Influence of Secondary Inorganic Aerosol on the Concentrations of PM$_{2.5}$ and PM$_{0.1}$ during Air Pollution Episodes in Hanoi, Vietnam

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ABSTRACT

The high concentration of PM$_{2.5}$ in Hanoi has been an issue of great concern. There were several periods during the winter when PM$_{2.5}$ concentrations were higher than the Vietnamese ambient air quality standards (NAAQS) and WHO guidelines for daily PM$_{2.5}$. In this study, the periods when daily PM$_{2.5}$ concentrations exceeded the NAAQS of 50 µg m$^{-3}$ for a minimum of two consecutive days were determined as episode periods. The study focuses on the impact of secondary inorganic aerosol (SIA) on PM$_{2.5}$ episodes in the dry winter period in Hanoi. To calculate SIA, water-soluble ions of daily PM$_{2.5}$ and PM$_{0.1}$ samples which were collected on the rooftop of a three-storeyed building at an urban site in Hanoi, Vietnam (HUST site) from October 14 to December 31, 2020, were analyzed. Levels and SIA of PM$_{2.5}$ and PM$_{0.1}$ at a transportation site (CEM site) in an episode period from December 20 to December 28, 2020 were also measured. The contribution of SIA on PM$_{2.5}$ and PM$_{0.1}$ during those episodes, the effects of meteorological conditions, and long-range transport were investigated. The results showed that SIA contributed on average 29.0% and 14.1%, respectively, to PM$_{2.5}$ and PM$_{0.1}$ concentrations during air pollution episodes at HUST. Those were higher than the average contribution percentages of total SIA to PM concentrations in non-episode periods for PM$_{2.5}$ (25.6%) and PM$_{0.1}$ (10.6%) at HUST. Among meteorological factors, wind speed largely affected PM$_{2.5}$ concentration and SIA of PM$_{2.5}$. Relative humidity, pressure, temperature, and radiation had a good correlation with SIA of PM$_{0.1}$ and a moderate correlation with PM$_{0.1}$. Concentration-weighted trajectory analysis demonstrated that PM$_{2.5}$ and SIA levels were also influenced by long-range transportation from the upper areas. This study highlighted the importance and served as pioneered research on SIA contribution to PM$_{2.5}$ episodes in the country.

Keywords: SIA, PM$_{2.5}$, PM$_{0.1}$, Air pollution episodes, Hanoi

1 INTRODUCTION

Particulate matter (PM) pollution is a common phenomenon of great concern in recent decades in Southeast Asia and in Hanoi specifically. PM can be classified by aerodynamic diameter. PM$_{2.5}$ is particulate matter with an aerodynamic diameter of less than 2.5 µm, and PM$_{0.1}$ is particulate matter with an aerodynamic diameter of less than 0.1 µm. PM$_{2.5}$ is the most concerning air pollutant in Hanoi because of its high annual levels exceeding the national ambient standards (NAAQS) QCVN 05/2013:BTNMT of 25 µg m$^{-3}$ and WHO guidelines of 5 µg m$^{-3}$. For example, the current annual
monitoring data at an urban and a transportation site from August 2019 to June 2020 were 46 and 49 μg m\(^{-3}\), respectively (Makkonen et al., 2023). Daily PM\(_{2.5}\) often increases to levels higher than the NAAQSs of 50 μg m\(^{-3}\) in the winter and spring. PM\(_{0.1}\) is also of concern in Hanoi because of its high levels (Huyen et al., 2023; Dung et al., 2020). Additionally, small particles within the PM\(_{0.1}\) range can later grow into bigger particles, increasing PM\(_{2.5}\) levels significantly.

Air pollution episodes are periods with high pollutant levels. Because higher levels of pollutants pose greater health effects, air pollution episodes significantly affect public health. Luong et al. (2017) showed that in Hanoi from 2010 to 2011, hospitalization rates of children under five years old increased by 1.4%, 2.2%, and 2.5%, respectively, for every 10 μg m\(^{-3}\) increase in PM\(_{10}\), PM\(_{2.5}\), and PM\(_{1.0}\). There is no official definition of a PM episode in Vietnam. In this study, the term pollution episode is defined as the period when daily average PM\(_{2.5}\) concentrations exceed the NAAQS of 50 μg m\(^{-3}\) for at least two consecutive days.

Because of the serious impact of air pollution episodes, there were many studies about air pollution episodes in the world as well as in the Southeast Asia (SEA) region. For instance, a study of PM\(_{2.5}\) episodes in 100 cities across the world from 2013 to 2017 (Morawska et al., 2021) showed that the frequency, magnitude, and duration of severe air pollution episodes have been increasing in 46 out of 100 cities. In SEA, several studies on the periods of high PM levels have been conducted (Sulong et al., 2017; Iaafar et al., 2018; Pinto et al., 1998; See et al., 2007; Huang et al., 2016; Kim Oanh and Leelasakultum, 2011; Chomaneet et al., 2020). Based on chemical compositions, different causes of high PM levels in SEA have been identified (Van et al., 2022 and references therein). Besides SEA, several studies about air pollution episodes were investigated in China, showing deep insights into the episode formation mechanisms (Tao et al., 2017; Wang et al., 2021; Yang et al., 2015; Shen et al., 2017). The chemical compositions of particles are important information to identify the emission sources and understand the transformation processes of particles. This is the scientific underpinnings for countries to propose effective management strategies to reduce the negative consequences of PM. Lying in SEA, next to China, with reports of several episodes in winter (Ly et al., 2018; Van et al., 2022), Vietnam has no studies that have been conducted digging into the chemical compositions of PM in episode periods. This study aims to fill this information gap, concentrating on secondary inorganic aerosol (SIA) components.

SIA are the main components of PM\(_{2.5}\) in episode periods in SEA as well as in normal periods (Van et al., 2022 and references therein). They are denoted ‘secondary’ since they are the products of physical and chemical processes after emission into the atmosphere. The main SIA contains NH\(_4^+\), SO\(_4^{2-}\) and NO\(_3^-\) (occurring as NH\(_4\)NO\(_3\), NH\(_4\)HSO\(_4\), and (NH\(_4\))\(_2\)SO\(_4\)). These SIA are produced when SO\(_2\), NO\(_x\), and NH\(_3\) undergo complex chemical reactions in the air, on droplets, and particles (Weiwers et al., 2010; An et al., 2019). SO\(_4^{2-}\), NO\(_3^-\), and NH\(_4^+\) are mainly derived from anthropogenic origin, as their precursor gases are largely emitted from transportation, energy production, and agricultural sources. Few studies on PM\(_1\)'s chemical constituents, including SIA, were conducted in Hanoi, such as Dung et al. (2020), Makkonen et al. (2023), and Huyen et al. (2021, 2023). However, they mainly concentrated on seasonal variations of SIA rather than focusing on SIA contributions during high-level periods.

Many studies in China, South Korea, Malaysia, and Europe demonstrated that the level of SIA increased in air pollution episodes, and this increment contributed to heavy pollution (Tao et al., 2017; Tao et al., 2014; Li et al., 2016a; Shen et al., 2017; Wang et al., 2021; Yang et al., 2015; Geun et al., 2016; Sulong et al., 2017; Weiwers et al., 2010; Allen et al., 2019). SIA’s main gaseous precursors are SO\(_2\), NO\(_x\), and NH\(_3\) (Weiwers et al., 2010). SO\(_2\) is released by coal-fired power plants and industrial sources such as cement, smelters, and industrial boilers. NO\(_x\) is mainly emitted from fuel combusions in transportation, coal-fired plants, and other industrial sources (Weiwers et al., 2010) and partly from bacterial processes, wildfires, and lightning (Weiwers et al., 2010; Thurston, 2008). Meanwhile, agricultural activities are the main source of emissions of NH\(_3\) (Weiwers et al., 2010; Behera et al., 2013). Thus, the reduction of gaseous precursors has been linked to downward trends in PM levels. Numerous studies have shown that reducing agricultural NH\(_3\) emissions can result in a reduction in PM\(_{2.5}\) (Wang et al., 2018; Cheng et al., 2021; Pozzer et al., 2017; An et al., 2019; Mar et al., 2016; Huang et al., 2012). A study in China also reported that the reduction of NH\(_3\) may even be more effective in reducing PM\(_{2.5}\) than decreasing SO\(_2\) and NO\(_x\) emissions (Li et al., 2016b). The absolute impact on PM\(_{2.5}\) reduction was found strongest in East Asia and China,
even for small source reductions (Pozzer et al., 2017). Simulations conducted in Europe and North America have not shown immediate changes when limiting agriculture NH₃ sources, however, a significant downturn can still be seen clearly when NH₃ emissions are systematically reduced (Pozzer et al., 2017).

This work aims to investigate the contribution of SIA to PM₂.₅ concentrations during air pollution episodes in Vietnam. Water-soluble ions in daily PM₂.₅ and PM₀.₁ samples were collected in a dry winter in Hanoi and analyzed. The percentage of SIA of PM₂.₅ and PM₀.₁ in episode and normal periods data were calculated to see the contribution of SIA to those PM levels. Pearson correlation and polar plots were applied to investigate the effects of meteorological factors on PM₂.₅ and PM₀.₁. The HYSPLIT, especially the concentration-weighted trajectory (CWT) model was applied to determine the effects of long-range transport on PMs and SIA.

2 MATERIALS AND METHODS

2.1 Sampling Site

The location of the monitoring site is shown in Fig. 1. The monitoring site was selected in Hanoi, the capital of Vietnam. More information about Hanoi’s characteristics and meteorological conditions can be found in the studies by Hien et al. (2002), Hai and Kim Oanh (2013), Ly et al. (2018), and Huyen et al. (2021). In short, Hanoi is an actively developed city with high pressure of rapid urbanization and a high increasing percentage of vehicles. Hanoi meteorology is divided into the northeast monsoon in winter and the southeast monsoon in summer. From October to December, northerly to northeasterly flow coming from the inland of China brings mainly dry and cold air (Hien et al., 2002). From January to March/April, air masses have to travel a long way over the Pacific Ocean before reaching North Vietnam via the Gulf of Tonkin bringing humic air (Hien et al., 2002). The meteorological conditions have been demonstrated to largely affect the air quality of the city (Hien et al., 2002; Hai and Kim Oanh, 2013; Ly et al., 2018; Huyen et al., 2021).

Fig. 1. Sampling site at Hanoi University of Science and Technology (HUST), Hanoi, Vietnam (21°00′18″N, 105°50′38″E), the Northern Monitoring Center (CEM) (21°2′56″N, 105°52′57″E) and additional data site (BAM) at American Club Hanoi, No. 21 Hai Ba Trung Street, Hoan Kiem district (21°1′25″N, 105°51′14″E).
The first sampling site was at the rooftop of a three-storeyed building at Hanoi University of Science and Technology (HUST) (No. 1 Dai Co Viet, Hai Ba Trung district, Hanoi, Vietnam (21°00′18″N, 105°50′38″E)). A detailed description of this site has been presented in the study of Huyen et al. (2021). In short, this site is surrounded by residential houses and is more than 100 m away from roads with heavy traffic. The PM level and composition at this sampling site can be influenced by different emission sources in this urban area, such as transportation, construction, and cooking activities. It can therefore be considered both a mixed site and an urban site. The second sampling site (CEM) was on the rooftop of a one-storeyed building at the North Center of Monitoring, Vietnam Administration of Environment. The sampling site is next to the six-lane Nguyen Van Cu Street. It can be considered as a transportation site.

2.2 PM<sub>2.5</sub> and PM<sub>0.1</sub> Monitoring and Additional Data

2.2.1 Sampling method

Our sampling methodology has been previously reported in our article on PM concentrations (Ha et al., 2023) as well as in the paper of Huyen et al. (2023) investigating the seasonable variation of PM components. A total of 72 daily PM<sub>2.5</sub> and 76 daily PM<sub>0.1</sub> samples were collected during the dry winter (October 14–December 31, 2020) at HUST for 23.5 hours from 10:00 to 9:30 of the next day (Ha et al., 2023). Nine PM<sub>2.5</sub> and PM<sub>0.1</sub> samples were collected from December 20 to December 28, 2020, at CEM with the same sampling time frame. PM<sub>2.5</sub> and PM<sub>0.1</sub> samples were collected on 47 mm quartz fiber (2500 QAT-UP, Pall Corp., USA) using a cyclone device (URG-2000-30EH University Research Glassware Corp., Chapel Hill, NC, USA) with a flow rate of 16.7 L min<sup>–1</sup> and on 55 mm quartz fiber (2500 QAT-UP, Pall Corp., USA) using Nanosampler II (Model 3182, KANOMAX, Suita, Japan) at a flow rate of 40 L min<sup>–1</sup>, respectively. Before sampling, each filter was baked at 350°C for 2 hours. After sampling, each filter was placed into a petri dish and kept separately in an aluminum bag. The samples were stored in a freezer at –20°C to avoid volatilization and additional reactions, before undergoing further analysis.

2.2.2 Analysis

a. Mass analysis

To determine the mass of PM, filters were weighted on a microbalance (readability 1 µg) in a humidity and temperature-controlled room. A detailed description of sample filter weighing was presented in the study by Ha et al. (2023).

b. Ion analysis

The water-soluble ion components in the analysis target included cations: K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup> and anions: Cl<sup>–</sup>, SO<sub>4</sub><sup>2–</sup>, NO<sub>3</sub><sup>–</sup> (WMO/GAW, 2003) by the ion chromatograph device ICS-1600, Dionex Corp., Sunnyvale, CA, USA. The process of determining the ionic composition was made in 2 main steps: extraction and sample analysis. The method has been presented in the study of Huyen et al. (2023).

2.2.3 Additional data

Hourly data of PM<sub>2.5</sub> from a Beta Attenuation Monitor (BAM), 2.1 km from the monitoring site (HUST) were obtained to compare with the study’s results. The observation site is presented in Fig. 1.

Hanoi meteorological data were collected through R software version 4.1.3. Among those data, wind speed (Ws), wind direction (Wd), relative humidity (RH), and temperature (Temp) were observed at Noi Bai International Airport (approximately 30 km away from the HUST sampling site). Other meteorological factors (surface pressure (Press), radiation (Rad), and rainfall data (Pr)) were measured at Hanoi DONRE sites, which were presented on the website (moitruongthudo.vn).

2.3 Data Analysis

R software version 4.1.3 with various support packages including BMA, psych, openair, worldmet, etc. was used to perform HYSPLIT, concentration-weighted trajectory, Pearson correlation, and polar plots.
HYSPLIT was used to determine the air mass trajectory. Concentration-weighted trajectory (CWT) analysis was then used to investigate the effects of the long-range transport on PM$_{2.5}$ and SIA levels in Hanoi. HYSPLIT data inputs were downloaded from the National Oceanic and Atmospheric Administration (NOAA) websites: ftp://arlftp.arlhq.noaa.gov/archives/reanalysis/ More details of the HYSPLIT model and CWT were presented in NOAA (2018). According to Cohen et al. (2010), mixing heights in Hanoi during 206 days of sampling time between 2005 and 2006 ranged from 270 m (early morning) and 920 m (late afternoon). In this study, 500 m in height was selected to simulate air trajectories to Hanoi.

3 RESULTS AND DISCUSSION

3.1 Characteristics of PM$_{2.5}$ and PM$_{0.1}$

3.1.1 PM$_{2.5}$ and PM$_{0.1}$ variations

The temperature during the research period ranged from 12°C–26°C, and relative humidity ranged from 38%–95% (Fig. S1). Those two parameters were well presented for dry winter periods. The detailed results of PM$_{2.5}$ and PM$_{0.1}$ at HUST are presented by Ha et al. (2023) and depicted in Fig. 2(a). PM$_{2.5}$ measured by BAM at a site 2.1 km away from the HUST site and PM$_{2.5}$ measured at CEM are presented in Fig. 2(b). PM$_{2.5}$ concentrations at HUST varied from 19 to 147 µg m$^{-3}$ (with an average of 59.5 µg m$^{-3}$) (Ha et al., 2023). For BAM data, PM$_{2.5}$ varied from 9 to 120 µg m$^{-3}$ with an average of 53 µg m$^{-3}$. The concentration trends of PM$_{2.5}$ in HUST and BAM sites are quite similar. The concentrations of PM$_{2.5}$ at CEM were in the same range (57–117 µg m$^{-3}$) as those of two other sites during the same period.

Seven air pollution episodes (as defined as two consecutive days with PM$_{2.5}$ higher than NAAQS of 50 µg m$^{-3}$) were identified during the sampling periods, lasting from two to eight days (Ha et al., 2023). Those determined episodes also fit well with data measured by BAM during the same sampling period (Fig. 1(a)). For further analysis, data from HUST, BAM, and CEM in the period of 20–28 December, which is an episode based on data at HUST, were compared. The averages of PM$_{2.5}$ in this period in these three sites were comparable at 82.1, 75.4, and 88.2 µg m$^{-3}$ at HUST, BAM, and CEM, respectively. The intensives of the episode (period) at HUST and CEM were nine days and at BAM was eight days. Furthermore, given that similar concentration trends of PM$_{2.5}$ have been demonstrated in four sites within 60 km in the Red River delta during previous winter periods (Ly et al., 2021), we can refer that PM$_{2.5}$ episodes often cover a large area and air pollution episodes from our sampling site can be indicative of high pollution conditions in the broader area.

PM$_{0.1}$ concentrations at HUST varied from 2 to 13 µg m$^{-3}$, with an average concentration of 6 µg m$^{-3}$ (Ha et al., 2023). The fractions of PM$_{0.1}$ to PM$_{2.5}$ in episode and non-episode periods were 9.2% and 15.5%, respectively. PM$_{0.1}$ in the investigation period at CEM varied from 9 to 16 µg m$^{-3}$ with an average of 13.1 µg m$^{-3}$, more than two times higher than the value of HUST and CEM sites at the same time (Fig. S2). The much higher levels of PM$_{0.1}$ in CEM, which is the road site, demonstrated the local effect of traffic on PM$_{0.1}$. The effect of traffic is less significant on PM$_{2.5}$. There is no regulated limit for PM$_{0.1}$ in Vietnam, thus, PM$_{0.1}$ concentrations in several cities in the world were used for comparison with our data (Table 1). The average concentration of PM$_{0.1}$ at HUST in this study was within the same range as those measured in the same/nearby sites of other studies (Dung et al., 2020; Huyen et al., 2021, 2023). Those levels were close to those in European cities. The PM$_{0.1}$ concentration in CEM was approximately two times higher than it was at HUST and almost equal to the value in Beirut.

3.1.2 Ion components in PM$_{2.5}$ and PM$_{0.1}$

a. Ion components and SIA percentage in PM$_{2.5}$ and PM$_{0.1}$ at HUST and CEM sites

Fig. 2(a) shows that the concentration trend of ion components in PM$_{2.5}$ at HUST followed quite well those of PM$_{2.5}$ concentrations. All PM$_{2.5}$ peaks observed during the sampling period, such as from November 4 to November 7, coincided with a high SIA concentration. The Pearson correlation factors of SIA (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$) and PM$_{2.5}$ were 0.77–0.84. The contribution of water-soluble ions to PM$_{2.5}$ and PM$_{0.1}$ concentration in air pollution episodes and non-episode periods are presented in Fig. 3. Total water-soluble ions contributed, on average, approximately 32.7% to the
Fig. 2. Water-soluble ions and PM$_{2.5}$ concentration: (a) at HUST site (from October 14 to December 31, 2020); (b) at CEM site (from December 20 to December 28, 2020). Note: The blue shades showed the episode period. The orange shades showed the non-episode period.

Table 1. PM$_{0.1}$ concentration compared to other studies (µg m$^{-3}$).

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Note: The values in the table correspond to the episode period.
PM$_{2.5}$ mass concentration during the sampling time, while SIA ($\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{NH}_4^+$) contributed an average of 27.5% (6.2%–51.6%). Among the analyzed ions during sampling time, $\text{SO}_4^{2-}$ contributed the highest fraction of PM$_{2.5}$ concentration of 12.7%, followed by $\text{NO}_3^-$ (8.2%) and $\text{NH}_4^+$ (6.6%). These SIA component ratios were also within the same range as those reported in Hanoi (Huyen et al., 2021; Hai and Kim Oanh, 2013) and other SEA countries (Van et al., 2022 and references therein). The ion concentrations at CEM (Fig. 2(b)) did not follow the trend of PM$_{2.5}$ as at HUST. The SIA contributed 29.0% of PM$_{2.5}$ at CEM during the investigation period, lower than it was at HUST in that period of 38.1% (Fig. 2(b)).

The trend of SIA ions in PM$_{0.1}$ also followed quite well with PM$_{0.1}$ variation (Fig. S2). The Pearson correlation factors of PM$_{0.1}$ and its SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ were 0.64, 0.39, and 0.56, respectively. The SIA contribution to PM$_{0.1}$ at HUST was 12.5% (3.0%–24.6%) during the whole sampling time. The SIA contribution to PM$_{0.1}$ at CEM was 7.9% (Fig. S3), lower than it was at HUST in the investigated period of 13.9%. These values are within the same range as the SIA contribution of 16.28 $\pm$ 2.67% at a nearby site presented in the study by Dung et al. (2020). The higher SIA contribution percentage in PM$_{2.5}$ than in PM$_{0.1}$ (approximated two times) can be explained by the fact that PM$_{2.5}$ was largely affected by long-range transportation, the PM$_{2.5}$ source was regional (Ly et al., 2021; Thuy et al., 2018) whereas PM$_{0.1}$ was mainly local (Dung et al., 2020). Several previous studies demonstrated a high contribution percentage of SIA in PM$_{2.5}$ in the region. For example, the percentage of SIA in PM$_{2.5}$ in Guangdong was high (Wen et al., 2022; Huang et al., 2014).

b. SIA percentages in PM$_{2.5}$ and PM$_{0.1}$ at HUST in haze and non-haze periods

There were no significant differences in average contribution percentages of total SIA to PM$_{2.5}$ concentration between episode (29.0%) and non-episode periods (25.6%) at HUST. This similar contribution percentage is different from the increment trend of SIA percentages when PM$_{2.5}$ increases higher than 50 $\mu$g m$^{-3}$ in Guangdong and higher than 100 $\mu$g m$^{-3}$ in Beijing (Huang et al., 2014) but not different from the unclear trend in Xi’an and Shanghai (Huang et al., 2014).
The contribution of SO$_4^{2-}$/NO$_3^{-}$/NH$_4^+$ to the PM$_{2.5}$ concentration in non-episode and episode periods at HUST were 12.7%/6.5%/6.4% and 12.6%/9.7%/6.7%, respectively.

For PM$_{0.1}$, the average contribution percentage of total SIA to PM$_{0.1}$ concentration increased from 10.6% in non-episode periods to 14.1% in episode periods. The contribution of SO$_4^{2-}$/NO$_3^{-}$/NH$_4^+$ to the PM$_{0.1}$ concentration in non-episode and episode periods at HUST were 3.8%/3.4%/3.4% and 5.2%/4.2%/4.7%, respectively. All ions had increasing contribution percentages in episodes compared with non-episode periods.

As described in Section 1, SO$_2$ and NO$_x$ (the precursors of sulfate and nitrate ions) are mainly emitted from transportation, power plants, and industrial sources, but NH$_3$ (precursor of NH$_4^+$) is mainly emitted from the agriculture field. The reductions of emissions from those sources, especially NH$_3$ from agriculture are anticipated to reduce the SIA levels, thus reducing PM$_{2.5}$ levels in long-term periods as well as during episodes.

The high concentration of Ca$^{2+}$, which contributed approximately 1.7% to PM$_{2.5}$ might be due to construction activities that took place in the vicinity of the sampling. K$^+$ contributed approximately 1.2% to the PM$_{2.5}$ concentration, which might be due to biomass and coal burning (Yu et al., 2018). However, no noticeable variation during the sampling time was observed for Na$^+$, Mg$^{2+}$, and Cl$^-$, which mainly originate from natural resources.

To further analyze the differences of each component of PM between episode and non-episode periods, the differential percentages were calculated and presented in Fig. 4. For PM$_{2.5}$, whereas SO$_4^{2-}$ almost remained constant between non-episode periods and episode periods (decreased by 0.4%), components excluding SO$_4^{2-}$ have increased. NO$_3^{-}$ increased by 49.4% in its contribution percentage. NH$_4^+$ percentage slightly increased by 4.3% compared to normal periods. For PM$_{0.1}$, the contribution of NO$_3^{-}$ increased by approximately 23.5% during the air pollution episodes. Meanwhile, the percentage of SO$_4^{2-}$ and NH$_4^+$ in PM$_{0.1}$ increased by approximately 37.6% and 35.0%, respectively.

Fig. 4 also presents differential percentages of meteorological parameters between episode and non-episode periods. The data shows a large change between episodes and non-episode periods. The wind speed and solar radiation had a remarkable change with pollution levels, whereas temperature and relative humidity remained approximately stable (the temperature increased by 2.3% and RH decreased by 10.3%). Specifically, wind speed during air pollution episodes decreased by 31.0% compared to non-episode periods. In contrast, solar radiation increased by
46.2%. This movement was consistent with the theory that increasing solar radiation promotes photos curated reactions leading to secondary particle formation.

3.1.3 Correlation of ion concentrations at the HUST site

The concentration of NH₄⁺ was strongly correlated with that of SO₄²⁻ and NO₃⁻, with correlation coefficients (R²) of 0.90 and 0.89, respectively (Fig. 5). From the result shown in Fig. 5, it could be inferred that NH₄⁺ combined with SO₄²⁻ to form both (NH₄)₂SO₄ and NH₄HSO₄. Besides, the R² of NH₄⁺ and Cl⁻ was 0.60, thus NH₄⁺ neutralized SO₄²⁻ to form ammonium sulfate and ammonium nitrate first, then the remaining NH₄⁺ combined with Cl⁻ to generate NH₄Cl. The high correlation coefficients of NH₄⁺ with SO₄²⁻ and NO₃⁻ were well in line with the research at the same site of Huyen et al. (2021), which also demonstrated that cations and anions in PM₂.₅ and PM₀.₁ had a high Spearman correlation coefficient.

3.2 Effects of Meteorological Factors, Long-range Transport on PM₂.₅ and PM₀.₁ and SIA Levels

3.2.1 Effects of long-range transport

To investigate the influence of long-range transport on PM₂.₅ levels, 72 h backward air trajectories to Hanoi over the study period were examined. Fig. 6 shows two main clusters of air trajectory to Hanoi (C1: northeast-originated air mass; C2: east-originated air mass) during the sampling periods. The winter of Vietnam was affected by the northeast monsoon, so the northeast and east were the two predominant directions (Dung et al., 2020; Ly et al., 2018; Hien et al., 2002). The frequency of air mass No. 1 which started inside China and then arrived in Hanoi in the northeast direction was 79.7%. In Vietnam, they passed Quang Ninh, Bac Ninh, and Hai Duong

![Fig. 5. Correlation between cation and anion during sampling time: (a) NH₄⁺ versus SO₄²⁻; (b) NH₄⁺ versus NO₃⁻; (c) NH₄⁺ versus Cl⁻.](https://doi.org/10.4209/aaqr.220446)
provinces. Another came from the South China Sea passing through Hai Phong, Hai Duong, and Hung Yen provinces in Vietnam with 20.3% of frequency. Hai Phong and Quang Ninh are two neighboring provinces with a high density of coal-fired power plants. It was found that they had various sources, including urban, traffic, industry, coal, and oil combustion (Chifflet et al., 2018; Hang and Kim Oanh, 2014). Hai Duong and Bac Ninh provinces were affected by local sources such as coal combustion (from the Pha Lai coal-fired power plant), biomass burning, traffic, and long-range transportation.

Fig. 7(a) shows the PM$_{2.5}$ CWT result. The CWT covered an area ranging from Gansu province (China) in the north to Nghe An province (located in north central Vietnam) in the south. The range of color from blue to red indicated increasing concentrations. The darker color indicated higher potential sources of pollutants. The darkest area of PM$_{2.5}$ was found around the Taklamakan and Gobi deserts, approximately 3000 kilometers from the sampling site. This was also the longest trajectory before entering the sampling site. The long-range transport related to the Gobi desert corresponded with the study by Cohen et al. (2010) which proved that the air mass from the Taklamakan and Gobi deserts contributed to air pollution episodes in Hanoi. High levels of PM$_{2.5}$ were also found in the southside of mainland China.

To our knowledge, no study has used CWT analysis for SIA in Vietnam up to date. Due to their lifetimes lasting days to weeks, SIA could be transported far away from the source areas (Allen et al., 2019). In this paper, CWT of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and Cl$^-$ were simulated, which is shown in Fig. 7(b). The CWT maps of all ions are relatively similar, with the regions of the highest CWT heat map of SIA around South China including Guanxi and the southern Guangdong provinces, nearby and along the ocean, similar to those of PM$_{2.5}$ CWT. However, the strongest CWT of PM$_{2.5}$ around the Taklamakan and Gobi deserts does not appear similarly in the map of SIA. It is anticipated
because of the different PM compositions in the Taklamakan and Gobi desert regions (rich in dust) and those in south China (high SIA percentage). For example, the percentage of SIA in PM$_{2.5}$ in Guangdong was demonstrated to be high (Wen et al., 2022; Huang et al., 2014).

3.2.2 Effects of meteorological factors on PM$_{2.5}$, PM$_{0.1}$, and their SIA at HUST

The Pearson correlation analysis between meteorological parameters and PM$_{2.5}$, PM$_{0.1}$, and their SIA (Table S1) shows that wind speed had a quite high correlation with PM$_{2.5}$ ($r = -0.68$), and its SIA ions ($r$ from $-0.59$ to $-0.56$). However, wind speed had a low correlation with PM$_{0.1}$ ($r = -0.35$) and its SIA ions ($r$ from $-0.35$ to $-0.24$). The reason for the different effects of wind speed on the SIA of PM$_{2.5}$ and PM$_{0.1}$ can be explained by the effect of wind speed on PM$_{2.5}$ and PM$_{0.1}$ levels. As the SIA of PM$_{2.5}$ had a strong correlation with PM$_{2.5}$ concentration ($r$ from 0.77 to 0.84), the diluted effect of high wind speed on PM$_{2.5}$ also reduced the levels of its SIA. However, as wind speed did not affect PM$_{0.1}$ levels, wind speed did not significantly affect its SIA. All other meteorological factors had no significant effects on PM$_{2.5}$, PM$_{0.1}$, and SIA of PM$_{2.5}$ ($|r| < 0.5$). It is interesting to note that the SIA of PM$_{0.1}$ was significantly affected by temperature, RH, and atmospheric pressure, radiation. RH had correlation factors of $-0.74$, $-0.62$, and $-0.73$ with SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$, respectively. The temperature had correlation factors of $-0.55$ with NO$_3^-$. Atmospheric pressure had correlation factors of $-0.58$, and $-0.53$ with NO$_3^-$, NH$_4^+$. Radiation had correlation factors of 0.64, and 0.54 with SO$_4^{2-}$, and NH$_4^+$, respectively. The effects of those meteorological factors on the SIA of PM$_{0.1}$ demonstrate the importance of those meteorological factors for the forming and depleting mechanism of those SIA ions in PM$_{0.1}$.

The polar plots of PM$_{2.5}$ (Fig. S4) show that low wind speed ($< 3$ m s$^{-1}$) in all directions is related to high PM$_{2.5}$ concentration. When wind speed is low, the air is relatively stagnant, and the wind direction does not significantly affect the PM$_{2.5}$ concentration. The highly effective effect of wind speed is well in line with the Pearson correlation analysis above. The polar plot pointed out the importance of the build-up of local emissions for high PM$_{2.5}$ episodes. For PM$_{0.1}$, wind speed up to 4 m s$^{-1}$ from the southwest is related to high PM$_{0.1}$ concentration. Low wind speeds from other directions did not link with comparable high PM$_{0.1}$ concentration as those with wind direction from the southwest. The results implied that there were local sources of PM$_{0.1}$ from the southwest. It is predicted that the source is mainly transportation as the southwest area of the site has a high density of transportation. The effect of transportation on PM$_{0.1}$ also agrees with the research of Dung et al. (2020). Results of polar plots confirm the previous discussion that PM$_{2.5}$ sources were more regional and PM$_{0.1}$ sources were more local. However, at low wind speeds, the build-up of local PM$_{2.5}$ significantly contributes to the PM$_{2.5}$ episode.

Further analysis of SIA compositions at low wind speed sampling periods (wind speed $< 2$ m s$^{-1}$) and high wind speed periods (wind speed $\geq 2$ m s$^{-1}$) at HUST showed a difference in average SIA percentages of 31.9% and 26.4%, respectively. Average SO$_4^{2-}$ percentages remain at 12.6% (6.7%–18.0%) in two periods, while the NO$_3^-$ proportion average in low wind speed periods of 11.9% (3.8%–24.6) was significantly higher than it in high wind speed periods of 7.4% (0.7%–18.4%). SIA percentage in low and high wind speeds is comparable to those in episode and non-episode because of the significant affection of wind speed to PM$_{2.5}$ concentrations as discussed above. Additionally, SO$_4^{2-}$/NO$_3^-$/NH$_4^+$ percentage distribution at high wind speed is quite similar to the regions of the highest CWT heat map such as Nanning (23.5%/5.7%/9.4% during February–March 2016 as claimed by Mao et al. (2021)), Pearl River Delta (15.2%/12.7%/11.1% in 2019 as stated by Yan et al. (2020)), indicating long-term transportation from these areas during strong wind periods.

4 CONCLUSIONS

This study investigated water-soluble ion components of PM$_{2.5}$, and PM$_{0.1}$ in air pollution episodes (daily average PM$_{2.5}$ concentrations exceeded the NAAQS of 50 µg m$^{-3}$ for a minimum of two consecutive days) and non-episode periods at an urban site (HUST) and an episode period at a transportation site (CEM) in dry winter periods in Hanoi, Vietnam. PM$_{2.5}$ concentration in a nearby urban site was also examined.
The PM$_{2.5}$ periods are similarly found at three sites within 6.2 km in Hanoi. This similarity confirms the large covering area of PM$_{2.5}$ episodes in the area. The average concentrations of PM$_{2.5}$ and PM$_{0.1}$ in episode periods were 74.6 and 6.8 µg m$^{-3}$, respectively. The average concentrations of PM$_{2.5}$ and PM$_{0.1}$ in non-episode periods were 31.5 and 4.9 µg m$^{-3}$, respectively. The fractions of PM$_{0.1}$ to PM$_{2.5}$ in episode and non-episode periods were 9.2% and 15.5%, respectively.

SIA contributed 29.0% and 14.1% to PM$_{2.5}$ and PM$_{0.1}$ composition during air pollution episodes, respectively at HUST. The SIA contribution in episodes was slightly higher than the contribution in non-episode periods for PM$_{2.5}$ (increasing 13%). The investigated episode period in a nearby transportation site, CEM has a similar SIA contribution to those at HUST. The CWT of PM$_{2.5}$ and its SIA demonstrated that PM$_{2.5}$ and SIA were affected by long-range transportation. The contribution of SIA in episodes was significantly higher than the contribution in non-episode periods for PM$_{0.1}$ of 10.6% at HUST (increasing 32%).

PM$_{2.5}$ were more regional as demonstrated by CWT and the fact that their concentrations and variations at nearby sites were quite similar. However, the results of the polar plot that the low wind speed correlated to high PM$_{2.5}$ also demonstrated that the build-up of local PM$_{2.5}$ significantly contributed to PM$_{2.5}$ episodes. PM$_{0.1}$ sources, on the other hand, were more local as their concentrations at the transportation site were double those at the urban site. Polar plot analysis with significantly higher PM$_{2.5}$ concentration when the wind direction was southwest suggested for a local source from the southwest.

Pearson correlations showed that wind speed affected PM$_{2.5}$ and its SIA concentrations but did not affect PM$_{0.1}$ and its SIA levels. RH, pressure, temperature, and radiation have high correlations with the SIA of PM$_{0.1}$ but no significant correlation with the SIA of PM$_{2.5}$.

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SUPPLEMENTARY MATERIAL

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REFERENCES


