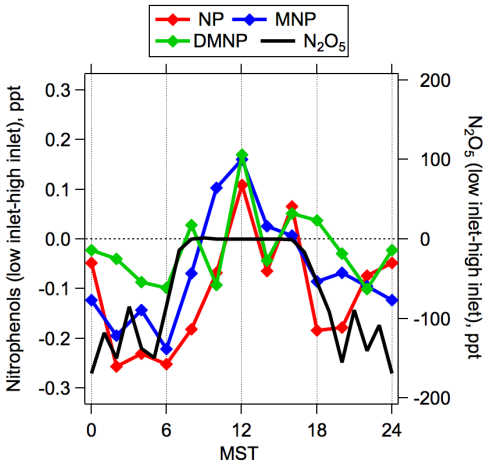

Figure 9. Diurnal profiles of vertical gradients for nitrated phenols measured in January 22 – February 1. The measured vertical gradient of N_2O_5 measured in February 6- 14 is also shown for comparison.

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Tables

Table 1. Sensitivities and detection limits of nitrated phenols in acetate ToF-CIMS

Species	Abbreviation	Ion	m/z	Sensitivity, ncps/ppt	Ratio to Formic acid[e]	Detection Limit, ppt[f]	
						Method 1	Method 2
Nitrophenol	NP	$C_6H_4NO_3^-$	138.0197	13.2[a]	2.6	0.18	0.45
Methylnitrophenol	MNP	$C_7H_6NO_3^-$	152.0353	16.6[b]	3.3	0.24	0.36
Dimethylnitrophenol + ethylnitrophenol	DMNP	$C_8H_8NO_3^-$	166.0510	16.6[c]	3.3	0.14	0.36
Dinitrophenol	DNP	$C_6H_3N_2O_5^-$	183.0047	10.3[d]	2.0	0.23	0.58

a: Average from calibrations of 2-NP (8.4 ncps/ppt) and 4-NP (18.0 ncps/ppt).

b: Calibration of 2-methyl-4-nitrophenol.

c: Using the same value as MNP.

d: Calibration using 2,5-dinitrophenol.

e: Based on the determined sensitivity of formic acid at 5.0 ncps/ppt during UBWOS 2014.

f: Method 1 is based on the random errors of observed counts follow Poisson distribution, whereas method 2 is calculated as the concentrations with counts at three times of standard deviations of measured background counts (see discussions in text and in Bertram et al. (2011)).

Table 2. Vapor pressure, enthalpy of evaporation (ΔH_{vap}) and calculated concentration fractions in particle phase (F_p) for several nitrated phenols

Species	Vapor pressure at 298 K, Torr[a]	ΔH_{vap}, kJ/mol[a]	F_p,
2-NP	0.20	53.1	$1.1\pm0.9\times10^{-4}$
4-NP	1.4×10^{-3}	80.0	$5.3\pm4.8\times10^{-2}$
2,4-DNP	8.4×10^{-3}	70.4	$4.6\pm4.4\times10^{-3}$
2,5-DNP	1.2×10^{-3}	68.5	$2.8\pm2.7\times10^{-3}$

a: Calculated from data in Schwarzenbach et al. (1988).

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Measurements of DNP using the acetate CIMS were challenging during UBWOS 2014, due to the influence of a fluorine ion ($C_3F_6HO_2^-$, m/z 182.9886) released from the heated Teflon inlet (see Figure S2 for peak fitting example). The release of $C_3F_6HO_2^-$ ion was supported by much higher signals of this ion from the long-heated inlet compared to the short-unheated inlet, when inlet-switching experiments were conducted in February 2-5 (Figure S1). We also observed that several other fluorine ions were released from the heated inlet ions, such as $C_2F_3O_2^-$, $C_3F_4O_2^-$ and $C_3F_5O_2^-$. The presence of $C_3F_6HO_2^-$ ion made it difficult to get accurate signals of the ion for of DNP (m/z 183.0047) for most of the time during UBWOS 2014, when the long-heated inlet was used (Figure S1). As a result, we will only use measured DNP data in the beginning of the campaign (January 18-22), when the long heated inlet was not connected to the acetate CIMS and no inlet switching was performed.