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of nitrated phenols

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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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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 ($-\text{NO}_2$) and hydroxyl groups ($-\text{OH}$) 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.,

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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 NO₃ radicals yield phenoxy (C₆H₅O) radicals, which react further with NO₂ to generate NP. In addition to benzene oxidation, C₆H₅O radical is also generated from the reaction of NO with phenyl peroxy (C₆H₅O₂) radicals, a product from reactions of some other aromatic precursors, e.g. benzaldehyde (Caralp et al., 1999). Further oxidation of nitrated phenols with nitration process will produce 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 NO₃ radicals (Atkinson et al., 1992; Bolzacchini et al., 2001) have been reported. Berndt and Boge (2003) also showed that the NP yield from OH oxidation of phenol increases at higher NO₂ concentrations. In addition to gas phase reactions, nitrated phenols are formed from aqueous-phase reactions in aerosol or cloud water (Vione et al., 2001, 2005). The importance of the aqueous reactions compared to gas-phase reactions is highly dependent on liquid water content in the atmosphere (Harrison et al., 2005b).

The sinks of nitrated phenols in the gas phase include reactions with OH radicals (Atkinson et al., 1992; Bejan et al., 2007), with NO₃ radicals (Atkinson et al., 1992), with chlorine atoms (Bejan et al., 2015) and photolysis (Bejan et al., 2007; Chen et al., 2011). It has been proposed that photolysis is the dominant gas phase atmospheric loss for nitrated phenols (Bejan et al., 2007). Despite the importance of photolysis of

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5 nitrated phenols, the photolysis frequency of nitrated phenols under ambient conditions was only reported in a single non-peer reviewed publication (1.4 % of photolysis frequency of NO_2) (Bardini, 2006). The chemical products from photolysis of nitrated phenols were proposed, but the proposed products were not fully evaluated against experimental results (Bejan et al., 2006). Nitrated phenols are also removed by various processes in the aqueous phase, including reactions with OH, NO_3 and photolysis (Vione et al., 2009).

10 Measurements of nitrated phenols have been mainly conducted using offline methods (Harrison et al., 2005a). Air samples are usually collected on filters or cartridges and then analyzed by liquid chromatography (LC) methods (Rubio et al., 2012; Harrison et al., 2005a; Delhomme et al., 2010). These detection methods are time-consuming and measurements as a function of the time of day are not usually possible (Delhomme et al., 2010). The lack of fast-response online measurements has prevented, at least partially, a thorough investigation of sources and sinks of nitrated phenols. Recently, 15 Mohr et al. (2013) deployed a chemical ionization mass spectrometer (CIMS) using acetate as the reagent ion to measure nitrated phenols online in the particle phase in winter in London and based on their measurements the authors concluded that nitrated phenols were mainly from wood burning in this region of the atmosphere.

20 In this study, we conducted high time resolution measurements of nitrated phenols in the gas phase at a site in an oil and gas production region in winter. High 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 25 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

An Aerodyne time-of-flight (ToF) CIMS (Lee et al., 2014) that uses acetate ($\text{CH}_3\text{C}(\text{O})\text{O}^-$) 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^{-1}) mixed with another flow of N_2 (2.5 L min^{-1}) 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 ($\text{CH}_3\text{C}(\text{O})\text{O}^- \cdot \text{CH}_3\text{C}(\text{O})\text{OH}$)/acetate ($\text{CH}_3\text{C}(\text{O})\text{O}^-$) at $0.4 \pm 0.1\%$. 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 $1-2 \times 10^6$ 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 h 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

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from the sample air and determine instrument backgrounds. During the UBWOS 2014 study, two CIMS inlets constructed from Teflon heated to $\sim 40^\circ\text{C}$ with similar lengths ($\sim 10\text{ m}$) placed at heights of 1 and 18.5 m above ground were switched automatically every 30 min during the period of 24 January–1 February, 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 1–5 February, 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 (Fig. 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 Sect. 3.3.

The ToF-CIMS data was processed using the TOFware software package (<https://sites.google.com/site/citofms/analysis-software/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). The fitted raw signals for the targeted compounds were normalized using an acetate signal at the level of 1×10^6 cps. The fitted m/z used for quantification of concentrations of nitrated phenols in the acetate CIMS are m/z 138.0197 for NP, m/z 152.0353 for MNP, m/z 166.0510 for dimethylnitrophenol + ethylnitrophenol (DMNP) and m/z 183.0047 for DNP. Some examples of high-resolution (HR) peak fitting to the m/z in the mass spectra of the ToF-CIMS are shown in Fig. S2. 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.

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

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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 between our instrument and that in Mohr et al. (2013) can be caused by many different instrumental conditions, 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 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) mass spectra fittings (0–10 %), 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)

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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).

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. 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 Fig. 2. 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 (23:00–01:00 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 3 shows two types of episodes encountered during UBWOS 2014. The first 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 $4.6 \pm 0.7 \times 10^{-3}$ pptppb⁻¹, which is comparable with the reported NP/NO_x emission ratios ($1\text{--}50 \times 10^{-3}$ pptppb⁻¹) 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

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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 (Fig. 2b). 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.

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 ($-5 \pm 5^\circ\text{C}$) 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 Fig. 1 and they were already included in MCM v3.2. The model ran in a time-dependent mode and a 48 h spin-up time was applied in the box model. Measured concentrations of various hydrocarbons, NO_x , NO_3 , O_3 and photolysis frequencies were used as constraints in the box model. The simulation period of the model was chosen to be 18–27 January, a pe-

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riod 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 ($5.8 \times 10^{-6} \text{ s}^{-1}$) was calculated from the decrease rate of NP concentration between 00:00–06:00 a.m. MST when the chemical loss was expected to be low (see Sect. 3.3.4). A higher physical loss rate ($2.0 \times 10^{-5} \text{ s}^{-1}$) during daytime was used to account for larger turbulent mixing during daytime (Edwards et al., 2014), which results in the decrease of concentrations of inertial tracers in the afternoon, e.g. benzene (Fig. 2) 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) (Fig. 1 Route 1). There are other possible chemical routes for photolysis of NP: producing phenoxy radicals ($\text{C}_6\text{H}_5\text{O}$) by losing NO_2 (Route2 in Fig. 1) and producing nitrophenoxy radical by hydrogen abstraction (Route3 in Fig. 1). The simulation test in Fig. S3 excludes phenoxy radicals ($\text{C}_6\text{H}_5\text{O}$) as the main product from photolysis of NP, since $\text{C}_6\text{H}_5\text{O}$ radical will re-form NP by reacting with NO_2 and it would make photolysis an ineffective sink for NP. The route producing nitrophenoxy radical will be discussed in Sect. 3.3.

The simulated results for phenol and NP from the base case of the box model are shown in Fig. 4. 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 ($2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K) removes phenol quickly (Fig. 6 and discussion in Sect. 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 (Fig. S4). Another simulation using calculated NO_3 concentrations from the equilibrium between NO_3 and N_2O_5 (Fig. S4) 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 Fig. 3a). However, a simulation using the measured phenol concentrations as a constraint in the box model, predicted much higher NP concentrations than measurements (Fig. S3). 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 Fig. 4 will be used in the following discussions.

3.2.2 NO_2 dependence of NP yields

As shown in Fig. 1, NP is generated from the reaction of NO_2 with phenoxy radicals ($\text{C}_6\text{H}_5\text{O}$) (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 ($\text{C}_6\text{H}_5\text{O}_2$) with NO. In addition to NO_2 , $\text{C}_6\text{H}_5\text{O}^\bullet$ radicals also react with NO and O_3 (Platz et al., 1998)

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(see Fig. 1), thus the yield of NP has been reported to depend on NO₂ concentrations in the atmosphere (Berndt and Boge, 2003).

In the MCM v3.2, only the reactions of C₆H₅O radical with O₃ and NO₂ are included and here we added the reaction of C₆H₅O with NO ($k = 1.88 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) 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 MST, as the effective yield of NP is reduced (Fig. 4). The small enhancement during the period of 11:00–17:00 MST in NP concentrations from the base simulation is absent in the simulation with the reaction of C₆H₅O with NO. The variations of modeled NP concentrations in the daytime from the new simulation are in better agreement with the measurements (Fig. 4). This indicates the reaction of NO and C₆H₅O radical should be considered to account for the NO₂ 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 NO₃ oxidation) is also performed. This simulation neglects any dependence of NP yield from phenol oxidation on concentrations of NO₂, O₃ and NO. We observed lower concentrations during both the day and night compared to the base simulation (Fig. 4). However, the enhancement of modeled NP in the period of 11:00–17:00 MST 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 NO₂ 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). 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 Her-

rmann (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 Supplement), based upon 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). The calculated fractions in particle (F_p) for 2-NP were generally very low (campaign average: $1.1 \pm 0.9 \times 10^{-4}$, 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 as the result of variations of both OA concentrations ($12.5 \pm 8.7 \mu\text{g m}^{-3}$, min: $< 1 \mu\text{g m}^{-3}$, max: $42.6 \mu\text{g m}^{-3}$) and ambient temperature ($-5 \pm 5^\circ\text{C}$, 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) ($8.4 \pm 7.5 \mu\text{g m}^{-3}$) in aerosol using the ISORROPIA model (Fountoukis and Nenes, 2007). The estimated F_p values based on aqueous phase 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 absorption partitioning theory, indicating partitioning of NP into particle aqueous phase was not important during UBWOS 2014.

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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):

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

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

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 ($\text{m}^2 \text{s}^{-1}$), ν 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 ($\text{m}^2 \text{m}^{-3}$). 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 ($\tau = 5$ 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 Fig. 5. 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. 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 Fig. 6. 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^{-1}) and NO_3 oxidation (19 ppt day^{-1}) are comparable on a daily basis. From morning to afternoon (08:00–15:00 MST), production of phenol is larger than the losses, resulting in continuous growth of phenol concentrations in this period. After 15.00 p.m., 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 Fig. 6, 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 ($\text{C}_6\text{H}_5\text{O}$) with NO_2 , so the contribution from different pathways to NP formation can be derived from source analysis of $\text{C}_6\text{H}_5\text{O}$ radicals (Fig. 6c). The production of $\text{C}_6\text{H}_5\text{O}$ radicals is dominated by the reaction of $\text{C}_6\text{H}_5\text{O}_2$ radicals with NO during daytime (71 % for 24 h average) and the reaction of phenol with NO_3 radicals at night (27 % for 24 h average). There are several sources contributing to the formation of $\text{C}_6\text{H}_5\text{O}_2$ 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 $\text{C}_6\text{H}_5\text{CO}_3$), 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 $\text{C}_6\text{H}_5\text{O}$ radicals (2 % for 24 h average), indicating phenol is not an important precursor for NP during daytime. The destruction of NP is mainly due to photolysis (17 ppt day^{-1}), with some

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contributions from NO_3 reaction (1.7 ppt day^{-1}). The 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 ($23.6 \text{ ppt day}^{-1}$) and loss rates ($23.1 \text{ ppt day}^{-1}$) of NP maintain a balanced budget of NP on a daily basis.

The different diurnal variations of production and loss rates of NP explain the measured diurnal profile of NP concentrations shown in Fig. 2. 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 a 100 % yield of HONO (upper limit) from photolysis of nitrated phenols, photolysis of NP, MNP and DMNP together accounted for a formation rate of HONO of $1.5 \pm 1.9 \text{ ppt h}^{-1}$ around noontime (09:00–15:00 MST) during UBWOS 2014. This photolysis source would increase the steady state concentrations of HONO by 0.5 ppt in early morning (07:00–08:30 MST) and 0.2 ppt during the noontime period (09:00–15:00 MST), 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. Measurements of DNP using the acetate CIMS were challenging during UBWOS 2014, due to the influence of a fluorine ion ($\text{C}_3\text{F}_6\text{HO}_2^-$, m/z 182.9886) released from the heated Teflon inlet (see

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Fig. 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 2–5 February (Fig. 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 (Fig. S1). As a result, we will only use measured DNP data in the beginning of the campaign (18–22 January), when the long heated inlet was not connected to the acetate CIMS and no inlet switching was performed.

The measured time series of DNP in 18–22 January is shown in Fig. 7. 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 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 ($NO_2C_6H_5O^*$), 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 Fig. 7. The agreement between measurements and simulation is quite good from the base simulation. DNP has also been also observed in the particle phase at significant fractions (Morville et al., 2006). Using the equilibrium absorption partitioning theory described in Sect. 3.3.3 and vapor pressure of two different DNP isomers (2,4-DNP and 2,5-DNP) (Table 2), we incorporated the calculated particle fractions of DNP (Table 2) in 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 concen-

trations measured in UBWOS 2014 is explainable by known chemical reactions in the gas phase.

As described in Sect. 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 (Fig. 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 (orange line in Fig. 7), which are not observed in our measurements. Combining the results in Sect. 3.2 and here, we exclude both phenoxy radical and 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 shown in Sect. 3.3.3, using the chemical composition 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 $8.4 \pm 7.5 \mu\text{g m}^{-3}$ (whole campaign average), or $8.4 \pm 7.5 \times 10^{-12}$ 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 here 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

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those measured at 1 m. As shown in Fig. 8, 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 (Fig. 8). 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, 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 the 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 produc-

tion 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.

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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Table 1. Calibration of acetate CIMS to nitrated phenols.

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

^a Average from calibrations of 2-NP (8.4 ncps ppt⁻¹) and 4-NP (18.0 ncps ppt⁻¹).

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

^c Using the same value as MNP.

^d Calibration using 2,5-dinitrophenol.

^e 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).

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Table 2. Vapor pressure, enthalpy of evaporation and calculated concentration fractions in particle phase for several nitrated phenols.

Species	Vapor pressure at 298 K, Torr ^a	ΔH_{vap} , kJ mol ⁻¹ ^a	F_p
2-NP	0.20	53.1	$1.1 \pm 0.9 \times 10^{-4}$
4-NP	1.4×10^{-3}	80.0	$5.3 \pm 4.8 \times 10^{-2}$
2,4-DNP	8.4×10^{-3}	70.4	$4.6 \pm 4.4 \times 10^{-3}$
2,5-DNP	1.2×10^{-3}	68.5	$2.8 \pm 2.7 \times 10^{-3}$

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

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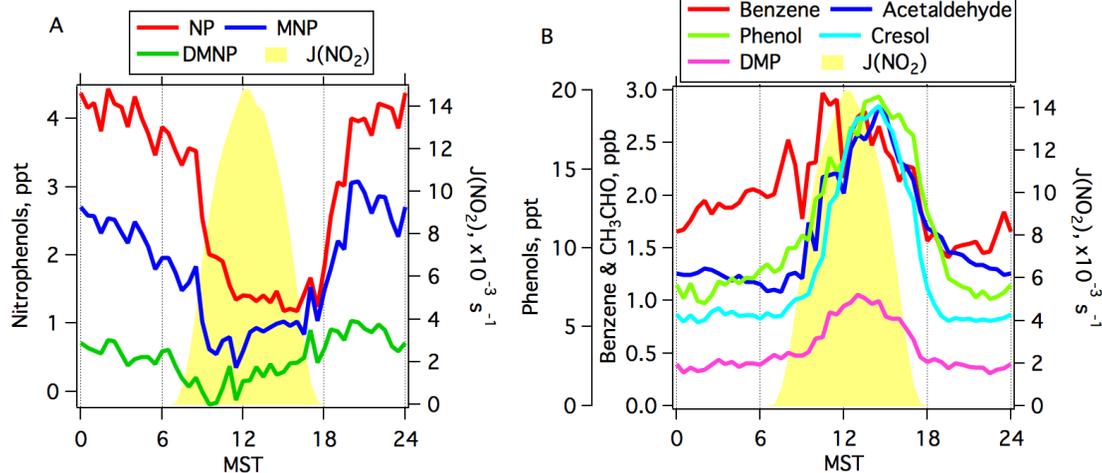


Figure 2. (a) Diurnal profiles of measured NP, MNP, DMNP. (b) Diurnal profiles of benzene, acetaldehyde, phenol, cresol and DMP. Photolysis frequencies of NO_2 are shown in both (a) and (b) for reference.

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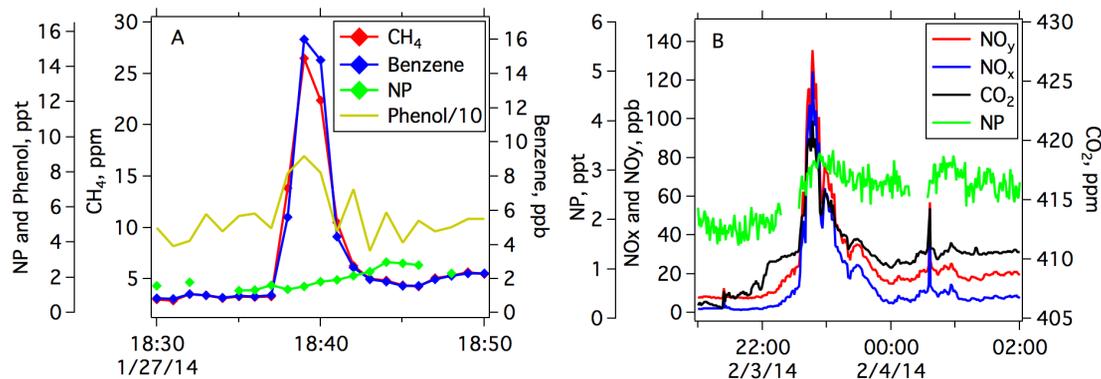


Figure 3. (a) An episode with high concentrations of methane and benzene on 27 January 2014 during UBWOS 2014. The source for this episode was fugitive emissions from oil and gas activities. (b) An episode with high concentrations of NO_y and CO₂ on 3 February 2014 during UBWOS 2014. The source for this episode was fuel combustion (e.g., vehicle exhaust and/or other combustion sources for oil and gas extraction).

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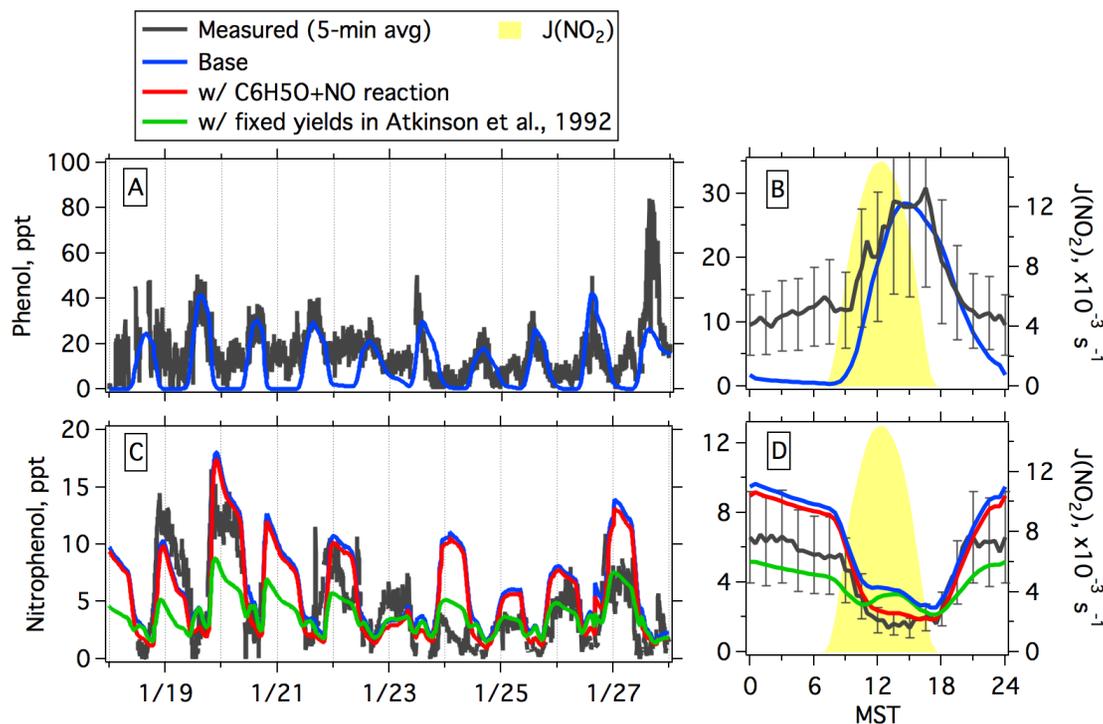


Figure 4. (a and c) Comparison of measured and modeled time series of phenol (a) and NP (c). (b and d) Diurnal profiles of measured and modeled concentrations of phenol (b) and NP (d). Photolysis frequencies of NO_2 are shown in (b) and (d) for reference. Error bars in (b) and (d) indicate the accuracies of concentrations of phenol (50%) and NP (40%), respectively.



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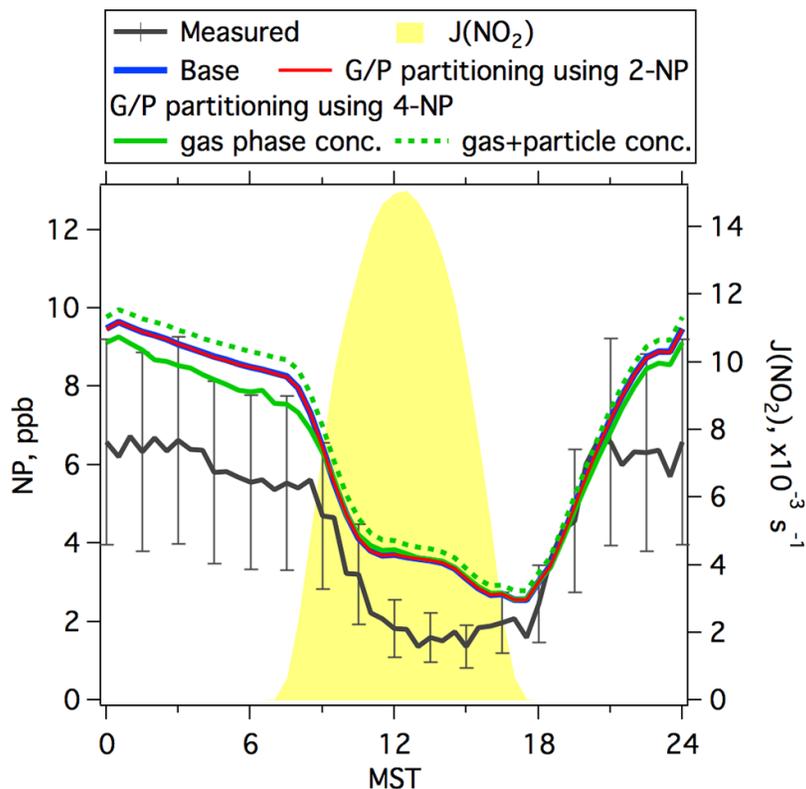


Figure 5. Diurnal profiles of measured and modeled concentrations of NP from base simulation and simulations considering gas/particle partitioning. Photolysis frequencies of NO_2 are shown in (b) and (d) for reference. Error bars indicate the accuracies of concentrations of NP (40 %).



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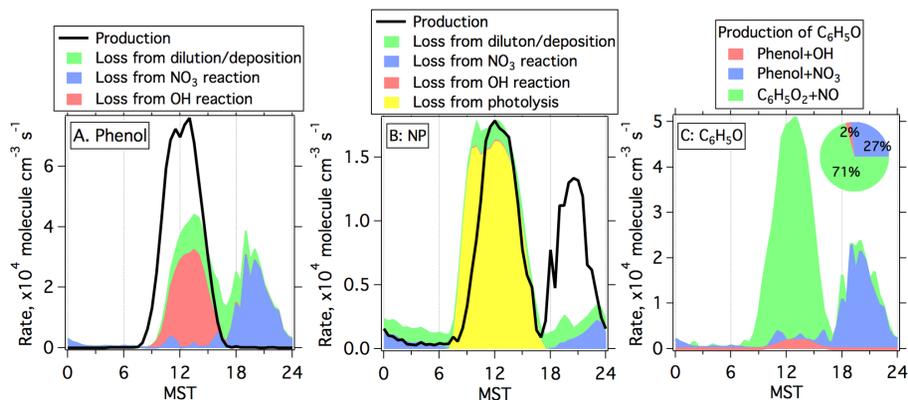


Figure 6. Diurnal profiles of production and loss rates from different pathways for phenol **(a)** and NP **(b)** derived from the base simulation of the box model. **(c)** Diurnal profiles of production rates from different pathways for $\text{C}_6\text{H}_5\text{O}$ radicals. The inserted pie in C shows contributions from three different pathways to the formation of $\text{C}_6\text{H}_5\text{O}$ radicals on a daily basis.

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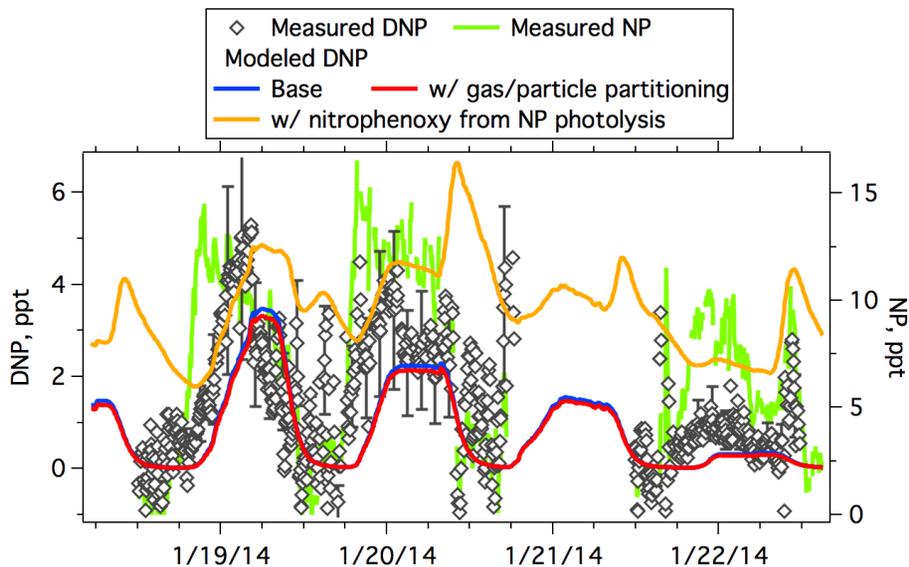


Figure 7. Comparison of measured and modeled time series of DNP. Measured time series of NP is also shown for comparison. Error bars indicate the accuracies of DNP concentrations (50 %).

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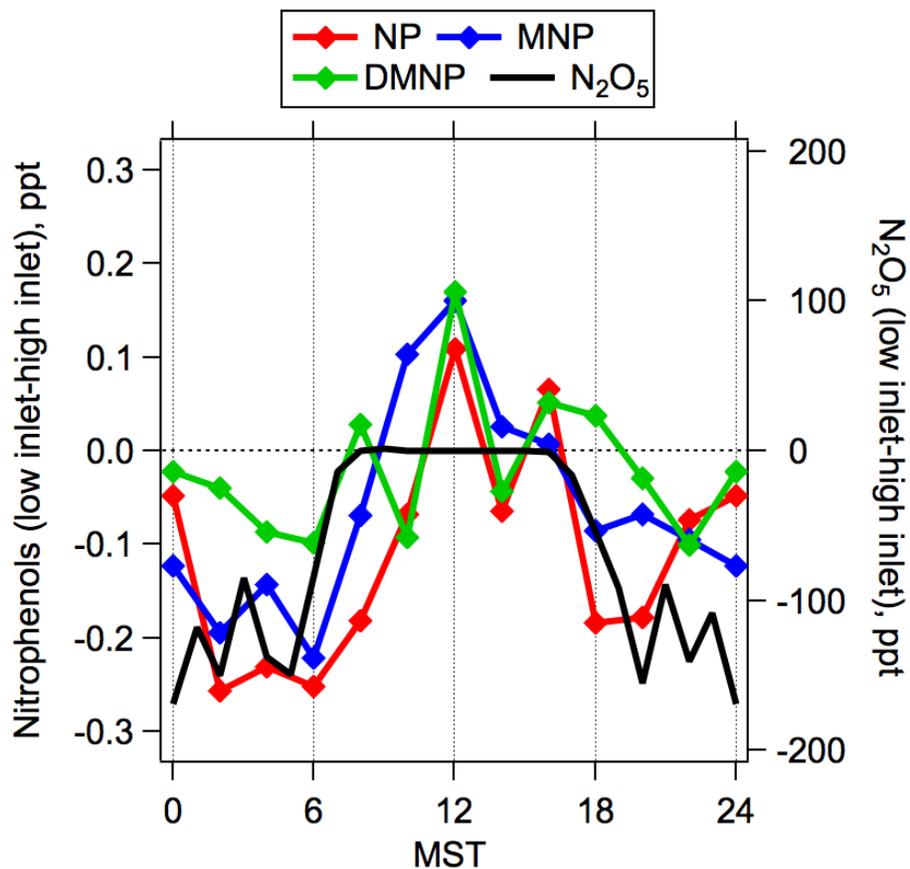


Figure 8. Diurnal profiles of vertical gradients for nitrated phenols measured in 22 January–1 February. The measured vertical gradient of N_2O_5 measured in 6–14 February is also shown for comparison.

