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Article

Investigating Dual Character of Atmospheric Ammonia on Particulate NH_4NO_3 : Reducing Evaporation Versus Promoting Formation

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Abstract: Ammonium nitrate (NH_4NO_3) constitutes a key component of fine particulate matter ($\text{PM}_{2.5}$), exerting significant implications for air quality and atmospheric chemistry. However, the dual regulatory role of ammonia (NH_3) in both the formation and evaporation of NH_4NO_3 under ambient atmospheric conditions remains inadequately understood. To investigate this, we conducted high-resolution field measurements at a clean tropical coastal site in China using an integrated system of Aerosol Ion Monitor-Ion Chromatography (AIM-IC), Scanning Mobility Particle Sizer (SMPS), and online OC/EC analyzers, complemented by thermodynamic modeling (E-AIM) and source apportionment via Positive Matrix Factorization (PMF) model. The E-AIM modeling indicated persistent deviations of NO_3^- in $\text{PM}_{2.5}$ from gas-particle equilibrium towards evaporation into gas phase even under $\text{NH}_{3\text{gas}}$ -rich conditions during the northeast monsoon, leaving that NH_4NO_3 in $\text{PM}_{2.5}$ was argued to be rapidly formed in fresh and/or non-precipitation-cloud-modified combustion plumes and subsequently underwent significant evaporation during atmospheric dispersion. Under the southeast monsoon conditions, sea-salt-aerosol-restricted reactions became dominant to form NO_3^- in $\text{PM}_{2.5}$ while NH_4NO_3 formation was suppressed despite plume influence. In scenarios of regional accumulation, elevated NH_3 concentrations suppressed NH_4NO_3 volatilization, enhancing the stability of NO_3^- in $\text{PM}_{2.5}$. PMF analysis identified five source factors, with NO_3^- in $\text{PM}_{2.5}$ mainly contributed by local power plant emissions and marine background, with notable seasonal variability. These results highlight the complex interplay between formation and evaporation pathways of NH_4NO_3 in $\text{NH}_{3\text{gas}}$ -rich coastal atmospheres.

Keywords: particulate nitrate; primary sources; gas-aerosol partitioning; atmospheric NH_3 ; source apportionment

1. Introduction

Ammonium nitrate (NH_4NO_3), a significant water-soluble inorganic component in atmospheric particles, plays a critical role in influencing regional visibility, cloud condensation nuclei (CCN) activity, and radiative forcing through its spatial distribution and gas-particle partitioning behavior [1–12]. The thermodynamic properties of NH_4NO_3 make its concentration highly sensitive to changes in ambient temperature (T) and relative humidity (RH) [2,13–20]. For example, elevated RH enhances the partitioning of both $\text{HNO}_{3\text{gas}}$ and $\text{NH}_{3\text{gas}}$ into the submicron particle phase, as well as the transfer of $\text{HNO}_{3\text{gas}}$ to supermicron particles through the neutralization of negative charges by non-volatile metal ions, thereby further regulating the formation and stability of NH_4NO_3 and nitrate metal salts [2,14,15,17–19]. Conversely, elevated temperatures and low humidity conditions tend to drive the dissociation of NH_4NO_3 back into the gas phase [17–19]. These coupled thermodynamic and chemical

interactions underscore the importance of elucidating the formation and depletion mechanisms of NH_4NO_3 in the atmosphere [9,11,21–23].

In the formation of NH_4NO_3 through the transfer of $\text{HNO}_{3\text{gas}}$ to submicron particles, $\text{NH}_{3\text{gas}}$, the primary component of atmospheric alkaline gases, serves as both a key precursor and a stabilizing agent [24–30]. Additionally, $\text{N}_2\text{O}_{5\text{gas}}$ contributes to nighttime nitrate formation through particle-phase condensation processes, during which $\text{NH}_{3\text{gas}}$ further enhances the stability of NH_4NO_3 aerosols, particularly under conditions of low alkali metal ion concentrations (such as Na^+ and K^+) in the submicron particles [31–36]. Globally, the primary source of NH_3 is agricultural activities, although transportation and industrial emissions in urban areas also contribute to NH_3 emissions [37–43]. Thus, the regulatory effect of NH_3 on NH_4NO_3 demonstrates significant spatial heterogeneity and concentration dependence [12,24,44–48]. Observational evidence suggests that when the NH_3 concentration exceeds the stoichiometric threshold required for the complete neutralization of sulfate, its role shifts from “precursor-limited” to “thermodynamic-limited,” fundamentally altering the pathways of NH_4NO_3 formation and its phase stability [10,48–53].

In contrast to previous studies that primarily focused on the formation pathways, environmental impacts, climatic effects, and policy implications of NH_4NO_3 , Shen et al. [23] provided comprehensive evidence showing that high concentrations of NH_4NO_3 during severe $\text{PM}_{2.5}$ (atmospheric particles with diameter less than $2.5\text{ }\mu\text{m}$) air pollution events are primarily due to prolonged, rapid conversion within combustion plumes under cold, humid and stable meteorological conditions, followed by subsequent evaporation along the plume dispersion track in ambient air. Using isotopic traces, Xiao et al. [54] found that nitrate in $\text{PM}_{2.5}$ primarily originated from primary combustion in a central Chinese city. Furthermore, two independent thermodynamic modeling studies in Beijing showed that thermodynamic force did not support the formation of NH_4NO_3 , even under $\text{NH}_{3\text{gas}}$ -rich atmospheres [49,55]. More recently, Sun et al. [8] and Yang et al. [44] identified high concentrations of NH_4NO_3 at approximately 400 meters in altitude in northern and eastern China, consistent with emission heights and plume rise from strong industrial sources. If NH_4NO_3 aerosols in ambient air primarily originated from primary emissions and prolonged combustion plumes, NH_4NO_3 evaporation would generally be expected to occur [56,57]. This raises the question: does atmospheric NH_3 play a role in reducing NH_4NO_3 evaporation or in promoting NH_4NO_3 formation in ambient air?

This paper aims to comprehensively investigate the dual regulatory roles of ammonia in both the formation and evaporation of NH_4NO_3 , using high-resolution data collected at a clean coastal site on a tropical island in China [58]. The simplicity and clarity of pollution sources at this location offer an ideal environment for isolating the effects of NH_3 , thereby enhancing the robustness of the analysis. By combining field observational data analysis, thermodynamic equilibrium modeling, and source apportionment analysis, this work provides novel scientific insights into the synergistic regulation of nitrate aerosols in $\text{PM}_{2.5}$. The findings are expected to offer theoretical foundations for improved air pollution mitigation strategies and for advancing our understanding of aerosol-climate interactions.

2. Materials and Methods

The sampling site for this study is situated on the third floor of a research building within a high-tech industrial park in southeastern Hainan Province (18.328°N , 109.169°E , Figure 1a-b). This region represents a typical land-sea transition zone, positioned approximately 1.9 km west of the South China Sea coastline [58]. It is seasonally influenced by alternating southeasterly and northeasterly monsoons under the overarching control of the East Asian monsoon system. To the south of the site, a 487-meter-high hill situated 1.3 km away acts as a local topographic barrier, fostering local circulation patterns under weak synoptic forcing. Between the sampling site and the hill lies the Huaneng Nanshan Power Plant—a natural gas-fired facility located 1.2 km to the south at the hill’s base (Figure 1cd). The plant has a total installed capacity of $2 \times 46\text{ MW}$ (new generators visible on the left side of Figure 1c) and 132 MW (original units largely obscured on the right side of Figure 1c), and serves as a major source of industrial air pollutant emissions in the area. Plumes from the facility are

occasionally observed traversing the sampling location. Additionally, within a 5 km radius of the park, the surrounding landscape comprises undeveloped wastelands and agricultural land, with approximately 2.3 km² designated for future development. A major traffic road is located 50 meters east of the sampling point, with traffic volumes reaching 810 vehicles per hour during peak periods (07:00-09:00 and 17:00-19:00), 24% of which are electric vehicles (zero-emission models), classifying it as a low mobile pollution source area.



Figure 1. Map of the sampling site: (a-b) High-resolution terrain map from Google Earth, with red markers indicating the sampling site and power plant locations, and blue markers showing the locations of the three national control points in Sanya. (c) Dispersion of emissions from the power plant under dry weather. (d) Dispersion of emissions under humid weather.

The study utilized an Aerosol Ion Monitor-Ion Chromatography system (AIM-IC) (Thermo Fisher, Waltham, MA, USA) for the continuous monitoring of both gaseous and particulate matter in the atmosphere. The detection limits for NO₃⁻ and NH₄⁺ were $5 \times 10^{-2} \mu\text{g m}^{-3}$ and $4 \times 10^{-4} \mu\text{g m}^{-3}$, respectively. The AIM-IC system was installed within the laboratory and connected to ambient air via a 2.5-meter-long stainless steel inlet tube (3.5 cm inner diameter), with the sampling probe positioned approximately 10 meters above ground level. Regular maintenance and calibration procedures were carried out throughout the observation period to ensure the accuracy and instrument stability. Data collected during two periods-November to December 2023 and June 2024 were used for analysis, capturing atmospheric composition under varying meteorological conditions. Detailed operational information for the AIM-IC system is available in our previous publications [18,58,59]. The AIM-IC system is equipped with two analytical columns, one for cations (Ion Pac CS20, 2 × 250 mm) and one for anions (Ion Pac AS 11-HC, 2 × 250 mm), along with two guard columns,

one for cations (CG20, 2 × 50 mm) and one for anions (AG 11-HC, 2 × 50 mm). Additionally, the system is equipped with a PM_{2.5} cyclone separator to ensure accurate sampling of fine particulates, operating at a flow rate of 3 L min⁻¹. The system provides hourly concentration data for reactive gases (NH₃, SO₂, HNO₃, etc.) and water-soluble ions (NH₄⁺, NO₃⁻, etc.). It is important to note that the HNO₃ signal measured by AIM-IC includes not only gaseous HNO₃ but also contributions from its atmospheric precursors, such as N₂O₅, a fraction of organic nitrate, and trace amounts of NO₂ in ambient air, similar to other acidic vapor species measured by the system [59]. Therefore, HNO₃^{*} was used instead of HNO₃ in the subsequent analysis.

Particle size spectrum data were measured simultaneously using a Scanning Mobility Particle Sizer (SMPS, Grimm, Germany). During sampling, the air was dried before entering a differential analyzer, where the number concentration size distribution from 11 to 1110 nm was obtained at a sampling flow rate of 0.3 L min⁻¹, with a 4-minute resolution and 112 sampling channels, providing high-precision particle size distribution data. Additionally, an OC-EC online analyzer (Model 4, Sunset, USA) was employed for the continuous monitoring of organic carbon (OC) and elemental carbon (EC) in PM_{2.5}. Owing to the relatively clean atmospheric conditions at the sampling site (annual mean PM_{2.5} < 10 µg m⁻³), OC and EC concentrations were monitored with a time resolution of 2 hours to improve signal-to-noise reliability. However, the OC-EC analyzer experienced frequent malfunctions. Data points identified as outliers due to instrument malfunction or external contamination events were excluded during quality control to ensure the accuracy and integrity of the dataset.

For model applications, this study utilized the Extended AIM Aerosol Thermodynamics Model (E-AIM, versions Model II and Model IV, available at: <http://www.aim.env.uea.ac.uk/aim/aim.php>) to simulate the gas-particle partitioning equilibrium of NH₄NO₃. E-AIM remains the only publicly available thermodynamic model capable of simultaneously resolving multiphase equilibrium processes involving both inorganic and organic aerosols. The core assumptions of E-AIM are as follows: (1) homogeneous internal mixing of aerosol components, and (2) thermodynamic equilibrium between aerosols and ambient gases [58,59]. In this study, both Model II and Model IV were used to calculate equilibrium partitioning among gaseous, aqueous, and solid phases. Model II is suitable across a broad range of relative humidity (0.1 < RH < 1.0) and accounts for the multiphase behavior of the NH₃-HNO₃-H₂SO₄-NH₄⁺-NO₃⁻-SO₄²⁻ (including solid salt precipitation and liquid water dissolution), resolving the distribution of species such as (NH₄)₂SO₄, NH₄NO₃, etc. Model IV extends the capabilities of Model II by incorporating Cl⁻ and Na⁺ to represent the influence of sea salt aerosols. Meteorological data were obtained from the China Meteorological Data Service Center (<http://data.cma.cn/>), and hourly PM_{2.5} mass concentration data were retrieved from three national monitoring sites in Sanya. Using the NOAA HYSPLIT model (<https://www.ready.noaa.gov/HYSPLIT.php>), 24-hour backward trajectories were calculated at a height of 500 m, reflecting air mass transport characteristics at the top of the boundary layer during the day or above it at night, with a time resolution of 1 hour.

To apportion the source contributions of NO₃⁻ in PM_{2.5} ([NO₃⁻]_{PM2.5}), the study integrated the modified particle number concentration spectrum (11-700 nm, with 39 size segments reduced from the original ones) with the [NO₃⁻]_{PM2.5} composition matrix using the Positive Matrix Factorization (PMF) model for positive matrix decomposition. This method clarified the contributions of various source aerosols to the formation and evolution of NO₃⁻. Strong new particle formation (NPF) events were excluded during the PMF analysis to minimize their dominant effect on the dataset. The study used the Q-value (Q/Q_{exp}) as a fitting evaluation index, comparing changes in Q-values across different factor solutions and considering residual distribution and the physical significance of factor spectra to determine the optimal solution[60]. After running the model 20 times with data from 2023 and 2024, the five best factors were identified, with a Q/Q_{exp} ratio of 1.12.

3. Results

3.1. Overview of Observational Results at the Coastal Site

Figure 2 illustrates time series of concentrations of major ions (including NO_3^- , NH_4^+ , SO_4^{2-} , and Na^+) and carbonaceous components (OC and EC) in $\text{PM}_{2.5}$, along with hourly measurements of NH_3 and HNO_3^* gases during the observation periods (14 November to 12 December 2023 and 7-20 June 2024). During the continuous observation in November 2023 (excluding 27-30 November), the $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ remained relatively low, fluctuating around $0.6 \pm 0.3 \mu\text{g m}^{-3}$, with a maximum value of only $1.7 \mu\text{g m}^{-3}$. However, between 27 and 30 November, several peaks in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ were observed, with the highest concentration reaching $3.9 \mu\text{g m}^{-3}$. A weak correlation was observed between $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and the corresponding SO_4^{2-} and NH_4^+ concentrations ($R^2 = 0.42$ and 0.52 , respectively; $P < 0.01$), whereas, SO_4^{2-} and NH_4^+ showed a strongly correlated ($R^2 = 0.91$; $P < 0.01$). These results suggested that NO_3^- in $\text{PM}_{2.5}$ partly existed as NH_4NO_3 , while SO_4^{2-} was primarily existed as NH_4^+ salts. Furthermore, no correlation was found between $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and Na^+ concentrations, indicating that aged sea salts, such as NaNO_3 , were not major contributors to the observed NO_3^- in $\text{PM}_{2.5}$. Additionally, NO_3^- in $\text{PM}_{2.5}$ and other ions exhibited significant diurnal variations, although the characteristics of these variations were inconsistent.

In contrast, the diurnal variations of the concurrently observed $\text{HNO}_3^*_{\text{gas}}$ were consistent clear, with peaks consistently occurring around noon and before sunset, and low values observed before sunrise (Figure 2c). Similarly, NH_3_{gas} showed a generally consistent diurnal pattern, characterized by peak concentrations shortly after sunrise and around midnight, and minimum concentrations occurring before and after sunset. A comparison of the diurnal variations of ions in $\text{PM}_{2.5}$ and the concurrently observed gases suggested that diurnal meteorological factors (such as T, RH, wind speed, wind direction, and sunlight) may significantly influence the concentration variations of each component. The sources of ions in $\text{PM}_{2.5}$ appear to be more variable than $\text{HNO}_3^*_{\text{gas}}$ and NH_3_{gas} .

Furthermore, during the one-month observation period, atmospheric NH_3_{gas} concentrations fluctuated around $8.2 \pm 3.3 \mu\text{g m}^{-3}$, with a maximum of $23 \mu\text{g m}^{-3}$ and a minimum of $2.5 \mu\text{g m}^{-3}$. In contrast, $\text{HNO}_3^*_{\text{gas}}$ concentrations remained much lower, fluctuating around $0.1 \pm 0.04 \mu\text{g m}^{-3}$, with the maximum of $0.3 \mu\text{g m}^{-3}$. Despite the fact that the formation of particulate $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ is governed by the product of NH_3 and HNO_3 concentrations[13], the markedly lower levels of $\text{HNO}_3^*_{\text{gas}}$ suggest that it was a more significant limiting factor for $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ formation in this environment. The carbonaceous components in $\text{PM}_{2.5}$, particularly OC, significantly exceeded the concentrations of inorganic ions, with concentration ranging from 4.7 to $12 \mu\text{g m}^{-3} \text{ C}$ ($6.7 \pm 1.3 \mu\text{g m}^{-3} \text{ C}$). The corresponding EC ranged from 0.2 to $1.5 \mu\text{g m}^{-3} \text{ C}$ ($0.4 \pm 0.1 \mu\text{g m}^{-3} \text{ C}$), which were slightly lower than $[\text{NO}_3^-]_{\text{PM}_{2.5}}$. The high OC and OC/EC ratios might be related to nearby cooking emissions, as suggested by the concurrently low SO_4^{2-} and NO_3^- concentrations [61].

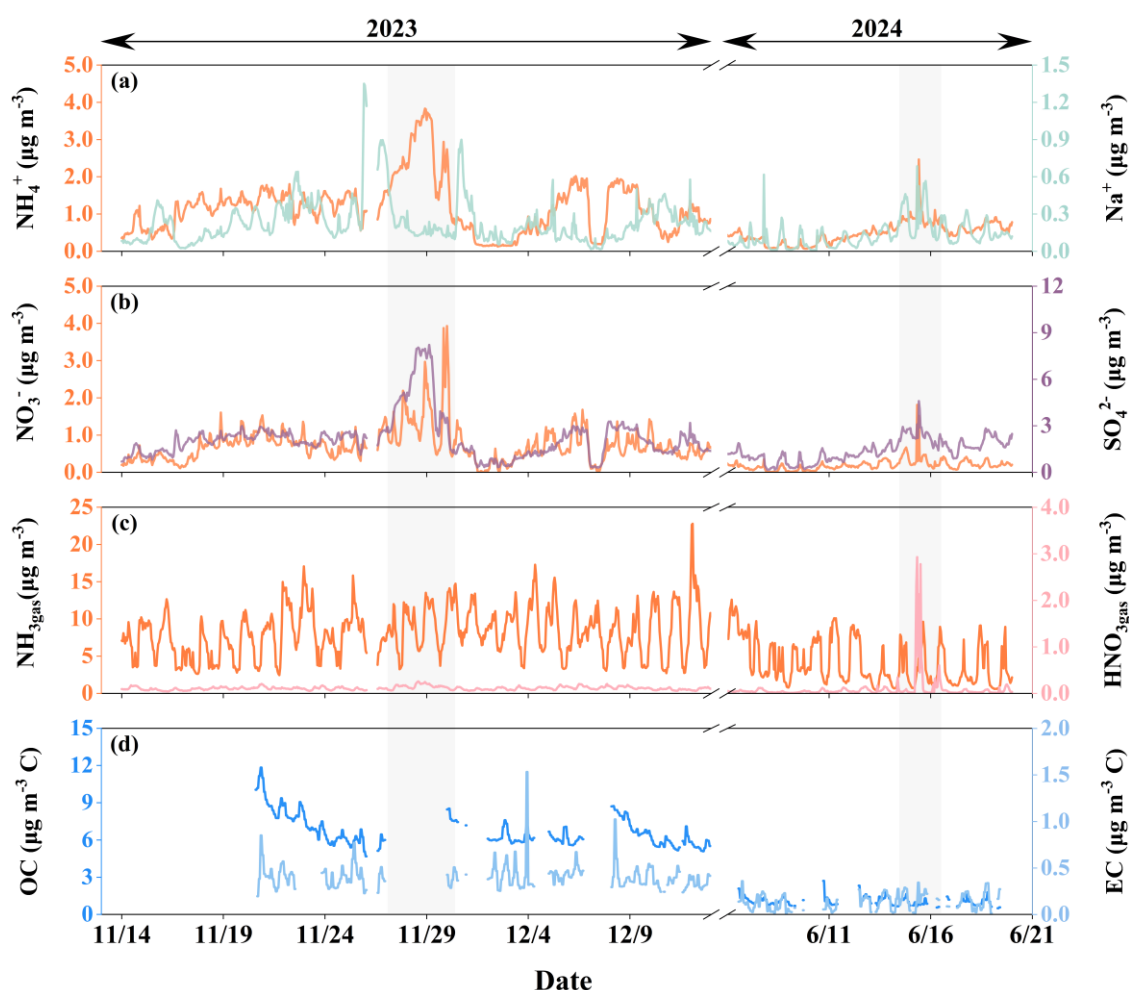


Figure 2. Time series of various species concentrations in PM_{2.5} during the study periods in 2023 and 2024. Panels (a-b) show the concentrations of NH₄⁺, Na⁺, NO₃⁻, and SO₄²⁻; panel (c) displays the concentrations of NH₃ and HNO₃^{*} gases; panel (d) shows OC and EC concentrations in PM_{2.5}.

Similar to the data from November-December 2023, the [NO₃⁻]_{PM2.5} in June 2024 remained at a low concentration level of $0.2 \pm 0.1 \mu\text{g m}^{-3}$, except for June 16. During this period, the maximum concentration observed was $0.7 \mu\text{g m}^{-3}$. However, on June 16, a distinct anomaly in [NO₃⁻]_{PM2.5} was observed, with a peak of $1.8 \mu\text{g m}^{-3}$, significantly higher than the concentrations on the preceding and following days. During the two-week observation period in June, [NO₃⁻]_{PM2.5} exhibited noticeable diurnal variation, but the timing and width of the daily peaks were inconsistencies, suggesting the complexity of its influencing factors. A weak correlation was observed between [NO₃⁻]_{PM2.5} and the corresponding SO₄²⁻ and NH₄⁺ concentrations ($R^2 = 0.46$ and 0.51 , respectively; $P < 0.01$), whereas SO₄²⁻ and NH₄⁺ were strongly correlated ($R^2 = 0.88$, $P < 0.01$). These results suggest that NO₃⁻ in PM_{2.5} partly existed in the form of NH₄NO₃, while SO₄²⁻ predominantly existed as NH₄⁺ salts. A significant correlation was found between NO₃⁻ and Na⁺ in PM_{2.5} ($R^2 = 0.64$, $P < 0.01$), indicating that aged sea salts, such as NaNO₃, may have contributed to the formation of NO₃⁻ in PM_{2.5}.

The diurnal variation of the concurrently observed NH_{3gas} concentrations also exhibited strong fluctuations, but the shape and timing of the peaks varied considerably. During the June observation period, the maximum and minimum NH₃ concentrations ranged were $13 \mu\text{g m}^{-3}$ and $0.5 \mu\text{g m}^{-3}$, respectively. Concentrations below $1 \mu\text{g m}^{-3}$ predominantly occurred between midnight and sunrise. The diurnal variation of HNO₃^{*}gas generally showed an inverse pattern to that of NH_{3gas}, except on 16 June. HNO₃^{*}gas concentrations fluctuated around $0.06 \pm 0.06 \mu\text{g m}^{-3}$, with the maximum of $0.6 \mu\text{g m}^{-3}$. However, nighttime concentrations remained below $0.1 \mu\text{g m}^{-3}$. On 16 June, between 06:00 and 12:00, HNO₃^{*}gas concentrations exceeded $2 \mu\text{g m}^{-3}$ during four separate intervals. The impact of high concentrations of HNO₃^{*}gas on [NO₃⁻]_{PM2.5} will be discussed later. Throughout the observation period,

the carbonaceous components in PM_{2.5} exhibited relatively low concentrations. Specifically, OC ranged from 0.5 to 2.7 $\mu\text{g m}^{-3}$ C ($1.1 \pm 0.4 \mu\text{g m}^{-3}$ C), and EC ranged from 0.01 to 0.4 $\mu\text{g m}^{-3}$ C ($0.1 \pm 0.1 \mu\text{g m}^{-3}$ C). These values were among the lowest compared with recent measurements in the U.S. [62]. This reduction in OC and EC concentrations can be attributed to the influence of the southwest monsoon, which brought air masses primarily from the ocean.

3.2. Thermodynamic Equilibrium Simulations for the Four Cases

To understand the causes for NO₃⁻ peaks in PM_{2.5}, thermodynamic equilibrium simulations were conducted to examine the gas-aerosol partitioning states. Figure 3 shows a comparison between the thermodynamic equilibrium simulations and observations for HNO_{3gas}, NH_{3gas}, and HCl_{gas}. During 27-29 November 2023, the simulated concentrations of HNO_{3gas} deviated from the 1:1 line in over 90% of the time, indicating that the NO₃⁻ in PM_{2.5} has not reached equilibrium with HNO_{3gas} and was undergoing volatilization into the gas phase. The degree of deviation was independent on the corresponding [NO₃⁻]_{PM2.5}, as indicated by the color scale in Figure 3. However, the simulation did not account for the presence of K⁺, which may bind with a fraction of NO₃⁻. K⁺ had an appreciable contribution in PM_{2.5} as analyzed in Section 3.3-3.6. This omission could partially explain the positive biased simulated HNO_{3gas}. Nevertheless, given the elevated levels of atmospheric NH₃ observed during this period, the potential impact of this error is expected to be minimal. Moreover, on 27 and 29 November, approximately 10% of the data points aligned with the 1:1 line, suggesting that NO₃⁻ in PM_{2.5} and gaseous HNO₃ reached equilibrium during these periods. Conversely, no negative deviations from the 1:1 line were observed, providing strong evidence that particulate nitrate formation did not occur. Recall that the observed HNO₃^{*} includes not only gaseous HNO₃ but also N₂O₅, organic nitrate and minor hydrolyzed NO₂. This may introduce a positive bias in the observed HNO_{3gas}, which could theoretically result in a negative deviation in the simulation. This effect is likely more pronounced at night, when N₂O₅ concentrations may exceed those of HNO₃. However, no such negative deviations were observed. Additionally, when NaCl is not considered in the model, a more pronounced positive bias in simulated HNO_{3gas} was observed on 28 and 29 November, especially those cases under conditions with higher [NO₃⁻]_{PM2.5} (Figure S1). This suggests that a portion of HNO_{3gas} may undergo heterogeneous reactions with NaCl to form particulate NaNO₃. However, the difference was negligible on 27 November.

On 16 June 2024, the modeled concentrations of HNO_{3gas} closely aligned with the 1:1 line for case with higher-[NO₃⁻]_{PM2.5}, and were positively deviated from the 1:1 line to some extent for other cases. Again, when NaCl was excluded from the model, a more pronounced overestimation of HNO_{3gas} was observed including some higher-[NO₃⁻]_{PM2.5} cases. Thus, it can be inferred that 1) NO₃⁻ associated with NH₄⁺ in PM_{2.5} was undergoing volatilization to HNO_{3gas}; 2) NO₃⁻ associated with Na⁺ was achieved the gas-aerosol equilibrium on that day.

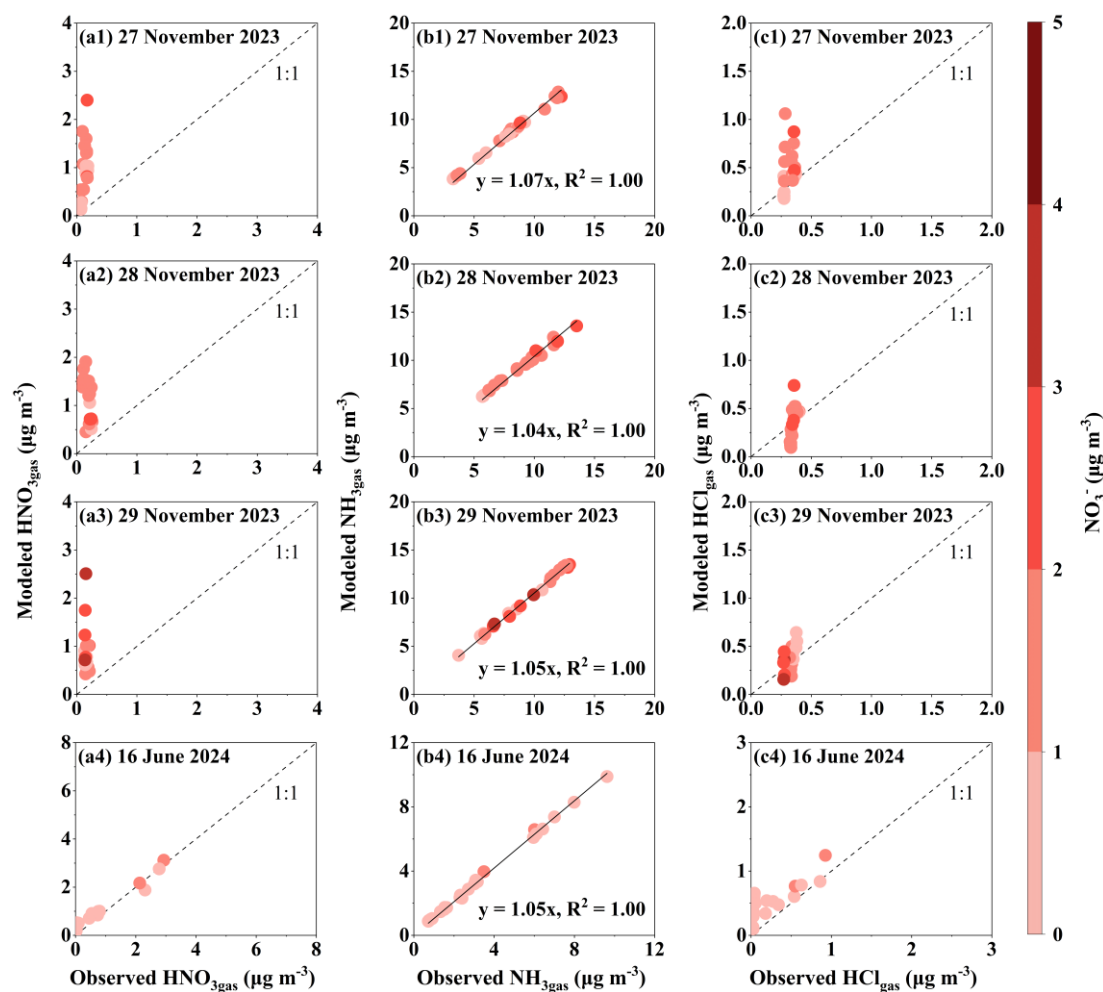


Figure 3. Comparison of modeled and observed gas concentrations for 27–29 November 2023, and 16 June 2024. (a) Modeled $\text{HNO}_{3\text{gas}}$ vs. Observed $\text{HNO}_{3\text{gas}}$. (b) Modeled $\text{NH}_{3\text{gas}}$ vs. Observed $\text{NH}_{3\text{gas}}$. (c) Modeled HCl_{gas} vs. Observed HCl_{gas} . The color bar indicates NO_3^- concentration in $\mu\text{g m}^{-3}$.

The simulated equilibrium $\text{NH}_{3\text{gas}}$ concentration slightly exceeded the observed value, primarily because the observed $\text{NH}_{3\text{gas}}$ concentration is sufficiently high, meaning the gas-particle equilibrium has minimal impact. The simulated HCl_{gas} concentration shows a mix of both positive and negative deviations from the 1:1 line. These inconsistencies may stem from the presence of sea salt and ammonium salts in externally mixed forms, which are treated as internally mixed in the thermodynamic simulation. Fresh sea salt tends to produce a positive deviation, whereas aged sea salt may lead to a negative one. Additionally, the observed HCl_{gas} includes contributions not only from HCl but also from Cl_2 and NO_2Cl [63], potentially introducing a positive measurement bias that could account for negative deviations in the simulated HCl concentrations.

From a theoretical perspective, the elevated atmospheric temperatures typical of tropical regions facilitate the attainment of gas-particle equilibrium for NH_4NO_3 , with equilibrium timescales on the order of minutes [64,65]. The simulation results for 16 June also corroborated this behavior. However, in particles produced by fresh combustion, NH_4NO_3 may be encapsulated by organic material [66–68], significantly prolonging the time required to reach equilibrium.

3.3. Case 1: Synergistic Effects of Primary Emissions and Meteorological Conditions on the Rapid In-Plume Formation and Subsequent Volatilization of Fresh Ammonium Nitrate

The case analysis is further conducted to characterize the NO_3^- peaks. Case 1 is based on observations obtained on 27 November 2023. Figure 4a–e displayed the concentrations of NO_3^- , NH_4^+ , and Na^+ in $\text{PM}_{2.5}$, along with the concurrent atmospheric $\text{NH}_{3\text{gas}}$ concentrations, particle number size

distributions, and changes in PM_{2.5} mass concentration at three national control sites in Sanya. They also included the correlation between the normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and the sum of particle number concentrations larger than 100 nm ($N_{>100}$) (as defined in the caption of Figure 4), as well as 24-hour air mass back trajectories for that day. Figure S2ab illustrated the correlations between NH_4^+ and NO_3^- , and between NH_4^+ and the equivalent concentrations of $(\text{NO}_3^- + \text{SO}_4^{2-})$ in PM_{2.5}. The results in Figure 4a revealed a bimodal distribution of $[\text{NO}_3^-]_{\text{PM}_{2.5}}$, with a lower peak at 09:00 and a higher peak at 21:00. PM_{2.5} mass concentrations at the three national control sites in Sanya also exhibited a similar bimodal distribution, except for a trough observed at the Junyue Sea-Beach station, which may be related to localized showers. This suggested that the increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ may have been a widespread phenomenon. However, the calculated air mass back trajectories indicated that 1) the sampling site was neither downwind nor upwind of the national control sites, and 2) the trajectories nearly overlapped during both peak and the non-peak period (Figure 4e). Therefore, it can be inferred that the atypical diurnal variations observed on that day were more likely due to local atmospheric processes rather than regional pollutant transport.

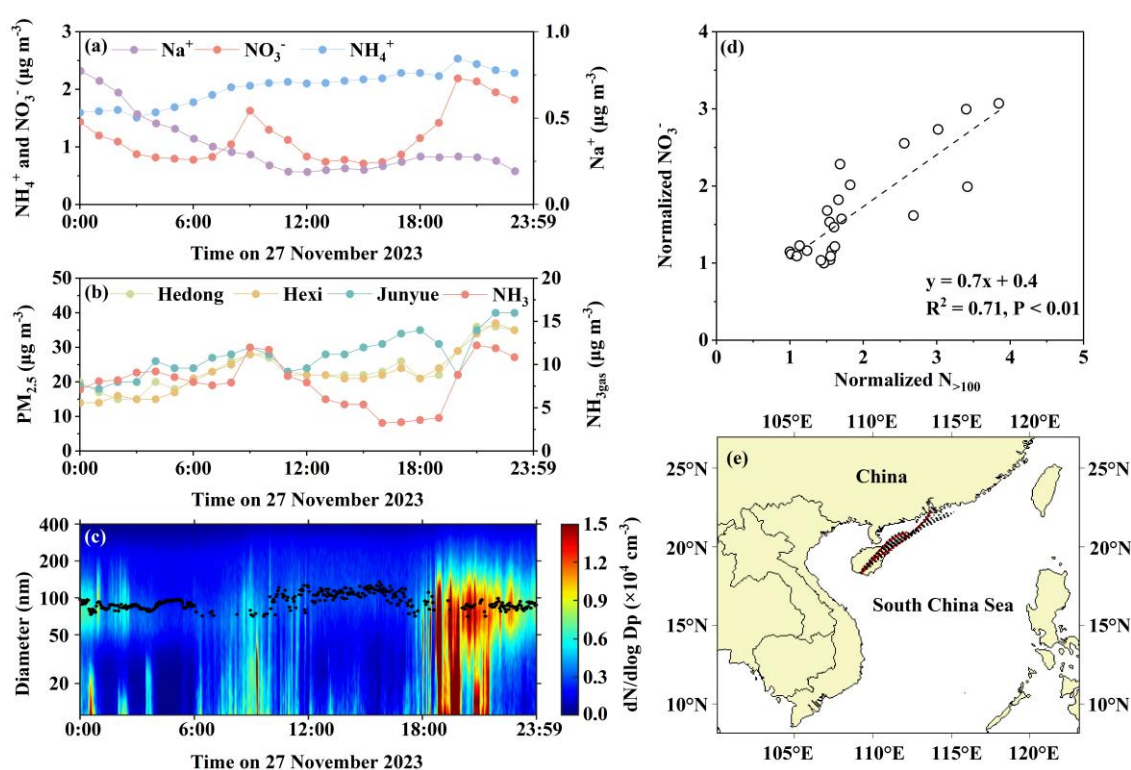


Figure 4. Observational and calculated data on 27 November 2023. (a) daily variations of NO_3^- , Na^+ , and NH_4^+ concentrations in $\text{PM}_{2.5}$; (b) daily variations of $\text{PM}_{2.5}$ mass concentrations at three national monitoring sites; (c) contour plotting of particle number size distributions; (d) correlation between normalized NO_3^- concentration and $N_{>100}$, with the normalized values calculated by dividing all NO_3^- concentrations by the minimum NO_3^- concentration and all particle counts by the minimum particle count; (e) 24-hour air mass back trajectories (red trajectories correspond to NO_3^- peaks).

The concentrations of NH_4^+ and Na^+ in $\text{PM}_{2.5}$ exhibited unidirectional increases and decreases in their diurnal variations, respectively, and did not show a statistically significant correlation with NO_3^- (Figure S2 and S3a). This indicates that sea salt and atmospheric $\text{NH}_{3\text{gas}}$ were not the primary controlling factors for the increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$. However, atmospheric $\text{NH}_{3\text{gas}}$ also displayed a bimodal distribution and a weak statistically significant correlation with NO_3^- ($R^2 = 0.32, P < 0.01$). A more detailed analysis revealed that changes in the concentration of $\text{NH}_{3\text{gas}}$ concentrations lagged behind those of $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ (Figure 4ab). Additionally, the strong correlation between the equivalent concentration of NH_4^+ and that of $(\text{NO}_3^- + \text{SO}_4^{2-})$ (Figure S2) suggested that NH_4^+ in $\text{PM}_{2.5}$

predominantly existed as inorganic ammonium salts. Thus, the delayed peaks of atmospheric NH_3gas are more likely attributed to the volatilization of NH_4NO_3 [8,23,56], supporting by the thermodynamic equilibrium stimulation analysis presented in Section 3.2. In this specific case, atmospheric NH_3gas likely played a role in restricting its volatilization as gaseous ($\text{HNO}_3 + \text{NH}_3$).

The particle number size distribution presented in Figure 4c indicated that, during periods of elevated $[\text{NO}_3^-]_{\text{PM}_{2.5}}$, the median accumulation mode particle diameter was notably smaller than during periods with lower $[\text{NO}_3^-]_{\text{PM}_{2.5}}$. Additionally, the normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ exhibited a strong positive correlation with the normalized $N_{>100}$, with a regression slope of 0.7. This strongly suggests that NH_4NO_3 primarily originated from primary sources [23,54,63,64]. The slope of less than unity also confirmed that NH_4NO_3 was undergoing volatilization (Figure 4d). Furthermore, the high-resolution particle number size distributions further demonstrated that, during the NO_3^- peak periods, the number concentration spectra fluctuated dramatically (Figure 4c), a typical feature indicative of the influence of nearby pollution sources.

3.4. Case 2: Biomass-Burning-Derived Potassium Salts and Cloud-Processing of KNO_3 and NH_4NO_3 by Mixing with Additional Anthropocentric Sources, Followed by NH_4NO_3 Volatilization

The second case occurred on 28 November 2023. On this day, the diurnal variation of $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ exhibited a distinct pattern compared to that on 27 November (Figures 4 and 5). Between 00:00 and 20:00, $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ remained relatively stable at $1.3 \pm 0.2 \mu\text{g m}^{-3}$ (Figure 4a), followed by a statistically significant increase to $1.5 - 3.0 \mu\text{g m}^{-3}$ ($P < 0.05$). Notably, no corresponding increase in $\text{PM}_{2.5}$ mass concentration was recorded at the three national control sites (Figure 5b). This suggested that the increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ was a localized phenomenon rather than a regionally distributed event. Simultaneous particle number size distributions revealed that, during the $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ increase, the median diameter of the accumulation mode particles decreased rather than increased (Figure 5c). Furthermore, a strong positive correlation was identified between the normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and the normalized $N_{>100}$ (Figure 5d), with the regression slope of 2.2, significantly exceeded unity. These findings suggested that $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ was influenced by primary sources; however, primary emissions alone cannot fully account for the observed increase.

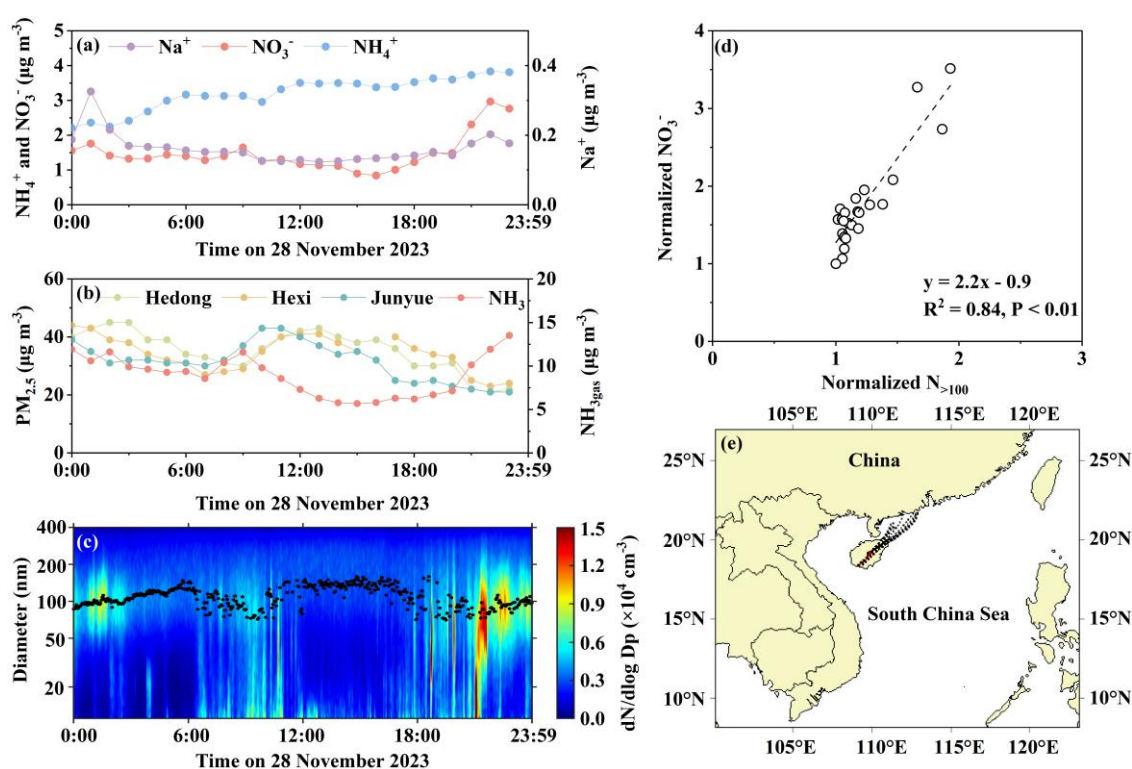


Figure 5. Same as Figure 4, except on 28 November 2023.

On 28 November, the concentrations of NH_4^+ and Na^+ in $\text{PM}_{2.5}$ exhibited diurnal variations similar to those observed on 27 November, although with substantially larger fluctuations. Although no statistically significant correlation was identified between $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and NH_4^+ concentrations in $\text{PM}_{2.5}$ ($P > 0.05$, Figure S2c), NH_4^+ showed a strong correlation with the equivalent concentrations of $(\text{NO}_3^- + \text{SO}_4^{2-})$, with a regression slope close to unity. Based on this, using 20:00-23:00 as the analysis window (t_0, t_1, t_2, t_3), the net increases in NH_4^+ concentrations at t_1 - t_3 relative to t_0 can be calculated by the difference. Assuming NH_4^+ was fully associated with $(\text{NO}_3^- + \text{SO}_4^{2-})$ at a 1:1 equivalent concentration ratio, the corresponding net increase in NO_3^- attributed to NH_4NO_3 at t_1 - t_3 was calculated to be $0.02 \mu\text{g m}^{-3}$, $0.04 \mu\text{g m}^{-3}$, and $0.05 \mu\text{g m}^{-3}$, respectively. These contributions account for 3.0%, 2.4%, and 4.2% of the total net increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ during the same periods. Recall that thermodynamic equilibrium stimulation analysis indicated the volatilization of NH_4NO_3 into gas phase. The significant increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ between 21:00 and 23:00 was likely related to the formation of other nitrates, such as KNO_3 and NaNO_3 . However, the minimal increase in Na^+ concentration in $\text{PM}_{2.5}$ during this period (Figure 5a) suggested that NaNO_3 may accounted for only a small fraction. In contrast, a marked increase in K^+ concentration was observed in $\text{PM}_{2.5}$ between 21:00 and 23:00 (Figure S4), indicating that biomass burning emissions may be a major contributor [69,70]. Concurrently, atmospheric NH_3 also increased (Figure 5b), which may similarly be attributed to biomass burning emissions [33]. Other anthropogenic or natural sources of NH_3 during nighttime are considered less likely [18,33,71]. It is noteworthy that, compared with 27 November, the nucleation mode in the particle number size spectrum nearly disappeared during the NO_3^- increase, suggesting that the biomass burning aerosols may have undergone atmospheric processing, such as cloud modification under non-precipitating conditions [60]. Therefore, the significant increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ during 21:00-23:00 was more likely driven by secondary formation processes within non-precipitating clouds, rather than direct primary emissions. Interestingly, a secondary increase in K^+ was also observed between 01:00 and 03:00 on the same day (Figure S4), accompanied by a pronounced rise in the particle number concentration within the accumulation mode (Figure 5c). Surprisingly, the increase in concentrations of NO_3^- and atmospheric $\text{NH}_{3\text{gas}}$ during this period were almost negligible. Therefore, primary biomass burning aerosols and non-precipitation modification alone were insufficient to explain the increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ between 21:00 and 23:00, leaving additional anthropogenic sources as co-contributors. Importantly, no significant shift was observed in the air mass back trajectories before and after the $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ increase (Figure 5e).

3.5. Case 3: Transition from Regional Transport to Local Combustion Sources Induces Strong Phase Instability and NH_4NO_3 Volatilization

On 29 November 2023, $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ exhibited two distinct periods: from 00:00 to 18:00 and after 18:00. During the first period, the concentration changes of NO_3^- and NH_4^+ were consistent with the trends observed in $\text{PM}_{2.5}$ concentrations at the national monitoring stations (Figures 6ab), suggesting a common regional source. In contrast, after 18:00, $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ rapidly increased from $1.4 \mu\text{g m}^{-3}$ to a peak of $3.9 \mu\text{g m}^{-3}$, without a corresponding rise in $\text{PM}_{2.5}$ concentrations at the national stations. Furthermore, the correlation between $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and NH_4^+ concentrations over the full day ($R^2 = 0.34$) was significantly lower than that during the first period ($R^2 = 0.92$) (Figure S2e). These results point to the hypothesis that the increase in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ after 18:00 was primarily attributable to local sources. Moreover, the air mass trajectories during the period of elevated $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ were in between two slightly separately trajectories before 18:00 (Figure 6e).

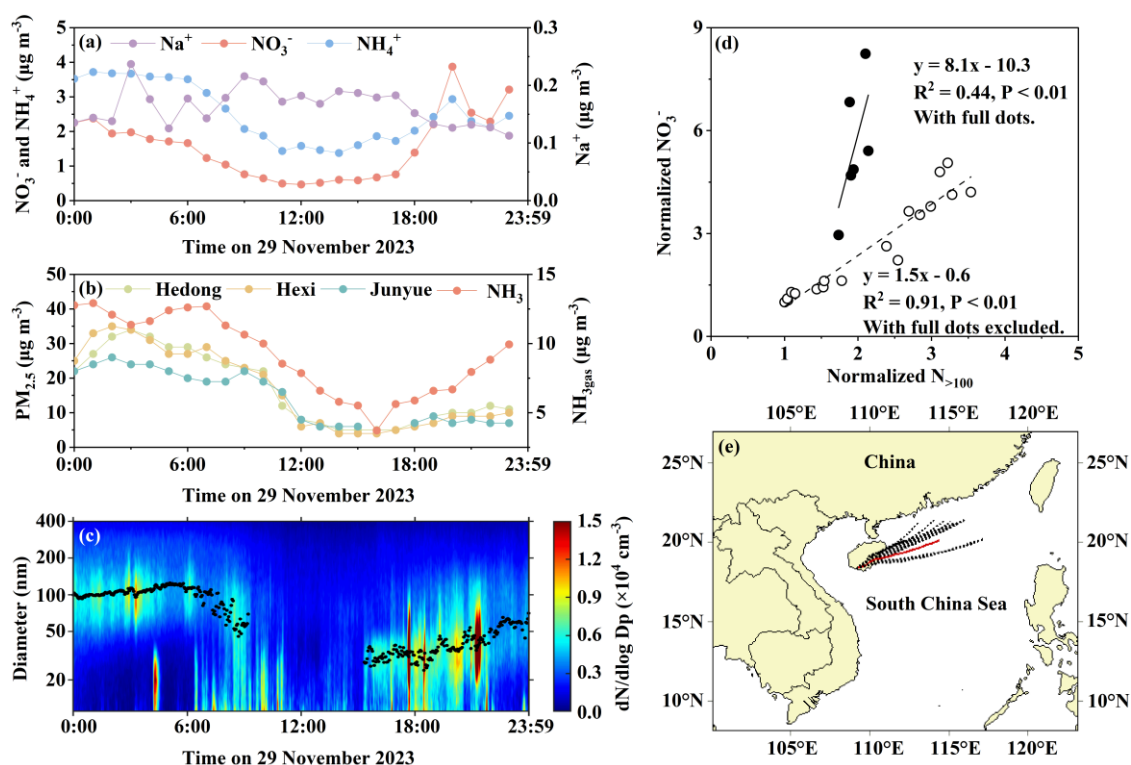


Figure 6. Same as Figure 4, except on 29 November 2023.

However, whether the equivalent concentrations were calculated using data from 00:00–23:00 or from 00:00–18:00, the results consistently showed that $[\text{NH}_4^+] = 0.9 * ([\text{SO}_4^{2-}] + [\text{NO}_3^-]) + 0.02$, with an R^2 of 0.99 and $P < 0.01$ (Figure S1f). This suggested that NO_3^- in $\text{PM}_{2.5}$ both before and after 18:00 primarily existed in the form of NH_4NO_3 . Consequently, the observed decrease in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ between 00:00 and 18:00, along with the declining proportion of NH_4NO_3 among ammonium salts, may be attributed to the volatilization of NH_4NO_3 , consistent with thermodynamic simulations aforementioned. However, the amount of $\text{NH}_{3\text{gas}}$ released through this process was considerably smaller than the total reduction in ambient $\text{NH}_{3\text{gas}}$ concentrations. The concurrent decline in atmospheric $\text{NH}_{3\text{gas}}$ levels may have further promoted the volatilization of NH_4NO_3 (Figure 6b).

Additionally, the diurnal variations of Na^+ and NO_3^- in $\text{PM}_{2.5}$ were nearly opposite (Figure S3c), indicating that NO_3^- associated with NaNO_3 in $\text{PM}_{2.5}$ was likely negligible. The particle number size distributions demonstrated that after 18:00, the particle number concentration was dominated by the smaller-sized Aitken mode (Figure 6c). The median Aitken mode diameters showed significant variation at minute-scale resolution and showed an overall increasing trend, although it remained significantly smaller than the accumulation mode diameter dominant before 06:00 that day. According to particle emission fingerprints from different sources reported in the literature [72], the particles observed after 18:00 were most likely emitted from combustion sources rather than formed via ambient nucleation processes [73].

Further analysis of the normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and $N_{>100}$ revealed a strong correlation during the period from 00:00 to 18:00, with a regression slope of 1.5. Once Again, primary emissions alone could not fully account for the observed $[\text{NO}_3^-]_{\text{PM}_{2.5}}$. However, it is likely that secondary NO_3^- formation occurred earlier during air mass transport to the observation site, considering that NH_4NO_3 appeared to have predominantly volatilized from the particle phase. This will be further confirmed in the following thermodynamic simulations. In contrast, after 18:00, the correlation between normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and $N_{>100}$ weakened significantly, and the regression slope increased to 8.1. The slope value alone implied that NO_3^- in $\text{PM}_{2.5}$ was mainly derived from secondary sources, although the observed $\text{HNO}_3^*_{\text{gas}}$ concentration remained relatively low (0.13–0.21 $\mu\text{g m}^{-3}$). Therefore, the pathway of large-scale N_2O_5 production, which could promote NH_4NO_3 formation, is ruled out. On the contrary,

NH_4NO_3 may have formed rapidly during the cooling of combustion plumes, followed by dilution and NH_3 -limited volatilization [23,54].

3.6. Case 4: Primary Emissions and Marine Aerosol Interactions Drive Diurnal Sea-Salt-Restricted Nitrate Formation Under Southeast Monsoon Influence

Figure 7a-h showed a unique case observed under the influence of southeast monsoon. During this period, the nearby natural gas-fired power plant was intermittently located directly upwind of the sampling site. On 16 June 2024, the concentrations of NO_3^- , Na^+ , and NH_4^+ in $\text{PM}_{2.5}$ exhibited distinct temporal patterns before and after 12:00 (Figure 7a). After 12:00, $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ exhibited a bell-shaped temporal that closely resembled the pattern of Na^+ in $\text{PM}_{2.5}$. The strong correlation between $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and Na^+ in $\text{PM}_{2.5}$ supported the heterogenous formation of NaNO_3 through the reaction of $\text{HNO}_{3\text{gas}}$ with sea-salt aerosols at the time [74]. In contrast, the observed low concentrations of $\text{HNO}_{3\text{gas}}$ and the thermodynamic simulations didn't support the formation of NH_4NO_3 during the moments. Note that the diurnal variation of Na^+ concentrations in $\text{PM}_{2.5}$ on that day was reasonably consistent with the tide height (Figure S5).

Before 12:00 on that day, the concentrations of NO_3^- , Na^+ , and NH_4^+ all increased synchronously, exhibiting a bimodal distribution with peaks at 07:00 and 09:00. Three peaks of $\text{HNO}_{3\text{gas}}$ were observed before 12:00 ranged from 2.1 to 2.9 $\mu\text{g m}^{-3}$, which were approximately an order of magnitude higher than other values recorded throughout the study. However, low concentrations of OC were recorded at only 1.3-1.6 $\mu\text{g m}^{-3}$ during the peak periods. Although the concentration of EC increased to 0.7 $\mu\text{g m}^{-3}$ between 08:00 and 10:00, the ratio of OC/EC was only 2.1, a typical value for primary particulate carbonaceous emissions [75]. Moreover, $\text{PM}_{2.5}$ levels at three national sites did not show a proportional rise during these peak times, indicating no large-scale influx of air pollutants. Therefore, the large sawtooth-pattern increases in $[\text{HNO}_{3\text{gas}}]$ and $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ were more likely associated with primary emissions from the nearby natural gas-fired power plant, rather than the secondary formation of $\text{HNO}_{3\text{gas}}$ in the atmosphere followed by the heterogeneous reaction with sea-salt aerosols [74]. In this case, the amount of sea-salt aerosols appeared to be a controlling factor for $[\text{NO}_3^-]_{\text{PM}_{2.5}}$, considering that no corresponding peak in $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ occurred concurrently with the third peak of $\text{HNO}_{3\text{gas}}$ in the absence of $[\text{Na}^+]_{\text{PM}_{2.5}}$ peak. The trough of $[\text{Na}^+]_{\text{PM}_{2.5}}$ at 08:00 was likely due to temporary wet scavenging when low cloud crossed over the hill (Figure S5).

Unlike those on 27-29 November 2023, there was no significant correlation between the normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and $N_{>100}$ with $P > 0.05$ on 16 June. The particle number size distributions showed an increase concentrations of accumulation mode particles after 08:00, which coincided with the increase in EC and NH_4^+ in $\text{PM}_{2.5}$. These results suggested that the strongest emissions from the nearby power plant likely occurred between 08:00 and 12:00, which were apparently consistent with these larger values of $\text{HNO}_{3\text{gas}}$.

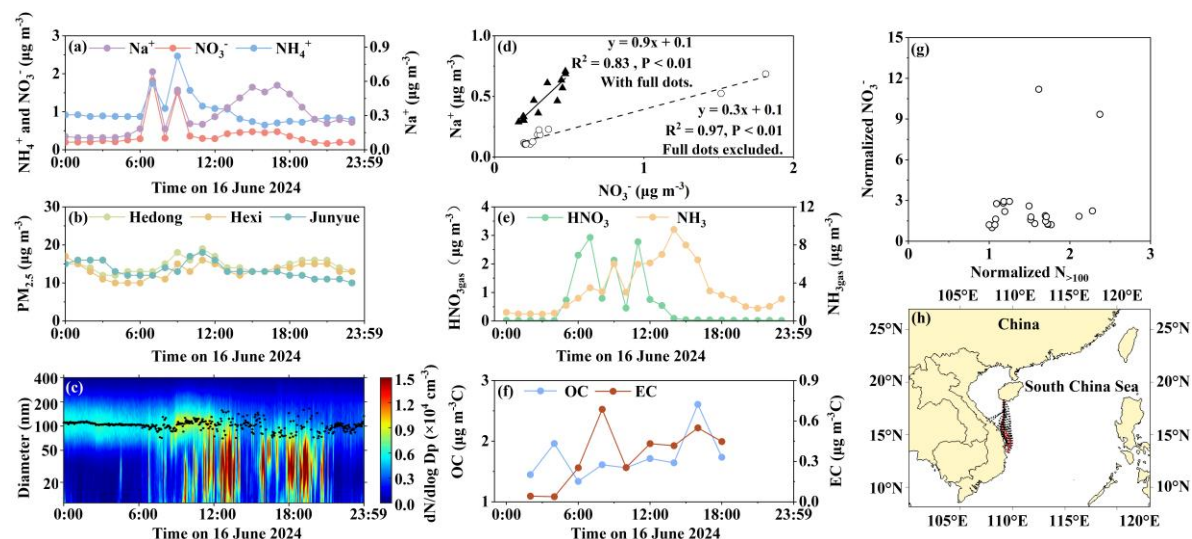


Figure 7. Observations and calculations on 16 June 2024. (a) daily variations of Na^+ , NO_3^- , and NH_4^+ concentrations in $\text{PM}_{2.5}$; (b) daily variations of $\text{PM}_{2.5}$ mass concentrations at three national monitoring sites; (c) contour plotting of particle number size distributions; (d) correlation between Na^+ and NO_3^- concentrations in $\text{PM}_{2.5}$ (empty and full symbols represent the values before and after 12:00); (e) daily variations of HNO_3^* and NH_3 concentrations; (f) daily variations of OC and EC concentrations; (g) correlation between normalized $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ and $N_{>100}$; (h) 24-hour air mass back trajectories (red trajectories correspond to peak periods).

3.7. Source Apportionment of NO_3^- in $\text{PM}_{2.5}$ During the Four Cases

The analysis of observation cases from 2023 and 2024 highlights the critical role of both primary and secondary sources in partitioning the gas-particle distribution of nitrate. Therefore, this study quantitatively evaluated the contributions of aerosols from various sources to nitrate using the PMF model (Figure 8). In November, NO_3^- in $\text{PM}_{2.5}$ was predominantly attributed to Factor 2 and Factor 5 only. Factor 5 contributed between 52% and 73%, while Factor 2 contributed between 26% and 46%. By contrast, on 16 June, Factor 1 made a limited contribution (4.6%), whereas the contribution from Factor 5 increased to 79%, and Factor 2 decreased to 16%.

Factor 1 exhibited a unimodal particle size distribution, with a median diameter centered approximately 40 nm. This source factor displayed distinct peaks during both morning and evening rush hours, suggesting a potential association with non-electric vehicular emissions [72,73,76,77]. The relatively weaker morning peak may be attributed to the widespread use of electric motorcycles for commuting in tropical regions. In contrast, Factor 2 presented a complex trimodal size distribution, with the dominant mode characterized by a median particle diameter exceeding 200 nm. Despite this, its total number concentration was the lowest among all five factors, approximately an order of magnitude lower than those of Factors 1, 3, and 4, indicating that it likely represents a regional background source, particularly of marine origin [72,78]. Factor 3 demonstrated a bimodal distribution, with prominent peaks at approximately 70 nm and a minor mode below 20 nm. This factor was likely attributed to emissions from Chinese-style cooking, where high-temperature oil use leads to substantial particle generation, particularly between 18:00 and 20:00. However, its contribution to NO_3^- in $\text{PM}_{2.5}$ was found to be negligible. Factor 4 was dominated by nucleation-mode particles, indicative of short atmospheric nucleation times. Its occurrence was more frequent during nighttime, implying that these events were likely influenced by transient coastal atmospheric conditions [78,79]. Correspondingly, this factor also exhibited minimal contribution to NO_3^- levels in $\text{PM}_{2.5}$. Lastly, Factor 5 displayed a bimodal particle size distribution and was primarily associated with emissions from a nearby natural gas-fired power plant (~1 km distance), with additional influence from regional background sources. Factor 5 exhibited a distinct trough in the particle size distribution around 100 nm, a feature resembling the Hoppel-effect modified distribution under an environmental supersaturation of 0.2%. This suggests that the gas-fired power plant plume, when emitted into an environment with a substantial temperature contrast, may promote the formation of microdroplets, thereby leading to an aerosol size distribution akin to that observed in non-precipitating cloud processing. Consequently, it is anticipated that Factor 5 will contribute a higher mass concentration of nitrate in winter compared to summer (Figure 8).

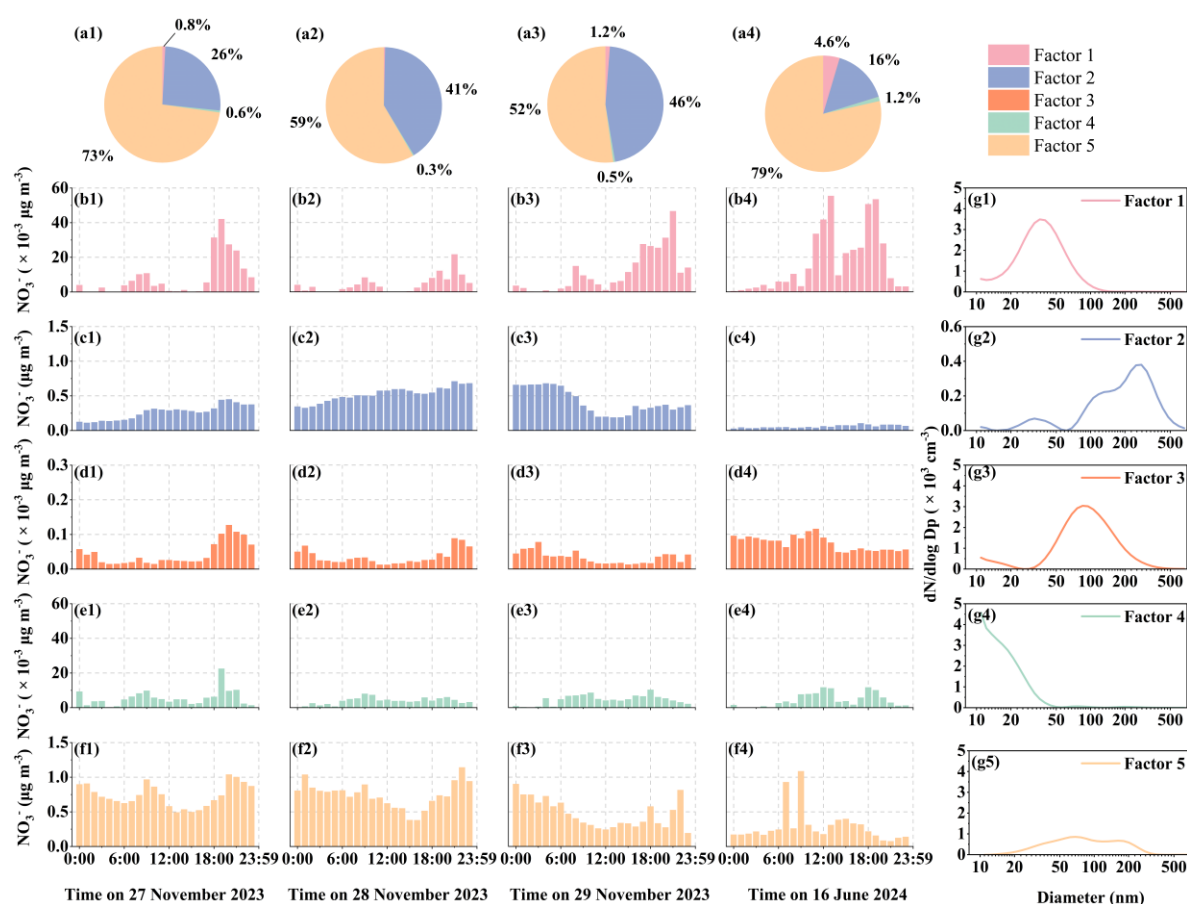


Figure 8. Source apportionment and daily variation of NO_3^- in $\text{PM}_{2.5}$. (a) Contribution of five factors to NO_3^- . (b-f) Daily variation in the contribution of each factor to NO_3^- . (g) The particle number size distribution profile of each factor.

As shown in Figure 1, the gas-fired power plant emits substantial amounts of water vapor droplets, which facilitate the formation of liquid-phase ($\text{NH}_4^+ + \text{NO}_3^-$). The residence time of the vapor droplets, ranging from several tens of seconds to a few minutes, is primarily influenced by ambient temperature and atmospheric humidity; lower temperatures and higher humidity extending their residence time [23]. This may account for the elevated NO_3^- concentrations observed in $\text{PM}_{2.5}$ during the humid November nights. It is evident that the ($\text{NH}_4^+ + \text{NO}_3^-$) formed rapidly through water vapor condensation and subsequent flue gas dilution is likely to volatilize from the particulate to the gas phase. Compared to Factor 2, Factor 5 appears to represent a more unstable component, as approximately 20% of high-concentration NO_3^- cases could not be resolved in the PMF analysis (Figure S6). In these instances, the PMF model clearly underestimates NO_3^- , possibly because the NO_3^- captured by the analysis reflects aged and relatively stable NH_4NO_3 . In contrast, high-concentration NO_3^- in $\text{PM}_{2.5}$ is relatively fresh and in the NH_3 -restricted volatilization process of NH_4NO_3 . It is worth noting that a slight difference in the extracted profile of each factor was observed when NO_3^- concentrations were used to replace those in the final particle size bin (Figure S7), which may be attributed to subtle differences in their respective sources.

4. Conclusions

This study systematically investigates the dual regulatory effects of atmospheric NH_3 on the formation and evaporation of NH_4NO_3 at a clean tropical coastal site. By integrating high-resolution field measurements, E-AIM modeling, and PNF source apportionment analysis, we demonstrate that NH_3 plays a role in suppressing the volatilization of NH_4NO_3 under varying atmospheric conditions rather than acting solely as a precursor promoting its formation.

Multiple case studies revealed that NH_4NO_3 in $\text{PM}_{2.5}$ originated from both primary emissions—particularly from local combustion plumes and in-cloud processing of KNO_3 and/or NH_4NO_3 , especially under the influence of the northeast monsoon. Under NH_3 -rich but HNO_3 -limited conditions, particle-phase NH_4NO_3 tended to volatilize as confirmed by thermodynamic modeling and various supporting lines of evidence. Source apportionment using the PMF model indicated that regional background transport and emissions from a nearby natural gas power plant were the dominant contributors to nitrate in $\text{PM}_{2.5}$. Under the southwest monsoon, the clean marine air mass was not conducive to NH_4NO_3 formation even when perturbed by plumes from local gas-fired power plants. In the case, the sea-salt-aerosol-restricted reactions between $\text{HNO}_3^*_{\text{gas}}$ and sea-salt aerosols dominantly contributed to NO_3^- in $\text{PM}_{2.5}$.

These findings challenge the conventional understanding of nitrate formation as purely precursor-limited, highlighting the importance of simultaneously accounting for formation and volatilization dynamics. This study refines the understanding of NH_4NO_3 behavior in ammonia-rich marine boundary layers and has important implications for optimizing future nitrate control strategies in coastal and urban environments.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Comparison of modeled and observed gas concentrations for 27-29 November 2023, and 16 June 2024 using the E-AIM with only three components including SO_4^{2-} , NH_4^+ and NO_3^- as inputs. (a) Modeled HNO_3 vs. Observed HNO_3^* . (b) Modeled NH_3 vs. Observed NH_3 . The color bar indicates NO_3^- concentration in $\mu\text{g m}^{-3}$. Figure S2: Correlations between NH_4^+ and NO_3^- , and NH_4^+ with the equivalent concentrations of $(\text{NO}_3^- + \text{SO}_4^{2-})$ in $\text{PM}_{2.5}$ from November 27-29, 2023, and June 16, 2024 (empty and full symbols represent the data before and after 18:00 in c), and; represent the data before and after 12:00 in g) and h)). Figure S3. Correlations between NO_3^- and Na^+ in $\text{PM}_{2.5}$ from November 27-29, 2023. Figure S4: (a-b) Correlations between NH_3 and NO_3^- on November 27-28, 2023. (c) K^+ Concentration from November 24 to December 3, 2023; Figure S5: (a) Sky picture taken on June 16, 2024. (b) Tidal height on June 16, 2024. Figure S6: PMF simulation closure validation results. (a-b) Closure of total particle size concentration before and after combination of particle size spectrum and $[\text{NO}_3^-]_{\text{PM}_{2.5}}$; (c) Closure of the channel with the largest particle size in the particle size spectrum; (d) Closure of $[\text{NO}_3^-]_{\text{PM}_{2.5}}$ (empty and full symbols represents the modeled values within 15% difference from the observations and beyond the 15% margins, respectively). Figure S7: Comparison of factor modes before and after replacing nitrate ion concentration in the last particle size channel.

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Abbreviations

AIM-IC, Aerosol Ion Monitor-Ion Chromatography; SMPS, Scanning Mobility Particle Sizer; E-AIM, Extended AIM Aerosol Thermodynamics Model; RH, relative humidity; T, temperature; $\text{N} + 2^*\text{S}$, the sum of the molar concentration of nitrate and twice the molar concentration

of sulfate; PM_{2.5}, particulate matter with the aerodynamic diameter below 2.5 µm collected by AIM-IC.

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