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Key Points:

- Nitrated phenolic compounds in particle, gaseous, and aqueous phases were simultaneously investigated
- Most nitrated phenolic compounds were distributed in the particle phase during cloud events
- Aqueous reactions increased the contents in aerosols and cloud droplets and altered the distribution patterns

Supporting Information:

Supporting Information may be found in the online version of this article.

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Atmospheric Nitrated Phenolic Compounds in Particle, Gaseous, and Aqueous Phases During Cloud Events at a Mountain Site in North China: Distribution Characteristics and Aqueous-Phase Formation

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Abstract Nitrated phenolic compounds in the atmosphere are receiving increasing attention due to their light absorption and biological toxicity. In this study, particulate, gaseous, and cloud water samples were simultaneously collected during cloud events at the summit of Mount Tai in northern China in spring, summer, and winter and the contents of 11 nitrated phenolic compounds were determined. The seasonal average concentrations of the total nitrated phenolic compounds in particles were in the range of 7.3–27.1 ng m⁻³, a little lower than those measured in the gas-phase (18.3–70.6 ng m⁻³). Their concentrations in cloud water were at the levels of 168.4–438.5 μg L⁻¹. 4-Nitrophenol and nitrosalicylic acids were the dominant compounds in particles, while 4-nitrophenol and 2,4-dinitrophenol were the most abundant in the gas phase and cloud water samples. During cloud events, most nitrated phenolic compounds were mainly distributed in the particle phase, except dinitrophenols which were mainly distributed in the gas phase in winter. The field-derived effective Henry's law coefficients were several orders of magnitude higher than their theoretical values in pure water. Moreover, the measured concentrations of particulate nitrated phenolic compounds were substantially greater than the theoretical predictions, especially in spring. The above results indicate that nitrated phenolic compounds were partly formed via aqueous-phase reactions inside the cloud droplets or on the wet particle surfaces, which changed their distribution patterns. The much higher ratios of 2,4-dinitrophenol to the sum of 4-nitrophenol and 5-nitrosalicylic acid in cloud water than those in particles further confirm the enhanced formation via aqueous processes.

Plain Language Summary Nitrated phenolic compounds, among the major components of brown carbon and hazardous substances, can affect air quality, regional climate, and human health. Here, simultaneous field observations of 11 nitrated phenolic compounds in gas, particle, and aqueous phases were conducted at a mountain site in northern China. The seasonal variations of them in the abundances and compositions are compared among different sample types. The distribution characteristics of nitrated phenolic compounds in particle, gaseous, and aqueous phases and the key influencing factors were analyzed. In addition, the aqueous-phase chemistry of 4-nitrophenol and 2,4-dinitrophenol was also explored. The results highlight the importance of aqueous-phase reactions on the formations of nitrated phenolic compounds and their atmospheric abundances and phase distributions during the cloud events.

1. Introduction

Nitrated phenolic compounds are important semi-volatile compounds with at least one hydroxyl- and one nitro-functional group connected to the benzene ring. They come from various emission sources and different formation pathways. Primary sources, including coal combustion, biomass burning, and vehicle exhaust, release large amounts of nitrated phenolic compounds into the atmosphere (Lu et al., 2019a, 2019b; H. L. Wang et al., 2020). Their atmospheric abundances also depend on the secondary formation from precursors such as aromatic hydrocarbons and phenolic compounds in the gas or aqueous phases (Harrison et al., 2005; M. Li

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et al., 2020). Previous studies have shown that nitrated phenolic compounds are among the major contributors to brown carbon (Mohr et al., 2013; Teich et al., 2017; Xie et al., 2017), and the absorption of near-ultraviolet and visible light (particularly at 370 nm) makes non-negligible impacts on radiative forcing and regional climate (Feng et al., 2013; Zhao et al., 2015). Gaseous and aqueous chemistry of nitrated phenolic compounds also lead to the formation of secondary organic aerosols which aggravate air quality and atmospheric visibility (Chow et al., 2016; Hallquist et al., 2009). In addition, trace levels of nitrated phenolic compounds can make adverse effects on human health and plant growth (Huang et al., 1995; Karim & Gupta, 2002; Natangelo et al., 1999).

Nitrated phenolic compounds have been detected in particle, gaseous, and aqueous phases at different locations (Harrison et al., 2005). These compounds in the gas phase readily partition into the particle and aqueous phases, following the Pankow's absorptive partitioning theory and the Henry's law, respectively. Our previous study simultaneously determined gaseous and particulate nitrated phenolic compounds at an urban site in northern China and found the dependence of the gas-particle partitioning on the particle size, the ambient temperature, and the compound volatility (M. Li et al., 2020). Several early field studies analyzed the existence of nitrated phenolic compounds in the gas and aqueous phases (e.g., dew water and cloud water) and found that those species with high Henry's law constants could efficiently partition into cloud water (Lüttke et al., 1997, 1999; Rubio et al., 2012). However, so far, there is lack of comprehensive understanding on the distribution characteristics of nitrated phenolic compounds in particle, gaseous, and aqueous phases, which are important for evaluating their atmospheric fate, long-range transport, and biological toxicity (Bidleman, 1988).

Aqueous processes have been recognized as an important formation pathway for nitrated phenolic compounds in laboratory studies. Specifically, phenol yielded 4-nitrophenol upon aqueous-phase reactions in the presence of nitronium ion (NO_2^+) (Heal et al., 2007). The electrophilic substitution of 3-methylcatechol with NO_2^+ formed non-ignorable amounts of methyl-nitrocatechols (Frka et al., 2016; Vidovic et al., 2018). Aqueous-phase nitration of salicylic acid acted as an important formation pathway for nitrosalicylic acid (Andreozzi et al., 2006). In addition, a recent field observation in Beijing indicated that aqueous-phase reactions of aromatic precursors were potential sources for 2,6-dimethyl-4-nitrophenol, 3-methyl-4-nitrophenol, and 2-methyl-4-nitrophenol (Y. J. Wang et al., 2019). Anti-correlations were observed between mononitrophenols (2-nitrophenol and 4-nitrophenol) and 2,4-nitrophenol in rainwater and cloud water, and the nitration of mononitrophenols was considered to be the major source of 2,4-nitrophenol (Lüttke et al., 1999; Vione et al., 2005). Nevertheless, though several aqueous-phase formation mechanisms of nitrated phenolic compounds have been proposed based on laboratory simulations, observation evidence in the real ambient atmosphere is still scarce.

In the present work, 11 nitrated phenolic compounds in particle, gaseous, and aqueous phases were simultaneously measured at the summit of Mount Tai in northern China. The distribution characteristics among different phases were presented and the influencing factors were analyzed. The field Henry's law coefficients and fractions in the particles were then calculated and compared with their theoretical predictions. The important roles of the aqueous formation for nitrated phenolic compounds in their abundances and distributions were also discussed.

2. Materials and Methods

2.1. Sampling Site

Sample collections were carried out at the summit of Mount Tai ($36^{\circ}16'N$, $117^{\circ}06'E$, 1,534 m a.s.l.) in the center of North China Plain. Mount Tai is the highest mountain in this region and the peak is located between the planetary boundary layer and the free troposphere. This site is rarely influenced by local anthropogenic activities and thus well represents the regional atmospheric environment. More detailed information can be seen in our previous study by Jiang et al. (2020). In this study, cloud water and fine particulate ($\text{PM}_{2.5}$) samples were simultaneously collected during 10 cloud events in spring (from 31 March 2018 to 7 April 2018), summer (from 25 July 2018 to 31 July 2018), and winter (from 28 November 2019 to 11 December 2019), while the gas-phase samples were only concurrently collected in spring and winter. Detailed atmospheric conditions during the sampling periods were shown in Table S1 in Supporting Information S1.

2.2. Sample Collections and On-Lime Measurements

Cloud water samples were collected by using a single-stage Caltech Active Strand Cloud Collector at a flow rate of $24.5 \text{ m}^3 \text{ min}^{-1}$, as described by Demoz et al. (1996). The cloud droplets were impacted on vertical six

rows of 500 μm diameter Teflon strings, and a cut size at the theoretical 50% collection efficiency was 3.5- μm droplet diameter (J. R. Li et al., 2017). Once the cloud event occurred, that is, ambient relative humidity >95% and atmospheric visibility <100 m, sampling was started immediately until the cloud disappeared. The cloud water was accumulated in a 500 mL closed polyethylene bottle. After collection, the cloud water sample was weighted, and the pH and conductivity were immediately measured on site with a Portable pH meter (pH/COND/TEMP METER, model 6350M). The remaining original sample was then filtered through 0.45 μm microfilters to remove insoluble particulate matters. Before and after sampling, the cloud collector was cleaned by using high-purity deionized water (resistivity: 18.2 $\text{M}\Omega\text{ cm}$). The field blank samples were obtained with spraying deionized water onto the Teflon strings. All samples were stored at 4°C until further chemical analyses and the aliquots for organic compounds analysis were preserved by adding a small amount of chloroform to act as a stabilizer and biocide (Guo et al., 2012).

A medium-volume sampler (TH-150A, Tianhong, China) was employed to collect $\text{PM}_{2.5}$ samples on the quartz-fiber filters (PALLFLEX, PALL Life Science, USA; 88 mm in diameter) with a flow rate of 100 L min^{-1} . To minimize the impact of cloud water on the collected particulate matters during fog events, the $\text{PM}_{2.5}$ sampler was modified by adding a cloud water collection device to separate and remove cloud droplets (detailed information can be found in Zhao (2019)). Before sampling, quartz-fiber filters were pre-heated at 600°C in a muffle furnace for 2 hr to remove the absorbed organic matters (OMs). Semi-volatile organic compounds (SVOCs) were collected with a high-volume air sampler (TE1000, Tisch, USA) at an average flow rate of 204 L min^{-1} . Particulate matters were first accumulated on the upper quartz-fiber filter and then the gas-phase SVOCs were absorbed by the polyurethane foam (PUF, Tisch, USA; 2.0 inches in height and 2.5 inches in diameter). The PUF were pre-cleaned with n-hexane and methanol successively for 2 hr via sonication. The sampling duration was 0.75–8 hr on foggy days, depending on the fog event. In the absence of fog, samples of $\text{PM}_{2.5}$ and SVOCs were collected at daytime (08:00–19:30, Beijing time) and nighttime (20:00–07:30) separately, with a duration of 11.5 hr. The sample collection was conducted from 22 March to 5 April in the spring of 2018 and from 21 November to 31 December in the winter of 2019, with sample sets of 25 and 69, respectively. However, in the summer of 2018, only five sets of fine particulate and cloud water samples were collected on foggy days (lack of SVOCs samples due to sampler failure). After collection, the filter and PUF samples were frozen in the dark at -20°C until laboratory analysis. Field blank samples for $\text{PM}_{2.5}$ and SVOCs were obtained by the same sampling procedure but without sucking ambient air. With consideration of limited uptake capacity of PUF due to the relatively low surface area (0.007–0.035 $\text{m}^2\text{ g}^{-1}$) (Li & Wania, 2021), before the field sampling, potential breakthrough of semi-volatile components in the high-volume sampler was tested with successional two PUF disks in different atmospheric conditions. Note that the sampling periods of SVOCs samples were not accurately consistent with those of cloud water and $\text{PM}_{2.5}$ samples, which would bring additional uncertainty to the fractions of targets in the gas phase.

In addition, trace gases including nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), carbon monoxide (CO), ozone (O_3), and sulfur dioxide (SO_2) were monitored by real-time optical analyzers (Model T200/T500U, T300U, and T400U, Advanced Pollution Instrumentation, USA, and Model 43C, Thermo Electron Corporation, USA, respectively). A Synchronized Hybrid Ambient Real-time Particulate Monitor (SHARP 5030, Thermo Fisher Scientific, USA) was also used to measure the online mass concentration of $\text{PM}_{2.5}$. Water-soluble inorganic ions including SO_4^{2-} , NO_3^- , Cl^- , Na^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ in fine particulate matters and acidic and alkaline trace gases covering HNO_3 , HCl, and NH_3 were determined by the Monitor for Aerosols and Gases (Applikon-ECN, Netherlands). In addition, meteorological parameters of temperature (T), relative humidity (RH), wind speed, and wind direction were obtained from the Taishan National Reference Climatological Station.

2.3. Sample Extraction and Analysis

Half of the filter sample was extracted with 15 mL methanol at constant temperature via sonication (KQ-300GDV, Kunshan, China) for three times and the extracted solution was evaporated to near-dryness using a rotary evaporator at room temperature. The residue was re-dissolved to 1.5 mL with methanol and then filtered through a syringe filter (0.22 μm , Minisart RC 4, Sartorius). Finally, the extracts were dried under a gentle flow of high-purity nitrogen and re-dissolved in 300 μL methanol containing 200 $\mu\text{g L}^{-1}$ 2,4,6-trinitrophenol as an internal standard. Cloud water samples with 15 mL (spring and winter samples) or 50 mL (summer samples) were used for analyte extraction, and the difference compared with particulate samples is that the solvent evaporation was conducted

under 40°C to accelerate the concentrating process. The PUF sample was cut into small pieces and then extracted in 55 mL of methanol with an ultrasonic bath for 45 min. The remaining procedures were consistent with particulate samples, except that after filtration, 10 μL methanol containing 20 $\mu\text{g mL}^{-1}$ 2,4,6-trinitrophenol was used as internal standard and the extracted solution was concentrated to 1 mL with nitrogen flow to reduce the potential loss (R. Li et al., 2019). All of the sample solutions were sealed and refrigerated at 4°C for future analysis.

Nitrated phenolic compounds in different sample solutions were then analyzed by an Ultimate 3000 ultra-high-performance liquid chromatograph (Thermo Scientific, USA) and detected with an ISQ EC mass spectrometer in negative mode equipped with an electrospray ionization source. Chromatographic separation was performed on an Atlantic T3 C18 column (2.1 \times 150 mm, 2.1 μm particle size, Waters, USA) and the column temperature was kept at 45°C. Eluents containing 0.1% acetic acid in methanol (A)/0.1% acetic acid in deionized water (B) flowed at a rate of 0.19 mL min^{-1} . The gradient program started with 1% A and held for 2.7 min. The proportion of A gradually increased to 54% with 12.5 min and kept for 1.0 min. It then changed gradually to 90% within 7.5 min and kept for 0.2 min. Finally, it returned to 1% during the period of 23.9–25.7 min and kept for the last 17.3 min. Eight mass-to-charge (m/z) ratios (138, 152, 154, 166, 168, 182, 183, and 197 amu) were recorded under the selected ion monitoring mode and the following 11 nitrated phenolic compounds were detected: 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC), 5-nitrosalicylic acid (5NSA), 3-nitrosalicylic acid (3NSA), 2,4-dinitrophenol (2,4DNP), and 4-methyl-2,6-dinitrophenol (4M2,6DNP). The target compounds were identified using separate standards based on the retention time and spectra. Multi-point curves for the mixed standard solutions were used to quantify these compounds after amendment with the internal standard signals.

The standards and other chemical reagents were purchased from Sigma-Aldrich (USA), Merck (Germany), J&K Chemical (China), and Atomax Chemicals (China). The determined average recovery rates of the target nitrated phenolic compounds of filter samples, PUF samples, and cloud water were 84.9%, 78.1%, and 80.7%, respectively. Field blank samples were treated and analyzed in the same ways as the collected samples, and concentrations in different sample solutions were corrected by subtracting the blank signals. The breakthrough rates, less than 10% for most nitrated phenolic compounds except for approximately 30% for 4-nitrophenol and 2,4-dinitrophenol, which have been considered in this study.

Additionally, the contents of organic carbons (OC) in the collected filter samples were measured by using a thermal/optical Carbon Aerosol analyzer (Sunset Laboratory, USA) with the protocol of NIOSH 5040. The concentrations of OM were estimated from the OC contents with a factor of 2.07 for nonurban areas in North China Plain (Yao et al., 2016). Note that the large pressure drop in the high-volume air sampler caused a significant loss of semi-volatile compounds in total suspended particulates (TSP) and led to apparent underestimation in the concentrations of total particulate nitrated phenolic compounds and total OC. Therefore, in this study the data of the $\text{PM}_{2.5}$ samples from the medium-volume sampler instead of the TSP samples from the high-volume air sampler were used to represent the contents in the particle phase.

2.4. Estimations of the Effective Partitioning Coefficients and F_p

Theoretical Henry's law constants H'_A for nitrated phenolic compounds were adopted from Sander (2015) at ambient temperature. The field-derived Henry's law coefficients of them in the cloud droplets (H_A^f , M atm^{-1}) were calculated according to Equation 1 (Sander, 2015; Xuan et al., 2020):

$$H_A^f = \frac{C_{\text{aq},i}^f}{C_{g,i}^f} \quad (1)$$

where $C_{\text{aq},i}^f$ (mol L^{-1}) and $C_{g,i}^f$ (atm) are the aqueous-phase concentration and the partial pressure of the compound i under equilibrium conditions, respectively.

The field-derived effective Henry's law coefficients of nitrated phenolic compounds in the particle droplets (H_p^f , M atm^{-1}) were calculated by Equation 2 (Shen et al., 2018):

$$H_p^f = \frac{C_{p,i}^f}{C_{g,i}^f M_i \text{ALWC} / \rho_{\text{water}}} \quad (2)$$

Table 1

Total Average Concentrations (Average \pm Standard Deviation) of Nitrated Phenolic Compounds in Particles (ng m^{-3}), Gas Phase (ng m^{-3}), and Cloud Water ($\mu\text{g L}^{-1}$) (Including Air Equivalent Concentrations [ng m^{-3}]) During Spring, Summer, and Winter at Mount Tai

Sample type	Spring ($N = 2$)	Summer ($N = 5$)	Winter ($N = 3$)
Particle (ng m^{-3})	16.4 ± 1.6	7.3 ± 4.4	27.1 ± 10.1
Gas (ng m^{-3})	18.3 ± 13.7	/	70.6 ± 20.4
Cloud water ($\mu\text{g L}^{-1}$)	438.5 ± 50.0	206.8 ± 104.4	168.4 ± 60.0
Cloud water (ng m^{-3})	15.5 ± 2.3	9.7 ± 6.4	8.9 ± 5.4

Note. N indicates the sample numbers.

where $C_{p,i}^f$ (ng m^{-3}) and $C_{g,i}^f$ (atm) are the measured abundances of compound i in particle and gas phases, respectively; M_i is the molecular weight of the nitrated phenol (g mol^{-1}); Aerosol liquid water content (ALWC) is estimated by a thermodynamic model ISORROPIA-II which was run in forward mode with the assumption of the particles at “metastable” system based on the measured particulate inorganic ions, trace gases, and meteorological parameters (Fountoukis & Nenes, 2007; Hennigan et al., 2015); ρ_{water} (g cm^{-3}) is the density of water. In this study, the average ALWC of fine particles during cloud events was $111.9 \mu\text{g m}^{-3}$.

The field and theoretical fractions of nitrated phenolic compounds in the particle phase (F_p) were determined based on the equilibrium absorption partitioning theory (Pankow, 1994) and estimated by Equations 3–5:

$$F_{p,i}^f = \frac{C_{p,i}}{C_{g,i} + C_{p,i}} \quad (3)$$

$$F_{p,i}^t = \left(1 + \frac{C_i^*}{C_{\text{OA}}}\right)^{-1} \quad (4)$$

$$C_i^* = \frac{M_i 10^6 \zeta_i P_{v,i}}{RT} \quad (5)$$

where $F_{p,i}^t$ and $F_{p,i}^f$ are the fractions in the particle phase in theory and in the field, respectively (Yuan et al., 2016); $C_{p,i}$ (ng m^{-3}) and $C_{g,i}$ (ng m^{-3}) are the particle- and gas-phase concentrations of compound i , respectively in this study; C_{OA} is the concentrations of organic aerosols (OA), calculated as OC multiplied by 2.07 (Yao et al., 2016); C_i^* is the effective saturation mass concentration ($\mu\text{g m}^{-3}$) which is calculated by Equation 5 (Williams et al., 2010); ζ_i is the activity coefficient of each nitrated phenolic compound which is unity and assumed as 1 in this work; R is the ideal gas constant ($8.2 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1} \text{ K}^{-1}$); T is the ambient temperature (K), and the average temperature during spring and winter observation period were 293 and 269K, respectively; $P_{v,i}$ is the liquid (or sub-cooled) vapor pressure of compound i at the specified temperature and was estimated using extended aerosol inorganic model by using the approach of Moller et al. (2008) (http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php). The data of boiling points and vapor pressures are provided in the Table S2 in Supporting Information S1.

2.5. Calculation of Scavenging Ratio

The scavenging ratio (SR) for $\text{PM}_{2.5}$ was determined according to Equation 6 (Y. Wang et al., 2011):

$$\text{SR} = 1 - C^*/C \quad (6)$$

where C^* is the concentrations of $\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$) during cloud events and C is the concentrations of these components during the 6 hours before cloud occurrence.

3. Results and Discussion

3.1. Concentrations and Compositions of Nitrated Phenolic Compounds in Different Phases

The average total concentrations of 11 nitrated phenolic compounds in particles, gas and cloud water during cloud events in three seasons were summarized in Table 1 (the average concentrations of individual compounds were listed in Table S3 in Supporting Information S1). The average concentrations of nitrated phenolic compounds in particles were 16.4 ± 1.6 , 7.3 ± 4.4 , and $27.1 \pm 10.1 \text{ ng m}^{-3}$ in spring, summer, and winter, respectively. Gaseous nitrated phenolic compounds were more abundant than those in particles, with average values of 18.3 ± 13.7 and $70.6 \pm 20.4 \text{ ng m}^{-3}$ in spring and winter, respectively. Their concentrations in both particle and gas phases exhibited the highest levels in winter, which is ascribed to the intensive pollutant emissions during the heating period in the regional scale. In addition, the weak diffusion conditions due to reduced solar radiation in winter also contributed to the accumulation of pollutants and relevant precursors. Furthermore, relatively high concentrations

Table 2
Concentrations of Nitrated Phenolic Compounds Concentrations in Aqueous-Phase in Previous Studies ($\mu\text{g L}^{-1}$)

Sampling site	Sampling type	Altitude (m a.s.l)	Sampling period	Type of nitrated phenolic compounds	Average concentrations	References
Holme Moss, UK	Cloud water	530	1999.03	4NP 2,4DNP	38.7	Hofmann et al. (2008)
	Rain water				3.6	
Fichtelgebirge mountains, Germany	Fog water	786	1997.05–10	4NP 2,4DNP	11.5	Hofmann et al. (2008) and Wrzesinsky and Klemm (2000)
Mount Brocken, Germany	Cloud water	1,142	1994.05	2NP 4NP 2,4DNP DNOC ^a	30.9	Lüttke et al. (1999)
Great Dun Fell, England	Gas	850	1993.04–05	2NP 4NP 2,4DNP DNOC ^a	24.6	Lüttke et al. (1997)
	Cloud water				6.1	
Vosges mountains, France	Cloud and rain water	~1,000	1991.04–06	4NP	5.5	Levsen et al. (1993)
Mount Tai, China	Cloud water	1,534	2008.06–07	4NP	1.6 ^b	Desyaterik et al. (2013)

^aDNOC = 2-methyl-4,6-dinitrophenol. ^bThe concentrations of 4NP reported by Desyaterik et al. (2013) were present here during the days which were not impacted by severe biomass burning.

of NO_x were observed in winter (4.73 ± 2.17 ppbv in winter vs. 2.09 ± 1.28 ppbv in spring), which meant intensive anthropogenic emissions and could facilitate the secondary formation of nitrated phenolic compounds via gas-phase oxidations of aromatic precursors in the presence of high levels of NO_x (Harrison et al., 2005; Yuan et al., 2016). The highest concentration in cloud water was observed in spring ($438.5 \pm 50.0 \mu\text{g L}^{-1}$), followed by summer ($206.8 \pm 104.4 \mu\text{g L}^{-1}$), and winter ($168.4 \pm 60.0 \mu\text{g L}^{-1}$). The elevated concentrations in cloud water in spring were mainly attributed to the low liquid water content in cloud (volume-weighted mean = 34.8 in spring, 54.6 in summer, 47.6 mg/m^3 in winter, respectively), the short duration of the cloud events, the high SR of particles (54%), and different concentrations and compositions of particulate matters before cloud events.

Table 2 compared the total concentrations of nitrated phenolic compounds in cloud water at Mount Tai with those in other mountain sites in previous studies. The aqueous-phase concentrations of nitrated phenolic compounds observed at Mount Tai were substantially higher than those reported in other mountain regions (Desyaterik et al., 2013; Hofmann et al., 2008; Levsen et al., 1993; Lüttke et al., 1997, 1999; Wrzesinsky & Klemm, 2000), which partly due to more nitrated phenolic compounds were identified and quantified in the present study and indicates the severe air pollution over the North China Plain during the sampling periods (characterized by concurrently very high concentrations of particulate matters and trace gases, as shown in Figure S1 in Supporting Information S1). However, when compared with those in cloud samples collected at Mount Tai in 2007, which were largely influenced by biomass burning (Desyaterik et al., 2013), the aqueous concentrations of 4-nitrophenol in the present study were relatively low. Gas-phase nitrated phenolic compounds in ambient air were rarely reported in previous studies. Compared with those determined in urban Jinan on normal days in 2016 (averagely 52.1 in spring and 36.7 ng m^{-3} in summer) (M. Li et al., 2020), the observed gas-phase nitrated phenolic compounds during foggy days at Mount Tai were lower, suggesting that anthropogenic activities in urban areas emitted large amount of gas-phase nitrated phenolic compounds and their precursors into the atmosphere. In addition, the concentrations of nitrated phenolic compounds in particles during foggy days in the present study were much higher than those observed during the no-fog periods at Mount Tai in summer in 2014 (2.5 ng m^{-3} on average) (L. W. Wang et al., 2018), which is attributed to that the cloud events at the summit of Mount Tai were usually accompanied by air pollution featuring with high loadings of particulate matters and thus high levels of particle-phase nitrated phenolic compounds were observed.

The compositions of nitrated phenolic compounds also exhibited large variation with sample types and seasons. As shown in Figure 1, in particulate samples, 4-nitrophenol and nitrosalicylic acids (i.e., 5NSA and 3NSA) were the dominant species among the 11 nitrated phenolic compounds, with average proportions of 27%–41% and 22%–36%, respectively, which was similar to that at Mount Tai in 2014 in our previous study by L. W. Wang et al. (2018). Nitrosalicylic acids have been identified primarily from secondary formation (M. Li et al., 2020; L. W. Wang et al., 2018), while 4-nitrocatechol are mainly associated with anthropogenic emissions such as biomass burning and can also be produced from the oxidations of aromatic precursors (Chow et al., 2016; Xie et al., 2017). Therefore, compared with urban sites in previous studies (M. Li et al., 2020; Y. J. Wang et al., 2019),

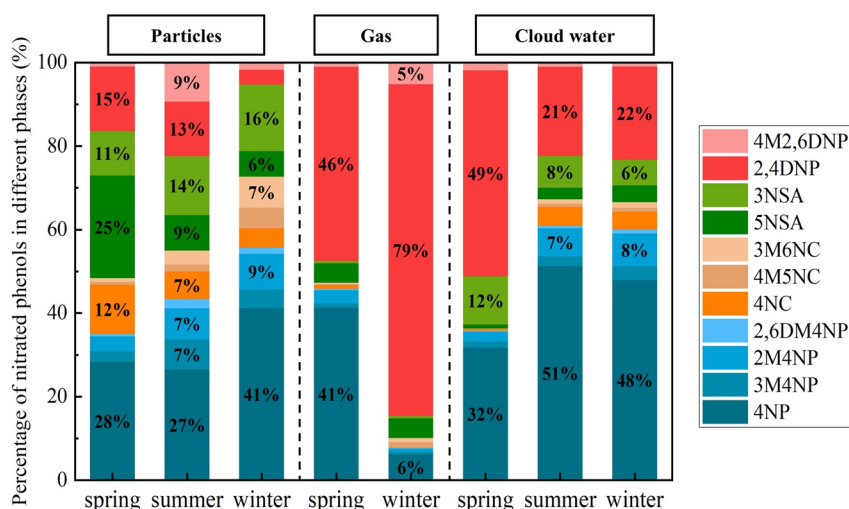


Figure 1. Fractions of individual nitrated phenolic compounds in particles, gas-phase and cloud water in spring, summer, and winter at Mount Tai.

particulate nitrosalicylic acids rather than 4-nitrocatechol dominating at Mount Tai indicates the more important role of secondary formation than primary emissions at the high mountain site. The chemical compositions of gaseous and aqueous samples exhibited distinct characteristics from that in the particle phase. Specifically, 2,4-dinitrophenol turned to be the predominant compound in the gas phase and cloud water when compared with the situation in particles, accounting for 46%–79% and 21%–49%, respectively. The extremely high levels and fractions of 2,4-dinitrophenol on foggy days have also been reported by Lüttke et al. (1997). Furthermore, the average proportions of dinitrophenols (i.e., 2,4-dinitrophenol and 4-methyl-2,6-dinitrophenol) (22%) in particles in summer were obviously higher than those in the other seasons. As described in the Master Chemical Mechanism (MCM v3.3.1), OH-initiated oxidations of benzene and toluene can yield phenol and cresol which are subsequently oxidized by OH or NO₃ radicals to produce nitrophenols and methyl-nitrophenols in the presence of nitrogen oxides. Then, the further oxidations of them with radicals and nitrogen oxides can generate dinitrophenols (Atkinson et al., 1992; Yuan et al., 2016). Thus, the relatively high fraction of dinitrophenols in particles in summer observed in this study is possibly due to large contributions from secondary formation in conditions of strong photochemical activities (e.g., 73.7 ppbv ozone on average) and the gas/particle phase partitioning. The highest proportion of dinitrophenols in cloud water appeared in spring instead of summer, which is possibly associated with the very low cloud water volume in spring (see Table S1 in Supporting Information S1) and relatively strong SRs with particles.

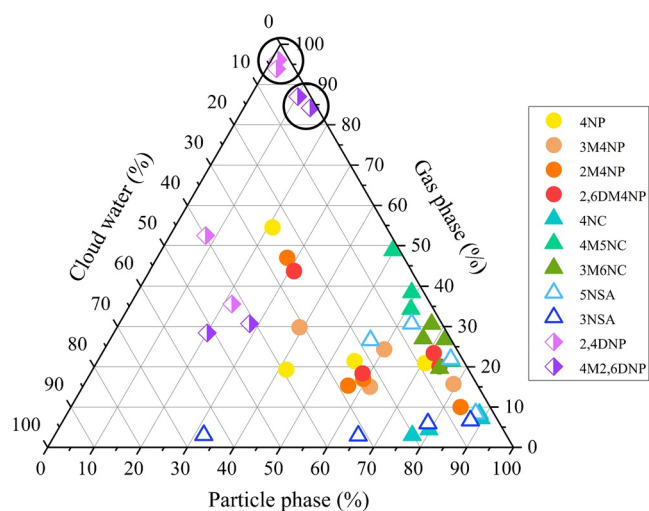


Figure 2. Ternary plot of nitrated phenolic compounds in the particle phase, gas phase, and cloud water (spring and winter samples were used here) and the black circles denote the distribution of dinitrophenols in winter.

3.2. Distribution Characteristics of Nitrated Phenolic Compounds

3.2.1. Distributions in Particle, Gas, and Aqueous Phases

In order to understand the distributions of nitrated phenolic compounds among particle, gaseous, and aqueous phase in spring and winter, their concentration data were normalized and a ternary plot was made. Before comparison, the cloud concentrations were converted to air equivalent concentrations with the aqueous concentration multiplied the liquid water volume collected and divided by the total collected air volume (Marinoni et al., 2004). As shown in Figure 2, the majority of most nitrated phenolic compounds distributed in the particle phase during cloud events. Specifically, 4-nitrophenol, methyl-nitrophenols (i.e., 3M4NP, 2M4NP, and 2,6DM4NP), 4-nitrocatechol, methyl-nitrocatechols (i.e., 4M5NC and 3M6NC), and nitrosalicylic acids (i.e., 3NSA and 5NSA) primarily appeared in the particle phase. As for dinitrophenols, their distribution characteristics exhibited

Table 3

Theoretical Predicted Values in Pure Water H_A^t and Field-Derived Henry's Law Coefficients H_A^f , and Theoretical Aqueous-Phase Concentrations of Nitrated Phenolic Compounds Predicted by Their Henry's Law Coefficients (C_{aq}^t) and Field Observed Concentrations (C_{aq}^f) at the Ambient Temperatures

Compounds	Theoretical H_A^t (M atm ⁻¹)	Field-derived H_A^f		Predicted C_{aq}^t (μg L ⁻¹)	Observed C_{aq}^f (μg L ⁻¹)
		Range (M atm ⁻¹)	Average (M atm ⁻¹)		
Spring					
4-Nitrophenol	7.4×10^4	5.2×10^5 – 2.5×10^6	1.5×10^6	11.4	139.0
2,4-Dinitrophenol	2.2×10^4	8.9×10^5 – 1.5×10^6	1.2×10^6	4.3	216.1
4-Methyl-2,6-dinitrophenol	2.9×10^4	1.6×10^6 – 2.3×10^6	1.9×10^6	0.1	8.3
Winter					
4-Nitrophenol	6.0×10^5	5.3×10^5 – 7.5×10^5	6.4×10^5	54.5	80.7
2,4-Dinitrophenol	6.9×10^4	2.9×10^4 – 3.4×10^4	3.1×10^4	84.8	37.5
4-Methyl-2,6-dinitrophenol	5.7×10^4	2.2×10^4 – 2.4×10^4	2.3×10^4	4.6	1.6

obvious seasonal differences. In winter, dinitrophenols mainly distributed in the gas phase (>80%). In spring, however, they scattered in three different phases, approximately half of them existing in the cloud water.

Overall, during the cloud events, most of nitrated phenolic compounds distributed in the particle phase instead of gas phase or aqueous phase. Their fractions in the particle phase on foggy days were substantially higher than those on cloud-free days in our previous study (M. Li et al., 2020). It indicates that part of the detected nitrated phenolic compounds possibly formed via aqueous reactions within the liquid water layer of fine particles at high humidity, as reported for nitrosalicylic acids and 2,6-dimethyl-4-nitrophenol in droplet-mode particles by Liang et al. (2020). Elevated humidity also favored the aqueous-phase formation of nitrocatechols within particles by decreasing the aerosol viscosity and facilitating the uptake of precursors (Y. J. Wang et al., 2019). Furthermore, the dominance of dinitrophenols in gaseous nitrated phenolic compounds in winter is in accordance to the previous study by Lüttke and Levsen (1997) in which the average concentration of gaseous 2,4-dinitrophenol on foggy days was seven times higher than those on cloud-free days and the concentrations of gaseous dinitrophenols were greater than those in the aqueous phase when cloud events occurred. The observed elevated concentrations and fractions of gaseous dinitrophenols in winter are mainly attributed to the enhanced formation in the gas phase in the presence of high levels of NO₂ during the winter sampling periods (as shown in Figure S1 in Supporting Information S1). Further measurements of the multi-phases partitioning of dinitrophenols are needed to get a comprehensive interpretation on the seasonal variations of dinitrophenols when compared with other nitrated phenolic compounds.

3.2.2. Gas-Aqueous Partitioning

With consideration of the available Henry solubility data and the relatively high fractions of 4-nitrophenol, 2,4-dinitrophenol, and 4-methyl-2,6-dinitrophenol in atmospheric gaseous- and aqueous phases, in this study we only analyzed the Henry's law-type partitioning process for these compounds. The field-derived gas-aqueous partitioning coefficients (H_A^f) for three nitrated phenolic compounds are listed in Table 3. The average values of H_A^f for the three nitrated phenolic compounds are in the range of 10^4 – 10^6 M atm⁻¹, following the order of $H_{A,4M2,6DNP}^f > H_{A,4NP}^f > H_{A,2,4DNP}^f$ in spring and $H_{A,4NP}^f > H_{A,2,4DNP}^f > H_{A,4M2,6DNP}^f$ in winter. H_A^f values also varied greatly with seasons, and these values in spring were significantly higher than in winter. When compared with the theoretical Henry's law coefficients (H_A^t) (also included in Table 3), in spring the field-derived H_A^f values are more than 1 order magnitude higher than the corresponding theoretical values (H_A^t), while in winter the H_A^f values are equal to or even lower than the theoretical values. Based on measured concentrations of gas-phase nitrated phenolic compounds and their Henry's law coefficients, we further estimated the theoretical aqueous concentrations of nitrated phenolic compounds (C_{aq}^t). In spring, the predicted aqueous-phase concentrations are much lower than the field measured values (C_{aq}^f), with a C_{aq}^t/C_{aq}^f ratio less than 0.12. It indicates that no more than 12% of the measured aqueous-phase nitrated phenolic compounds originated from gas-liquid partitioning, while most of them were generated from other sources. In winter, nevertheless, the theoretically predicted aqueous concentrations of dinitrophenols were a little higher than the measured values, suggesting that dinitrophenols in cloud water mainly came from gas-aqueous partitioning.

The discrepancies in the Henry's law coefficients between the theoretical predictions and the field-derived measurements are mainly attributed to the changeable atmospheric conditions, complex cloud droplet properties, and potentially other sources of nitrated phenolic compounds. In this study, H_A^f and H_A^i values have been unified under the same temperature, and the influence of temperature change can be generally neglected in spring and winter. The effect of pressure on predicted values can also be ignored under the condition of less than 1 atm according to the previous study on hydrogen peroxide by Lind and Kok (1986). In addition, the acidity of the cloud droplet possibly brought influences on the solubility of nitrated phenolic compounds. However, as reported by Lüttke and Levsen (1997), only 2,4-dinitrophenol can partly dissociate within the pH range of the cloud water samples, so the present study did not consider the influence of pH on H_A^i . Besides, ionic strength in cloud droplets is usually higher than pure water and the ionic concentration probably influences the gas-aqueous partitioning process. It has been reported that the solubility of 4-nitrophenol is to a certain degree facilitated in the inorganic salt solution (Guo & Brimblecombe, 2007; Shen et al., 2018). However, the “salting-in” effect cannot fill the gap in the Henry's law coefficients between predictions and measurements. In addition, the cloud scavenging of activated particles could also be the potential source for nitrated phenolic compounds in cloud water. To assess the relative contributions of different possible sources to nitrated phenolic compounds in cloud water, theoretical calculations were applied here by taking 4-nitrophenol as an example. Assuming that 4-nitrophenol in the gas phase and cloud water reached an equilibrium, based on the average gaseous concentration of 4-nitrophenol determined at Mount Tai (7.6 ng m^{-3}) and the Henry's law coefficient in spring ($7.4 \times 10^4 \text{ M atm}^{-1}$), a theoretical concentration of 0.4 ng m^{-3} for 4-nitrophenol in cloud water was obtained in the condition of the mean LWC of 0.035 g m^{-3} . It was significantly lower than the mean observed aqueous concentration of 4.9 ng m^{-3} , with a contribution of approximately 10%. With assumption of the same cloud SR of particulate 4-nitrophenol as $\text{PM}_{2.5}$ (i.e., 54%), maximum of 3.0 ng m^{-3} 4-nitrophenol would be efficiently scavenged by cloud water droplets. This amount accounts for at most 60% of the observed 4-nitrophenol concentration in cloud water, which suggests the scavenging of particulate 4-nitrophenol was likely one of the major sources of the compound in cloud water. In addition to gas-aqueous partitioning and particulate matter scavenging, the nitrated phenolic compounds in the cloud water can also be produced from the aqueous nitration and oxidation reactions from their aromatic precursors (Harrison et al., 2005). Therefore, in spring, the much higher Henry's law coefficients of nitrated phenolic compounds in cloud water in the field than in theory are partly attributed to the aqueous formation within cloud droplets.

3.2.3. Gas-Particle Partitioning

The gas-particle partitioning of nitrated phenolic compounds varied greatly with species and seasons, and apparent discrepancy existed between the observed and predicted fractions in the particle phase (F_p). As shown in Figure 3, in spring, in theory, nitrophenols (i.e., 4NP, 3M4NP, 2M4NP, and 2,6DM4NP) and dinitrophenols (i.e., 2,4DNP and 4M2,6DNP) were primarily in the gas-phase ($F_{p,i}^i < 10\%$), while 4-nitrocatechol, 4-methyl-5-nitrocatechol, and nitrosalicylic acids were mostly in the particle phase ($F_{p,i}^i > 50\%$). However, the field observed methyl-nitrophenols, methyl-nitrocatechols, and nitrosalicylic acids were mainly distributed in the particle phase ($F_{p,i}^f > 50\%$), while 4-nitrophenol and dinitrophenols were mainly partitioned into the gas phase ($F_{p,i}^f < 50\%$). Except for the low-volatile nitrocatechols (i.e., 4-nitrocatechol and 4-methyl-5-nitrocatechol) and nitrosalicylic acids, the field-derived $F_{p,i}^f$ values of most nitrated phenolic compounds were much higher than the predicted values by using the Pankow's equilibrium absorption partitioning theory. It indicates that the gas-particle partitioning process cannot maintain their abundances in particles, and part of the particulate nitrated phenolic compounds are expected to come from other sources or processes. Compared with the situation in spring, the proportions of most nitrated phenolic compounds in the particle phase increased in winter due to the enhanced gas-particle partitioning at low temperature. Nevertheless, the observed fraction in the particle phase of 2,4-dinitrophenol was obviously lower than the predicted value in winter, suggesting that more 2,4-dinitrophenol formed in the gas phase rather than aqueous phase in the conditions of high levels of NO_2 .

The predicted gas-particle partitioning coefficients of nitrated phenolic compounds in the present study are generally comparable with those obtained in the recent previous studies based on the equilibrium absorption partitioning theory by Cai et al. (2022) and Yuan et al. (2016). As reported by Cai et al. (2022), the estimated average F_p values for 4-nitrophenol, methyl-nitrophenols, 2,6-dimethyl-4-nitrophenol, 4-nitrocatechol, methyl-nitrocatechols, and nitrosalicylic acids in winter were 17.7%, 40.1%, 71.5%, 95.5%, 98.8%, and 100%, respectively. The estimated particle-phase fraction of 4-nitrophenol in the same season during the Uintah Basin Winter Ozone Study was $0.053\% \pm 0.048\%$ on average in the study of Yuan et al. (2016). The variations of the estimated F_p values among

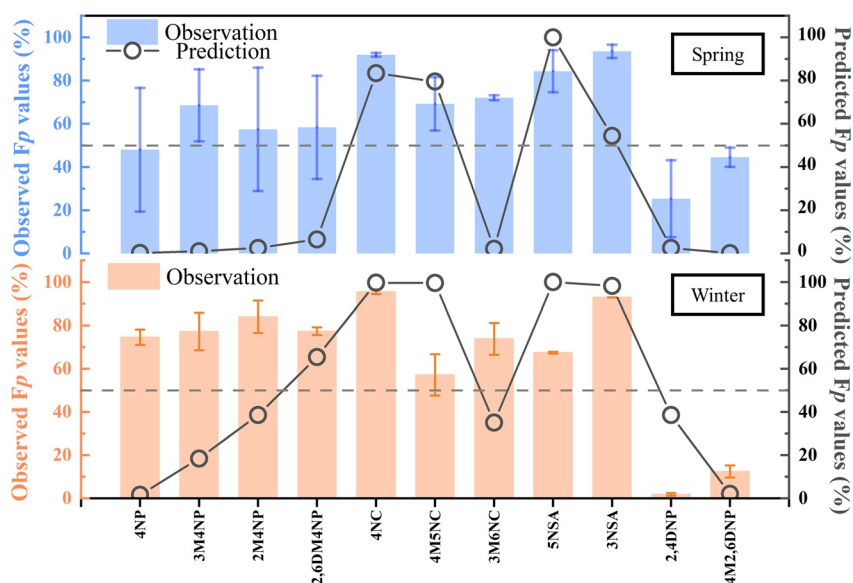


Figure 3. The field-derived and theoretically predicted fractions of nitrated phenolic compounds in the particle phase in spring and winter.

these studies arise mainly due to the different meteorological conditions, organic aerosol concentrations, and estimation pathways of F_p . In addition, in this study, the measured average F_p values of 4-nitrophenol in spring and winter were 48% and 75%, respectively, comparable to those values measured in urban Jinan (54% in spring and 47% in summer) and downtown Rome (82% in cold season) (Cecinato et al., 2005; M. Li et al., 2020). The measured F_p values in this study were higher in comparison to those reported in Beijing (17% in summer) and Iowa City (30% in autumn), which is ascribed to the lower temperature and higher liquid water content of aerosol particles on foggy days at Mount Tai that were more favorable for the partitioning of gas-phase nitrated phenolic compounds into the particle phase.

As for the discrepancy in F_p values between observations and predictions, the aerosol liquid water content was one of the major influencing factors. Hennigan et al. (2008) have shown that the predicted ALWC and F_p exhibited strong increases when ambient RH was larger than 70%, because the uptake of water on particles altered the partitioning of semi-volatile compounds. Based on the measured concentrations of gas-phase nitrated phenolic compounds, the modeled ALWC and their Henry's law coefficients, we estimated the theoretical particle-phase concentrations of these compounds (C_p^t) and field-derived effective Henry's law constants (H_p^f) in the particle droplets (as shown in Table S4 in Supporting Information S1). The average predicted C_p^t of 4-nitrophenol, 2,4-dinitrophenol, and 4-methyl-2,6-dinitrophenol were 5.1×10^{-3} , 3.9×10^{-3} , and 1.9×10^{-4} ng m⁻³, respectively, only accounting for less than 1% of the measured particle-phase concentrations, indicating that more nitrated phenolic compounds existed in the particle phase rather than expected by Henry's law at high humidity conditions during cloud events, so we do not further consider the dissolution of gaseous nitrated phenolic compounds into the aqueous phase of the determined particles. Furthermore, the average H_p^f values of nitrated phenolic compounds were more than two orders magnitudes higher than those in pure water. Excluding the slight improvement in solubility due to the "salting-in" effect, the large difference in gas-particle partitioning between field measurements and theoretical predictions is mainly attributed to the accelerated heterogeneous uptake on aerosols surfaces and aqueous-phase formation within the aerosol droplets at high humidity conditions (Y. J. Wang et al., 2019). It is possible that a large fraction of particulate nitrated phenolic compounds was probably generated from aqueous reactions and the aqueous chemistry increased their abundances in the particle phase, especially during cloud events. In addition, some other factors may also account for the enhanced concentrations of nitrated phenolic compounds in the particle phase. For instance, the presence of water-soluble organics, metals, and mineral dusts in the particles probably facilitated the absorption of gaseous nitrated phenolic compounds. Note that the uncertainty in the measurement data in particular in the gas phase caused by the samplers may also contribute to the apparent difference in gas-particle partitioning coefficients between field measurements and theoretical predictions and further integrated field studies with advanced sampling techniques are required.

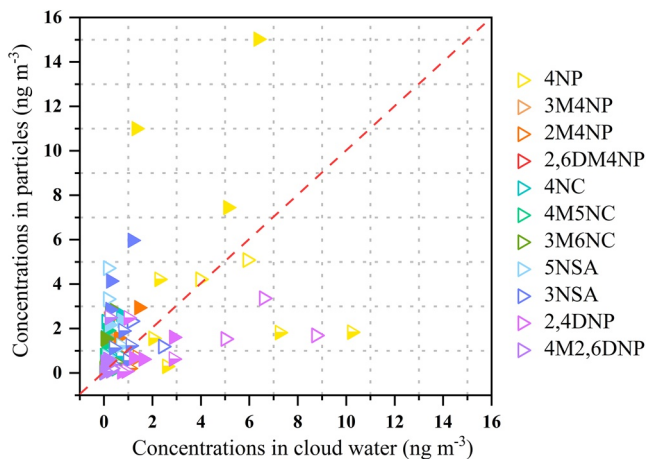


Figure 4. Distributions of nitrated phenolic compounds between the particle phase and cloud water. Data points for spring, summer, and winter are marked by hollow, half hollow, and solid triangles, respectively. The “1:1 line” indicates the distributions characteristics between cloud water and particulate matters.

3.2.4. Distributions Between Particle and Aqueous Phase

Figure 4 plots the distributions of the 11 nitrated phenolic compounds between particle and aqueous phases during the 10 cloud events in spring, summer, and winter (all data are expressed as air equivalent concentrations, ng m^{-3}). As shown, nitrated phenolic compounds are mostly distributed above the 1:1 line. Specifically, most compounds (e.g., methyl-nitrophenols, 4-nitrocatechol, methyl-nitrocatechols, nitrosalicylic acids, and 4-methyl-2,6-dinitrophenol) had high fractions in particles, while the fractions of most of the 4-nitrophenol and 2,4-dinitrophenol were large in cloud water in this study (especially in summer). It is well known that hygroscopic particles can act as cloud condensation nuclei (CCN) and transfer into cloud droplets by absorbing water. Particles can also be scavenged into droplets by collision, inertial impaction, interception, and diffusion (Herckes et al., 2013). The average scavenging efficiency for $\text{PM}_{2.5}$ by cloud is approximately 52% at Mount Tai (Y. Wang et al., 2011). Therefore, nitrated phenolic compounds in cloud water mainly came from the following pathways: (a) the transfer of those existing in the CCN into cloud water; (b) the scavenging of particulate nitrated phenolic compounds into cloud water; (c) the uptake of gas-phase nitrated phenolic compounds (and their precursors) into water droplets (Blando & Turpin, 2000); and (d) secondarily production in cloud water from precursors (Lüttke et al., 1999). The higher fractions

of 4-nitrophenol and 2,4-dinitrophenol in cloud water than other nitrated phenolic compounds are partly due to their relatively high vapor pressures, which are conducive for them to dissolve into cloud droplets, and are also attributed to the additional production in cloud water via aqueous reactions.

Then we further compared the concentrations of 4-nitrophenol and 2,4-dinitrophenols in particles and cloud water during the pre-cloud, cloud, and post-cloud periods for the five cloud events (No. 1, 2, 8, 9, and 10) in spring and winter. As shown in Figure 5, in spring, 2,4-dinitrophenol exhibited higher concentrations in cloud water than particles during cloud events. At the same time, obvious increase in particulate 2,4-dinitrophenol concentrations was observed during cloud events when compared to pre-cloud and post-cloud periods, indicating elevated ALWC promoted the aqueous formation within particles. However, in winter, substantially higher concentrations

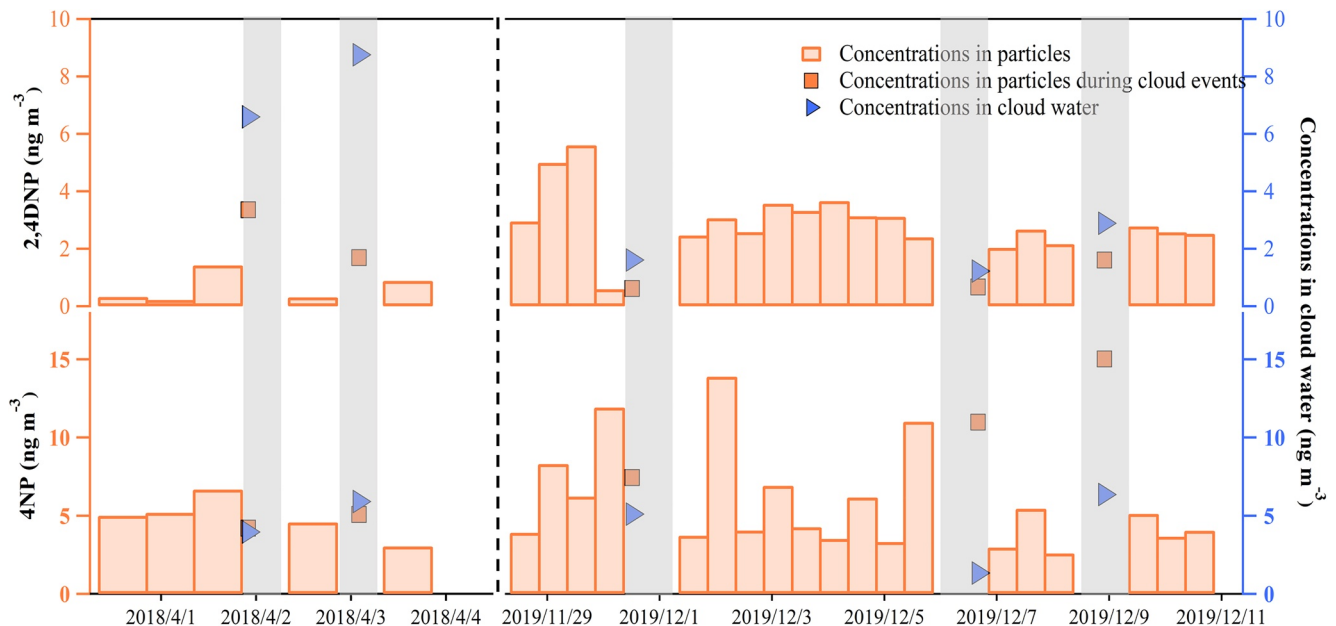


Figure 5. Concentrations of 4-nitrophenol and 2,4-dinitrophenol in cloud water (air equivalent concentrations, ng m^{-3}) and particles during the pre-cloud, cloud, and post-cloud periods. The cloud events were marked by gray shadings.

Table 4
The 2,4-Dinitrophenol/(4-Nitrophenol + 5-Nitrosalicylic Acid) Ratios in Cloud Water and Particles During Cloud Events (D = Daytime and N = Nighttime)

Cloud events	Date	Ratio in cloud water	Ratio in particles
No. 1	01 April 2018 N	0.62	0.45
No. 2	03 April 2018 N	0.60	0.17
No. 3	29 July 2018 D	0.35	0.19
No. 4	30 July 2018 D	0.29	0.01
No. 5	30 July 2018 N	0.39	0.28
No. 6	31 July 2018 N	0.37	0.89
No. 7	31 July 2018 N	0.48	0.59
No. 8	30 November 2019 D	0.31	0.08
No. 9	06 December 2019 D	0.79	0.05
No. 10	08 December 2019 N	0.40	0.09

of 2,4-dinitrophenol were observed in cloud water than in particles and significant decrease in particulate concentrations was noticed during cloud events when compared to pre-cloud and post-cloud periods. It is possible due to that the efficient scavenging by cloud droplets reduced the contents in the particle phase on foggy days. The increased particulate 2,4-dinitrophenol during the post-cloud period suggests that 2,4-dinitrophenol in cloud droplets could partly release back into the particle phase following with the evaporation of the cloud (Ehrenhauser et al., 2012). As to 4-nitrophenol, it also showed generally comparable or relatively high concentrations in particles during cloud events (especially during the cloud events No. 2, 9, and 10) when compared with pre-cloud and post-cloud periods, reflecting a combined result of both cloud scavenging and aqueous uptake and formation. Particularly, the particulate 4-nitrophenol concentrations during the cloud events No. 9 and 10 were quite high when compared to those in cloud water, indicating that the liquid water layer on aerosols surfaces possibly enhanced the gas-particle partitioning of 4-nitrophenol and the aqueous formation. However, during the cloud events No. 1 and 8, 4-nitrophenol in particles presented lower levels than pre-cloud periods, similar to the change in the PM_{2.5} mass concentration. It can be attributed to the scavenging process by the rapidly increased cloud droplets during these cloud events (T. Li et al., 2018). As shown above,

the distribution characteristics of 4-nitrophenol and 2,4-dinitrophenols between the particle or aqueous phases varied greatly among different cloud events in this study, which can be associated with the atmospheric conditions, liquid water contents and chemical compositions of cloud droplets, and properties of nitrated phenolic compounds. Further studies for the multi-phase nitrated phenolic compounds were warranted to obtain comprehensive understanding on the chemical composition, formation mechanism, and re-distribution altered by cloud processes.

3.3. Aqueous Phase Formation in Cloud Droplets for Nitrated Phenolic Compounds

As mentioned before, aqueous-phase formations have an essential influence on the abundances and distribution patterns of nitrated phenolic compounds during cloud events, especially for mononitrophenols (i.e., 4-nitrophenol and 2-nitrophenol) and dinitrophenols. Here, we further explored the possibility of aqueous formation processes for 4-nitrophenol and 2,4-dinitrophenol in the real atmosphere.

Previous laboratory studies have shown that 4-nitrophenol can be yielded from aromatic compounds in an aqueous solution. As important nitrating agents, dinitrogen pentoxide (N₂O₅) and nitryl chloride (ClNO₂) serve as the reservoirs of NO₃⁻ and NO₂⁺ in the atmosphere and the produced NO₂⁺ readily react with phenol to yield 4-nitrophenol (Heal et al., 2007). The aqueous-phase phenol nitration by nitrate radicals and NO₂ acts as an additional formation pathway for 4-nitrophenol. The nitration of phenol by nitrous acid (HONO) and peroxyxynitrous acid (HOONO) in an aqueous solution can also produce 4-nitrophenol (Harrison et al., 2005). In addition, there are other aqueous-phase formation pathways for 4-nitrophenol from nitration of phenol or benzene in the presence of nitrate and nitrite in the condition of photolysis (Vione et al., 2003) or catalysis by hematite (α-Fe₂O₃) (Arimoto et al., 2002). The above previous findings demonstrate that various kinds of phenol nitration in aqueous solutions readily produce 4-nitrophenol, which explains why high levels of 4-nitrophenol appeared in particles and cloud water during cloud events.

As for 2,4-dinitrophenol, it can be formed from the reactions of mononitrophenols with the photolysis products of nitrites or nitrous acid in the presence of NO₂ (Vione et al., 2005). Andreozzi et al. (2006) also found that the nitration of 5-nitrosalicylic acid in aqueous solutions initiated by HNO₃ served as the another source of 2,4-dinitrophenol. With consideration of the potential formation of 2,4-dinitrophenol from 4-nitrophenol and 5-nitrosalicylic acid, the ratio of 2,4-dinitrophenol relative to the sum of 4-nitrophenol and 5-nitrosalicylic acid was calculated to evaluate the relative production of 2,4-dinitrophenol. The ratios in particle and aqueous phases during the 10 cloud events were summarized in Table 4. As shown, the 2,4DNP/(4NP + 5NSA) ratios in cloud water were in the range of 0.29–0.79 and most of the ratios were higher than those in particles (range from 0.01 to 0.89). It suggests that a large fraction of 2,4-dinitrophenol in the cloud water was produced via aqueous reactions.

Based on the previous field observations, the mean 2,4DNP/(4NP + 5NSA) ratio in cloud water at Mount Broken under the influence of fresh polluted air masses was 0.09 (Lüttke et al., 1999). At the summit of Great Dun Fell, high ratios (2.8 on average) were observed due to the strong aqueous formation within cloud droplets (Lüttke et al., 1997). Additionally, this 2,4DNP/(4NP + 5NSA) ratio exhibited notable seasonal variations, with high values occurring in spring and low values in summer and winter, demonstrating that aqueous nitration served as the major source for 2,4-dinitrophenol in spring at Mount Tai and led to high levels of 2,4-dinitrophenol in cloud water.

4. Conclusions

Nitrated phenolic compounds in ambient particles, air, and cloud water were simultaneously determined during cloud events in spring, summer, and winter at the summit of Mount Tai, China. The average total concentrations of nitrated phenolic compounds were in the range of 7.3–27.1, 18.3–70.6 ng m⁻³, and 168.4–438.5 μg L⁻¹ in particles, the gas phase, and cloud water, respectively, generally higher than those reported at mountain sites elsewhere. Among the 11 nitrated phenolic compounds, 4-nitrophenol and nitrosalicylic acids were the most abundant compounds in particles, while 4-nitrophenol and 2,4-dinitrophenol comprised the largest fractions in the gas phase and cloud water. During cloud events, most nitrated phenolic compounds were partitioned into particles, while the distributions of dinitrophenols presented differences that mainly existed in the gas phase in winter. Further estimation based on the Henry's law shows that the observed concentrations of nitrated phenolic compounds in cloud water in spring were much higher than the theoretically predicted values, suggesting that the aqueous-phase reactions together with the cloud scavenging of particles and the uptake from the gas increased the contents of nitrated phenolic compounds in the cloud water. In addition, the observed fractions of nitrated phenolic compounds in the particle phase were substantially higher than those predicted based on Pankow's absorption partitioning theory, indicating aqueous reactions also occurred in the liquid water layer on particle surfaces. The aqueous production of nitrated phenolic compounds could account for the discrepancies between the predicted fractions in the particle phase and those measured in ambient particles. During cloud events, aqueous formation together with the relatively high vapor pressures led to high fractions of 4-nitrophenol and 2,4-dinitrophenol in cloud water. The nitration of aromatic precursors of phenol and benzene, and mononitrophenol and nitrosalicylic acid were responsible for the aqueous formation of 4-nitrophenol and 2,4-dinitrophenol, respectively.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data presented in this paper are freely accessible from the following link: <https://data.mendeley.com/datasets/yxbrjnpfsp/1>.

Acknowledgments

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