

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):

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

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-nitrophenol. 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-dinitrophenol 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, NO_x 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, CH₄ 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 CH₄ 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 C₃H₄F₂OH⁺ 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.

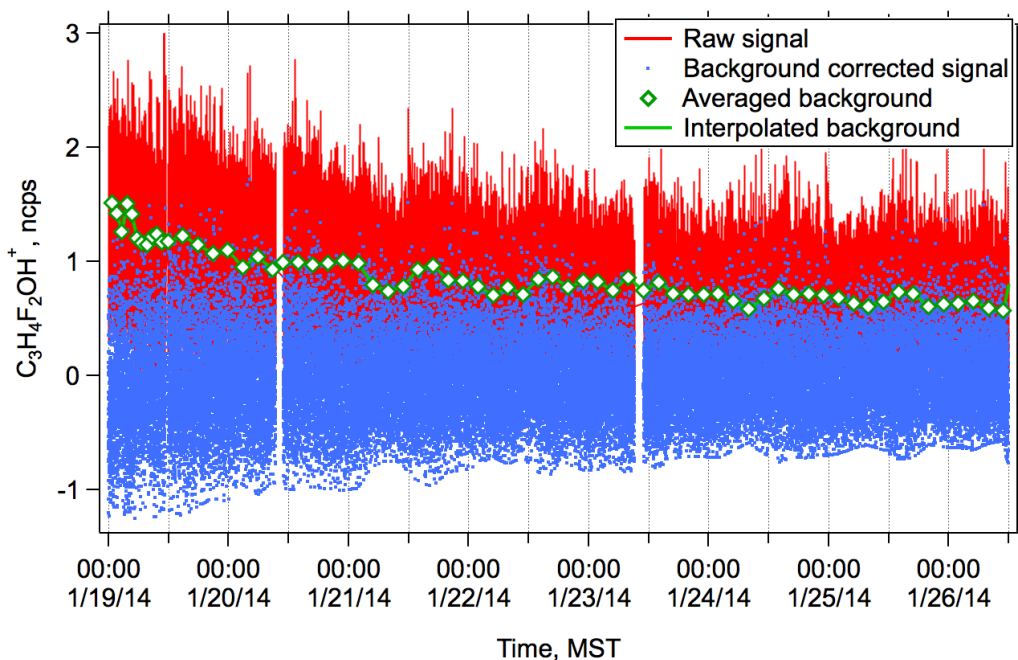


Figure R1. Time series of the raw signals, averaged background signals, interpolated background signals and background-corrected signals for the $C_3H_4F_2OH^+$ ion in PTR-TOF during UBWOS 2014. The background-corrected signal is symmetrically scattered around zero, indicating no measurable signal in 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 (O₂⁻), m/z 34.9694 (Cl⁻), m/z 44.9982 (CHO₂⁻), m/z 59.0139 (C₂H₃O₂⁻), m/z 61.9884 (NO₃⁻), m/z 143.9840 (C₃F₄O₂⁻), m/z 162.9824 (C₃F₅O₂⁻), m/z 193.9808 (C₄F₆O₂⁻) and m/z 243.9776 (C₅F₈O₂⁻). 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. C₈H₁₀O₂⁻ 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.

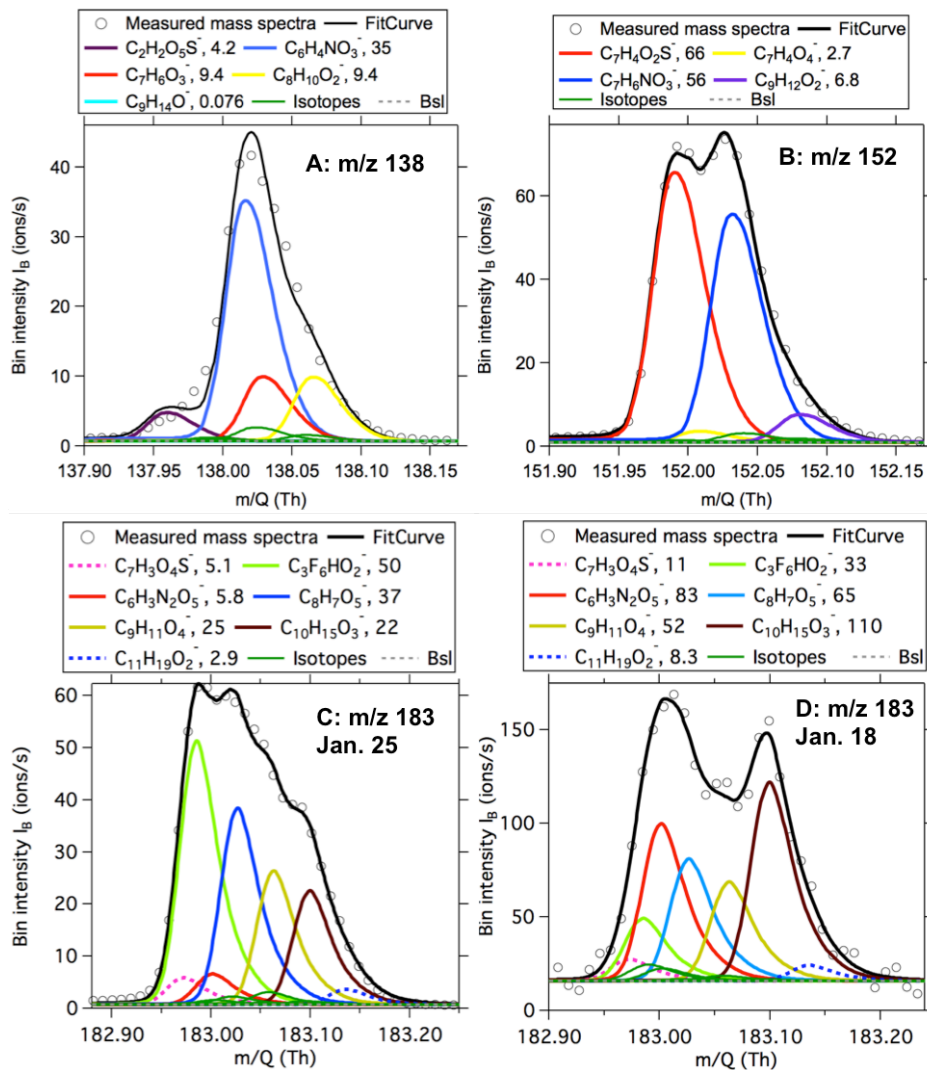


Figure R2 (Figure 2 in the revised manuscript). High-resolution peak fitting to the averaged mass spectra of acetate ToF-CIMS for m/z 138 (A), m/z 152 (B) and m/z 183 (C) on January 25, 2014 and m/z 183 (D) on Jan. 18, 2014 during UBWOS 2014. The dark green lines indicate the calculated isotope signals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

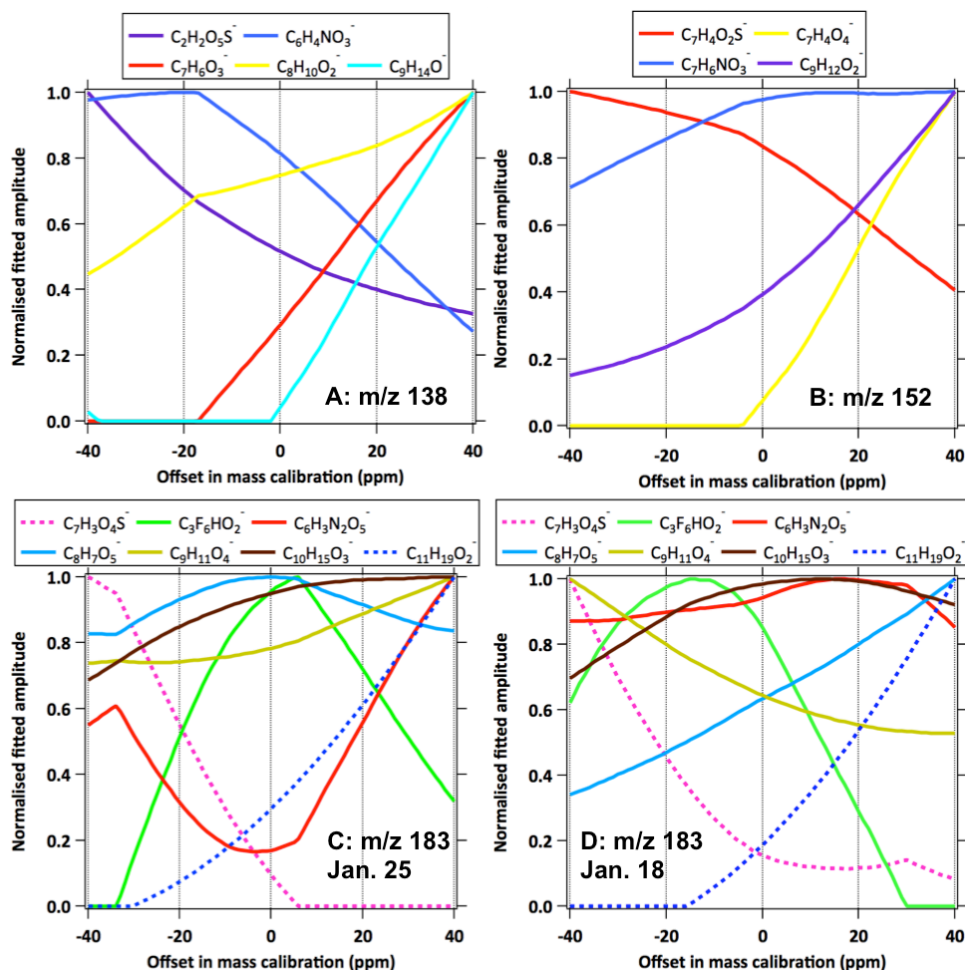


Figure R3 (Figure S2 in the revised manuscript). Sensitivity of the fitted ion intensities to mass calibration errors for ions at m/z 138 (A), m/z 152 (B) and m/z 183 (C) based on the averaged mass spectra on January 25, 2014 and m/z 183 (D) based on the averaged mass spectra on January 18, 2014 (see 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.

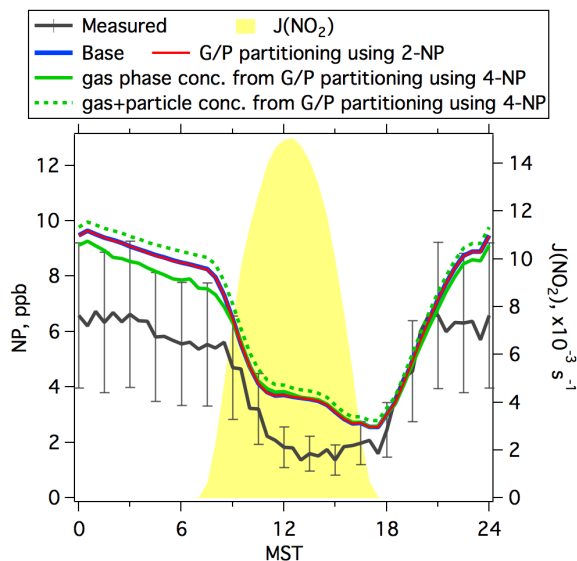


Figure R4. Diurnal profiles of measured and modeled concentrations of NP from the base simulation and the simulations considering gas/particle partitioning. Photolysis frequencies of NO₂ are shown for reference. Error bars indicate the accuracies of concentrations of NP (40%).

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).

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+3 σ) 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.

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 + NO₂. 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 C₆H₅O radicals and NO₂ is an ineffective sink for NP, since C₆H₅O radical will re-form NP by reacting with NO₂. 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 C₆H₅O 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 $1.4\% \times J(NO_2)$) 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 $1.4\% \times J(NO_2)$ yields HONO at a 100% yield (upper limit),...”

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

Reply: Done.

References:

- Bardini, P.: Atmospheric Chemistry of Dimethylphenols & Nitrophenols, PhD, University College Cork, Corcaigh, 2006.
- Cappa, C. D., Lovejoy, E. R., and Ravishankara, A. R.: Evidence for liquid-like and nonideal behavior of a mixture of organic aerosol components, *Proc Natl Acad Sci U S A*, 105, 18687-18691, 10.1073/pnas.0802144105, 2008.
- Corbin, J., Othman, A., D. Allan, J., R. Worsnop, D., D. Haskins, J., Sierau, B., Lohmann, U., and A. Mensah, A.: Peak-fitting and integration imprecision in the Aerodyne aerosol mass spectrometer: effects of mass accuracy on location-constrained fits, *Atmospheric Measurement Techniques*, 8, 4615-4636, 10.5194/amt-8-4615-2015, 2015.
- Cubison, M. J., and Jimenez, J. L.: Statistical precision of the intensities retrieved from constrained fitting of overlapping peaks in high-resolution mass spectra, *Atmospheric Measurement Techniques*, 8, 2333-2345, 10.5194/amt-8-2333-2015, 2015.
- Edwards, P. M., Brown, S. S., Roberts, J. M., Ahmadov, R., Banta, R. M., deGouw, J. A., Dube, W. P., Field, R. A., Flynn, J. H., Gilman, J. B., Graus, M., Helmig, D., Koss, A., Langford, A. O., Lefer, B. L., Lerner, B. M., Li, R., Li, S. M., McKeen, S. A., Murphy, S. M., Parrish, D. D., Senff, C. J., Soltis, J., Stutz, J., Sweeney, C., Thompson, C. R., Trainer, M. K., Tsai, C., Veres, P. R., Washenfelder, R. A., Warneke, C., Wild, R. J., Young, C. J., Yuan, B., and Zamora, R.: High winter ozone pollution from carbonyl photolysis in an oil and gas basin, *Nature*, 514, 351-354, 10.1038/nature13767, 2014.
- Hoyer, v. H., and Peperle, W.: Dampfdruckmessungen an organischen Substanzen und ihre Sublimationswärmen, *Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie*, 62, 61-66, 1958.
- Koss, A. R., de Gouw, J., Warneke, C., Gilman, J. B., Lerner, B. M., Graus, M., Yuan, B., Edwards, P., Brown, S. S., Wild, R., Roberts, J. M., Bates, T. S., and Quinn, P. K.: Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event, *Atmospheric Chemistry and Physics*, 15, 5727-5741, 10.5194/acp-15-5727-2015, 2015.
- Mackay, D., Shiu, W.-Y., Ma, K.-C., and Lee, S. C.: Handbook of physical-chemical properties and environmental fate for organic chemicals, CRC press, 2006.
- Müller, M., George, C., and D'Anna, B.: Enhanced spectral analysis of C-TOF Aerosol Mass Spectrometer data: Iterative residual analysis and cumulative peak fitting, *International Journal of Mass Spectrometry*, 306, 1-8, <http://dx.doi.org/10.1016/j.ijms.2011.04.007>, 2011.
- 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.
- Stark, H., Yatavelli, R. L. N., Thompson, S. L., Kimmel, J. R., Cubison, M. J., Chhabra, P. S., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Methods

- to extract molecular and bulk chemical information from series of complex mass spectra with limited mass resolution, *International Journal of Mass Spectrometry*, 10.1016/j.ijms.2015.08.011, 2015.
- Yatavelli, R. L. N., Stark, H., Thompson, S. L., Kimmel, J. R., Cubison, M. J., Day, D. A., Campuzano-Jost, P., Palm, B. B., Hodzic, A., Thornton, J. A., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Semicontinuous measurements of gas-particle partitioning of organic acids in a ponderosa pine forest using a MOVI-HRToF-CIMS, *Atmos. Chem. Phys.*, 14, 1527-1546, 10.5194/acp-14-1527-2014, 2014.
- Yuan, B., Veres, P. R., Warneke, C., Roberts, J. M., Gilman, J. B., Koss, A., Edwards, P. M., Graus, M., Kuster, W. C., Li, S. M., Wild, R. J., Brown, S. S., Dubé, W. P., Lerner, B. M., Williams, E. J., Johnson, J. E., Quinn, P. K., Bates, T. S., Lefer, B., Hayes, P. L., Jimenez, J. L., Weber, R. J., Zamora, R., Ervens, B., Millet, D. B., Rappenglück, B., and de Gouw, J. A.: Investigation of secondary formation of formic acid: urban environment vs. oil and gas producing region, *Atmos. Chem. Phys.*, 15, 1975-1993, 10.5194/acp-15-1975-2015, 2015.