A Comparison Study of Chemical Compositions and Sources of PM_{1.0} and PM_{2.5} in Hanoi

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ABSTRACT

We simultaneously collected 85 pairs of 24-h PM_{1.0} and PM_{2.5} samples from a new urban area in Hanoi, Vietnam, and analyzed their chemical compositions with particle-induced X-ray emission (PIXE) and ion chromatography (IC) to obtain input data for source apportionment via positive matrix factorization (PMF). Sulfate, ammonium, and black carbon (BC) composed the majority of the mass in both size fractions, and the PMF models clearly differentiated the contribution of long-range transport (LRT) aerosols, which accounted for more than two-thirds of the measured PM-bound sulfate and ammonium concentrations, from those of the six *in situ* sources, viz., resuspended road dust, primary vehicular emissions, coal fly ash, biomass burning emissions, construction dust, and sea salt. Whereas LRT aerosols, coal fly ash, and primary particulate vehicular emissions mainly occurred in the PM_{1.0}, resuspended road dust and biomass-burning fly ash tended to appear in the PM_{1.0-2.5}; hence, we can characterize the anthropogenic emissions in this area by examining the profile of the PM_{1.0} rather than the PM_{2.5}. Additionally, air masses with inland trajectories originating in northern China and countries northwest and southwest of Vietnam contained more ammonium, sulfate, and BC than those that passed over the East Sea. Finally, the LRT aerosols exhibited high acidity in the PM_{1.0} but neutrality in the PM_{2.5}.

Keywords: Submicron particles, LRT, Nitrate formation rate, Particle size partitioning, Back trajectory, Hanoi, Vietnam

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1 INTRODUCTION

Ambient fine particulate matter with an aerodynamic diameter smaller than 2.5 μm (PM_{2.5}) is among the criteria air pollutants and its mass concentration is regulated with ambient air quality standards by many countries. Particulate matter with an aerodynamic diameter less than 1.0 μm (PM_{1.0}) contributes greatly to PM_{2.5}, accounting for 50 to 90% of its mass concentration in the urban atmosphere (Lee *et al.*, 2006; Deshmukh *et al.*, 2011; Zhang *et al.*, 2018).

PM_{1.0} comprises many harmful substances emitted from fuel combustion either as primary emissions (such as diesel black carbon [BC] and trace metals) or as secondary aerosols from gaseous precursors by nucleation or by condensation on existing particles (Whitby, 1978; Hildemann, 1991; Huang *et al.*, 2003). PM_{1.0} has been regarded as a better indicator for vehicular emissions in roadside environments than PM_{2.5} because it minimizes the interference from natural sources (Lundgren *et al.*, 1996; Lee *et al.*, 2006). Exposure to PM_{1.0} has also been shown to have a more significant association with health effects (hospital admission, cardiovascular diseases, and mortality rate) than exposure to PM_{2.5} and PM₁₀ (Lin *et al.*, 2016; Hu *et al.*, 2018; Yin *et al.*, 2020). However, studies on the physicochemical characteristics and sources of ambient PM_{1.0} are fairly limited compared to the number of studies on PM_{2.5} and PM₁₀.

In this work, we characterize chemical species and sources of PM_{1.0} in an area of Hanoi under rapid urbanization, where the air quality is affected by increasing emissions from traffic, coal

briquette burning for cooking, biomass burning, and construction activities. We compared the contents of trace elements and water-soluble ions (WSI) in $PM_{1.0}$ with those in $PM_{2.5}$ collected simultaneously at the site to identify the differences in chemical compositions between the two size fractions. The chemical composition data were then used to characterize the sources affecting the site using the positive matrix factorization (PMF) method. Based on the PMF model, the differences between $PM_{1.0}$ and $PM_{2.5}$ in the compositions and contributions of both local and remote sources could be identified. The transport pathways and the contributions to $PM_{1.0}$ and $PM_{2.5}$ of remote emissions that affect the site through long-range transport of air pollutants were identified by backward-trajectory analysis.

We hope the results of the comparative analysis in this work will shed more light on the characteristics of $PM_{1.0}$ and $PM_{2.5}$ sources in Hanoi and provide a basis for developing abatement and pollution control measures.

2 METHODS

2.1 Sample Collection

The sampling site was located in a residential area within Hanoi's Cau Giay district, approximately 5 km northwest of the city center. This district has a population density of 14,000 persons km^{-2} and a road density of 3.33 $km\ km^{-2}$ (JICA, 2007). Motorbikes are the dominant form of transportation in Hanoi, accounting for 81% of all trips versus 11% and 4% trips by buses and cars, respectively (World Bank, 2011). Two bus routes are running within 100 m of the sampling site. Coal-fired industrial and power plants are located far to the south, but burning coal briquettes is popular for cooking in households and eateries in this area.

The air sampling instruments were set up in a shelter erected on the rooftop of the three-story office of the Institute for Nuclear Science and Technique. Particulate matter was collected with 0.4 μm pore filters using a dichotomous air sampler (Zambelli Twin Dust; Aquaria Tech s.r.l., Italy). The air sampler had two collection channels that can be paired with two different sampling heads that work alternately. The U.S.-made sharp-cut cyclone collector SCC-2.229 (BGI, Inc.) and the EU- $PM_{2.5}$ sampling head were used to collect $PM_{1.0}$ and $PM_{2.5}$, respectively. The airflow rate was automatically adjusted to 16.7 $L\ min^{-1}$ based on ambient temperature and barometric pressure in the controller's operating mode. Due to high PM mass loading at the sampling site, the cyclone system could not be run continuously for a full 24 h because of filter clogging. Thus, the sampler was operated alternating time on and time off (2 h on followed by 2 h off) throughout the 24-h period to provide a representative sample during that day. The sampling duration was 23.5 h starting from 9:00 a.m. local time to 8:30 a.m. on the following day. The Nuclepore polycarbonate filters were pre- and post-weighed to determine the gravimetric mass of the collected materials using a Mettler Toledo balance of 1 μg readability placed in a dedicated room with controlled temperature (25°C) and relative humidity (40%). The filters were pre- and post-conditioned in this controlled environment for 2 days before and after sampling. An electrostatic charge eliminator was used to neutralize charges accumulated on the filters before weighing. After being weighed, the loaded filters were kept in a refrigerator at 4°C to minimize the evaporation of volatile components until further analysis.

85 pairs of $PM_{1.0}$ and $PM_{2.5}$ samples were collected from November 2015 through June 2016, encompassing three seasons, i.e., winter (November–February), transitional and spring (March–April), and early summer (May–June). The sample collection was stopped in June–August because it was too hot at the sampling station. Four types of air masses that govern the meteorological conditions in northern Vietnam during the sampling period and drive the temporal variations in particulate pollution and source impacts at the sampling site are described in Section 3.3.

2.2 Chemical Analysis

The loaded filters were analyzed for BC, elemental components, and WSI using optical reflectance, ion chromatography (IC), and particle-induced X-ray emission (PIXE) methods, respectively. The BC content was measured using a smoke stain reflectometer provided by the International Atomic Energy Agency as part of the Asia-Pacific Regional Cooperation Agreement (RCA) for air pollution (Hopke *et al.*, 2008). The BC content was operationally defined based on the amount of

reflected light that is absorbed by the filter sample and a mass absorption coefficient recommended by RCA to convert the measured reflectance to $\mu\text{g m}^{-3}$ (Hien *et al.*, 2004; Hopke *et al.*, 2008).

After BC measurement, the filter was cut into two halves. The first half was analyzed by IC at the Institute for Nuclear Science and Technique in Hanoi, and the other half was reserved for elemental analysis by the PIXE method using the 3 MeV proton 5SHD2 Pelletron at Hanoi University of Natural Sciences.

A Dionex DX-600 system with chemical suppression and conductivity detection was used for the IC analysis. In the IC method, the filters were extracted ultrasonically by deionized water with the resistivity of $18 \text{ M}\Omega \text{ cm}^{-1}$ in 20 min and then were filtered to remove insoluble residues. The weak base eluent (1.7 mm NaHCO_3 + 1.8 mm Na_2CO_3) with a flow rate of 2.5 mL min^{-1} and the weak acid eluent (22 mm H_2SO_4) with a flow rate of 2 mL min^{-1} were used for anion and cation detection, respectively. The detection limits were about 5 ng m^{-3} for SO_4^{2-} , NH_4^+ , Na^+ , and Ca^{2+} and 10 ng m^{-3} for Cl^- , NO_3^- , K^+ , and Mg^{2+} . For the PIXE analysis, the filter samples were exposed to the 3 MeV proton beam of the 5SHD2 Pelletron accelerator and the X-rays emitted were detected using an Si(Li) detector. Measurement values were well above the detection limits for the species of Fe, Si, S, K, Pb, and Zn that were included in the input data for receptor modeling. The detection limits for these elements were $10\text{--}20 \text{ ng m}^{-3}$. As and Cr, the good tracers for coal burning, were detected in several samples, but in most samples, the measured values were lower than the detection limits. Blank Nuclepore filters were analyzed and the measured concentrations of species were blank-corrected accordingly.

2.3 Methodology and Input Data

In this work, the sources of $\text{PM}_{1.0}$ and $\text{PM}_{2.5}$ were derived from the measured concentrations of species using the PMF modeling method. PMF was developed by Paatero and Taper (1994) and has become the most common tool for source apportionment in studies of ambient air particulate matter (Belis *et al.*, 2013; Norris and Brown, 2014). As in other receptor modeling methods, the goal of PMF is to derive the source profiles and source contributions from the measured concentrations of species by solving the chemical mass balance (CMB) equation:

$$\mathbf{X}(n \times m) = \mathbf{G}(n \times p) \cdot \mathbf{F}(p \times m) + \mathbf{E}(n \times m) \quad (1)$$

where $\mathbf{X}(n \times m)$ is the concentration matrix of m species in n samples, $\mathbf{G}(n \times p)$ is the source contributions matrix of p sources in n samples, $\mathbf{F}(p \times m)$ is the source composition matrix of m species in p sources, and $\mathbf{E}(n \times m)$ is the model uncertainties.

In PMF, the elements of $\mathbf{G}$ and $\mathbf{F}$ are constrained to be non-negative. For this purpose, the influence of each input concentration value is weighted based on its measurement uncertainty (Paatero and Taper, 1994; Norris *et al.*, 2009). The factors resolved by the PMF model are interpreted as representing sources that impact the sampling site. The PMF results for a different number of factors and multiple values of F_{peak} were explored to obtain the optimal factor solution. For this purpose, a number of criteria were applied, including the comparison between $Q(\text{robust})$ and $Q(\text{true})$ and between the measured and PMF modeled species mass, but the key criterion was extracting realistic and reasonable source profiles and contributions.

In this study, the U.S. EPA PMF V5 software (Norris and Brown, 2014) was used to build the PMF model. The input data for $\text{PM}_{1.0}$ and $\text{PM}_{2.5}$ consisted of 8 WSI (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and 7 elements (BC, Al, Fe, Si, Mg, K, Pb, Si, and Zn). There are no missing values in the input array. Sulfur was not included in the input data to avoid double-counting its mass (Belis *et al.*, 2014) because S almost perfectly correlates with sulfate (Table 2). PM mass concentration was also included as an independent variable to provide estimated source contributions to the observed PM masses. However, to avoid the influence of the uncontrolled PM mass errors associated with, e.g., sampling loss of nitrate and water bound to aerosols, the PMF model was obtained from the base run using input data without PM mass. The experimental uncertainties u_{ij} were composed of a measurement error and a concentration-dependent component to account for the model error associated with, e.g., the variation in source profiles and chemical transformations of species in the atmosphere (Norris and Brown, 2014; Belis *et al.*, 2014).

The factor model with the optimal number of extracted factors and minimum rotational ambiguity was chosen among numerous solutions of the PMF base run following recommendations

in Norris and Brown (2014). The physical consistency requirements on the PM_{1.0}-to-PM_{2.5} ratio (Section 3.1.2) and on the ion-versus-element relationships (Section 3.1.3) were also used to help obtain the optimal solution of the PMF base run. Finally, the PMF bootstraps were run to estimate the stability and uncertainties of the factor model.

3 RESULTS AND DISCUSSION

3.1 Measurement Results, Data Validation, and Interpretation

3.1.1 PM mass concentrations

The mean ($\pm$ standard deviation) 24-h mass concentrations of PM_{1.0} and PM_{2.5} were 30.1 ($\pm$ 13.9) $\mu\text{g m}^{-3}$ and 44.5 ($\pm$ 21.0) $\mu\text{g m}^{-3}$, respectively (Table 1). PM_{2.5} levels exceeded the WHO 24-h guideline of 25 $\mu\text{g m}^{-3}$ on 69 of the total 85 sampling days (81%). The monthly mean PM_{2.5} mass concentration was highest in January 2015 (52.1 $\mu\text{g m}^{-3}$) and lowest in May 2016 (32.1 $\mu\text{g m}^{-3}$), reflecting the influence of the atmospheric conditions governed by the East Asian monsoon regime with northeast monsoon in winter and southeast monsoon in summer (Hien *et al.*, 2004).

3.1.2 Validation of the measured values based on the PM_{1.0}-to-PM_{2.5} concentration ratio

The measured data can be validated by consistency tests based on the requirement that the PM_{1.0}-to-PM_{2.5} concentration ratio should not exceed 1 (with tolerance to account for measurement uncertainties). The statistics in Table 1 and the PM_{1.0}-to-PM_{2.5} concentration ratios displayed in Fig. 1 are consistent with this requirement, except for several cases related to BC, Cl⁻, and NH₄⁺, which are present predominantly in PM_{1.0}. These extreme cases were flagged, but not removed from the data set.

The consistency test based on the PM_{1.0}-to-PM_{2.5} ratios helped provide information on the partitioning of chemical constituents between the two fractions. The major crustal elements of Fe, Al, and Si were found to be depleted in PM_{1.0}, accounting for only 13–38% of the PM_{1.0}

Table 1. Summary statistics of 24-h mass concentrations of species in PM_{1.0} and PM_{2.5} ($\mu\text{g m}^{-3}$) and the PM_{1.0}-to-PM_{2.5} concentration ratios.

	PM _{1.0}		PM _{2.5}	
	Mean	SD	Mean	SD
Mass	30.1	13.9	44.5	21.0
BC	6.28	2.88	6.50	3.19
Al	0.09	0.08	0.29	0.14
Ca	–	–	1.36	1.50
Ca ²⁺	0.55	0.66	1.39	0.86
Cl ⁻	0.51	0.74	0.42	0.56
Cu	0.02	0.02	0.02	0.02
F ⁻	0.03	0.02	0.04	0.03
Fe	0.12	0.09	0.32	0.14
K	0.75	0.63	0.85	0.33
K ⁺	0.56	0.47	0.72	0.40
Mg	0.33	0.21	0.39	0.13
Mg ²⁺	0.21	0.13	0.25	0.33
Na ⁺	0.29	0.29	0.48	0.44
NH ₄ ⁺	2.23	1.27	2.35	1.92
NO ₃ ⁻	0.09	0.22	0.15	0.14
Pb	0.07	0.08	0.07	0.05
S	2.21	0.10	2.58	1.78
SO ₄ ²⁻	6.34	3.11	8.66	5.40
Si	0.37	0.29	1.00	0.49
Zn	0.27	0.53	0.48	0.80

Fig. 1. The mean ($\pm$ standard error) of the measured $\text{PM}_{1.0}$ -to- $\text{PM}_{2.5}$ concentration ratios.

concentration mass, and more concentrated in the $\text{PM}_{1.0-2.5}$ fraction. Conversely, another major crustal species K (K^+) accounts for 81% (94%) of the $\text{PM}_{1.0}$ mass, suggesting an anthropogenic origin, i.e., biomass burning. Trace metals Pb, Cu, and Zn from primary vehicular emissions occurred mainly in submicron particles. Sulfate, nitrate, and ammonium also occurred mainly in the submicron size range, but the much lower $\text{PM}_{1.0}$ -to- $\text{PM}_{2.5}$ ratios for sulfate and nitrate than for BC and ammonium suggest significant contributions from absorption of sulfuric and nitric acids on the surface of coarse particles (Section 3.2.2).

Thus, like in the highly polluted cities of Beijing and Changzhou, China (Ye *et al.*, 2017; Zhang *et al.*, 2018), in Hanoi, anthropogenic components are more accumulated in $\text{PM}_{1.0}$ while natural components contributed more to $\text{PM}_{2.5}$.

3.1.3 Relationship between soluble ion and total element

The measurement values were also validated by another physical constraint, i.e., the concentration of any soluble ion should be less than that of the respective element. The proportion of a chemical element E occurring in aerosols as a soluble cation or anion I can be estimated based on the coefficient a in the following linear regression relationship (Hien *et al.*, 2005; Watson *et al.*, 2008):

$$[I] = a[E] + b \quad (2)$$

where the square brackets denote the concentration of the species inside. The regression parameters a , b , and the coefficient of determination R^2 are shown in Table 2.

In the case of sulfate versus total sulfur, the ratio of SO_4^{2-} to S is 3:1 if all the S is present in the aerosols as SO_4^{2-} . This was almost the case in this work with a slope of 3.01 ± 0.06 , a close to zero intercept (0.08 ± 0.15), and a significant correlation between SO_4^{2-} and S ($R^2 = 0.97$). Thus, 97% of sulfur was present in $\text{PM}_{1.0}$ as sulfate, and both PIXE and IC measurements were valid. A similar situation was found for $\text{PM}_{2.5}$. The regression parameters showed that 91% of potassium occurred

Table 2. Parameters a , b , and R^2 in the linear regression of ionic versus elemental concentrations (values in the brackets are standard errors).

	$[I]$	$[E]$	a	b	R^2
$\text{PM}_{1.0}$	SO_4^{2-}	S	$3.01 (\pm 0.06)$	$-0.08 (\pm 0.15)$	0.97
$\text{PM}_{2.5}$	SO_4^{2-}	S	$3.05 (\pm 0.08)$	$+0.3 (\pm 0.2)$	0.96
$\text{PM}_{1.0}$	K^+	K	$0.93 (\pm 0.03)$	$0.002 (\pm 0.02)$	0.91
$\text{PM}_{2.5}$	K^+	K	$0.79 (\pm 0.03)$	$6.0 (\pm 3.3)$	0.90

Table 3. Mean mass concentrations of PM_{1.0} and major chemical constituents ($\mu\text{g m}^{-3}$) in Asian cities.

	PM _{1.0}	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	OC	BC	Ca ²⁺	Literature
HK	44	10.7	1.9	2.5	9.6	15.8	0.07	Cheng <i>et al.</i> (2011)
Xian	127	18.9	12.4	7.2	1.7	–	1.9	Shen <i>et al.</i> (2010)
Guangzhou	52.4	11.3	4.6	3.4	6.8	5	0.3	Tao <i>et al.</i> (2012)
Beijing	86.19	7.37	11.01	4.47	21.22	–	0.32	Shao <i>et al.</i> (2018)
Kaohsiung	68	14.3	11.3	7.89	–	–	–	Lin and Li (2004)
Kanpur	123	10.9	16.0	13.2	–	–	–	Gupta <i>et al.</i> (2013)
Delhi	–	15.0	24.3	2.19	–	–	–	Prakash <i>et al.</i> (2018)
Delhi	–	10.3	16.6	18.4	–	–	0.3	Acharja <i>et al.</i> (2020)
Hanoi	30.1	6.34	0.09	2.23	–	6.28	0.55	This work

in PM_{1.0} as soluble K⁺ ions with an average proportion of $a = 0.93$. The corresponding figures for PM_{2.5} were 90% and $a = 0.79$.

3.1.4 Chemical compositions of PM_{1.0} and PM_{2.5}

Sulfate, BC, and ammonium were the most abundant species with a combined contribution of 50.3% of the PM_{1.0} mass. These species remain the most abundant in PM_{2.5} but with a lower combined contribution of 38.4%. Next was potassium and calcium, which were more abundant than their major crustal counterparts of Si, Al, Fe, and Mg, indicating the strong impact of biomass burning and construction dust. Zn originating from traffic was also more abundant than the major crustal elements of Fe and Al in both fractions. Meanwhile, nitrate was depleted in both the PM fractions with concentrations much lower than those reported in other Asian cities (Table 3). Nitrate could be lost due to evaporation of semi-volatile ammonium nitrate (Cabada *et al.*, 2004), but this sampling artifact could not be quantified.

3.2 Source Apportionment by Positive Matrix Factorization

3.2.1 Results and interpretation

The optimal PMF solutions were achieved with an *Fpeak* parameter of approximate zero and seven factors, representing seven sources for each PM fraction. The alternative six- and eight-factor solutions have also been explored. However, the six-factor solution explained much less variances of most species while in the eight-factor solution, the PM_{1.0}/PM_{2.5} requirement was violated for many species.

In Figs. 2(a) and 2(b), the profiles of these sources were plotted as the percent of each species apportioned to the factor (the sum of the species concentrations for the seven factors is 100). The contributions of these sources to the observed average concentrations of the most abundant species of sulfate and ammonium are shown in Figs. 3 and 4 for PM_{2.5} and PM_{1.0}, respectively. The source name is assigned based on the source fingerprints that have a high percent apportioned to the factor (Figs. 2(a) and 2(b)). Thus, mineral elements Al, Fe, and Si were the fingerprints for resuspended road dust (Factor 1), mineral elements for coal fly ash (Factor 2), Ca²⁺ and Mg²⁺ for construction dust (Factor 3), Cl⁻ and Na⁺ for sea-salt aerosols (Factor 4), Zn and Pb for traffic (vehicle tire and brake wear; Factor 5), and K and K⁺ for biomass burning (Factor 6). Coal fly ash was distinguished from resuspended road dust due to the high enrichment in K relative to other major crustal elements (Al, Fe, and Si) in coal. Pb and Zn were also enriched in coal like what was observed by Hsu *et al.* (2016). K and K⁺ were mostly associated with the biomass burning factor, in which BC was abundant. BC was also associated with the road dust factor indicating the presence of BC in surface soil, which comes from the incomplete combustion of plant materials and fossil fuels (Schmidt and Noack, 2000). Concerning sea-salt aerosols, it is worth noting the high Cl⁻-to-Na⁺ concentration ratio in Factor 4, i.e., 1.7 and 3.6 for PM_{1.0} and PM_{2.5}, respectively, as compared to the ratio for seawater of 1.8, suggesting other sources of chloride (Faxon and Allen, 2013) existed but were not resolved from the sea-salt factor in the PMF model.

The sources assigned to Factors 1–6 represent primary emissions and are common to those reported elsewhere (e.g., Belis *et al.*, 2013; Hsu *et al.*, 2016; Crilley *et al.*, 2017). The secondary inorganic aerosols of nitrate, sulfate, and ammonium resulting from the gas-to-particle conversion

Fig. 2(a). Source compositions of PM_{1.0} are calculated as the percent of species apportioned to the corresponding factor (sum of each species in all factors is 100).

Fig. 2(b). Source compositions of PM_{2.5} are calculated as the percent of species apportioned to the corresponding factor (sum of each species in all factors is 100).

Fig. 3. Contributions of sources to the observed average concentrations of sulfate and ammonium in $\text{PM}_{2.5}$.

Fig. 4. Contributions of sources to the observed average concentrations of sulfate and ammonium in $\text{PM}_{1.0}$.

of gaseous precursors SO_2 , NO_2 , and NH_3 in the atmosphere are associated with these primary sources, but most sulfate and ammonium are associated with Factor 7, which will be assigned as regional or LRT aerosols.

Nitrate was predominantly associated with coal fly ash followed by sea-salt and construction factors in both the PM fractions. The presence of nitrate in the sea-salt factor indicates the formation of sodium nitrate on sea-salt particles during transport from the sea as a result of the substitution of chloride by nitrate (Pathak *et al.*, 2003). Additionally, the association of nitrate with alkaline ions (Ca^{2+} , Mg^{2+} , and K^+) in coal fly ash and construction factors indicated that nitrate was formed through uptake and heterogeneous reactions of nitrogen gases, HNO_3 , and other trace gases on the surface of mineral dust particles (Zhang and Carmichael, 1999; Hien *et al.*, 2005; Perez *et al.*, 2008).

Similarly, the uptake and heterogeneous reactions of H_2SO_4 and sulfur gases on the surface of Ca-rich dust particles explained the presence of sulfate in the construction and road dust factors (Figs. 2(a) and 2(b)). Factor 2 (coal) contained sulfate and nitrate but some sulfuric and/or nitric acids were presumably also present in this factor to maintain the balance with large amounts of alkaline ions and ammonium. In contrast, sulfate in Factor 7 was completely neutralized by ammonium (in $\text{PM}_{2.5}$), indicating aerosols had a long atmospheric lifespan after having traveled far from the sources.

Factor 7 was nearly free from mineral dust and other species related to *in situ* emissions and was almost uncorrelated with the six remaining factors, as shown by the G-space (source contribution) analysis results (Norris *et al.*, 2014). Therefore, sulfate and ammonium associated with Factor 7 were not related to *in situ* emissions but came from long-range transport with air

mass arrived at the site on the sampling day. The dependence of Factor 7 contributions on the air mass trajectory type found in Section 3.3 justified this argument.

On average, about 60% (range: 0–87%) of observed sulfate concentrations in $PM_{2.5}$, equivalent to an average of $5204 \mu\text{g m}^{-3}$, came from long-range transport (Fig. 3). In $PM_{1.0}$, the LRT component was stronger, constituting 67% (range: 0–99%) of the observed sulfate, equivalent to an average of $4152 \mu\text{g m}^{-3}$ (Fig. 4). Nitrate was insignificant in Factor 7 (Fig. 3) possibly because ammonium nitrate may have evaporated during long-range transport before reaching the sampling site (Pathak *et al.*, 2003).

The mean molar ratio of sulfate to ammonium in $PM_{2.5}$ is slightly above 1, suggesting sulfate was fully neutralized and existed as ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$. Meanwhile, in $PM_{1.0}$ a 16% cation equivalent deficit was found, indicating some portion of sulfate (30%) may have existed as ammonium bisulfate (NH_4HSO_4), a precursor of ammonium sulfate (Chen *et al.*, 2019). Besides sulfate and ammonium, the LRT aerosols carried large amounts of BC, accounting for 34% and 20% of observed concentrations in $PM_{1.0}$ and $PM_{2.5}$, respectively.

3.2.2 Contributions of sources to PM mass

As expected, all the sources resolved by PMF for $PM_{1.0}$ existed in $PM_{2.5}$ with little differences between source profiles (Figs. 2(a) and 2(b)). However, there were apparent differences in the contributions of sources to the species concentrations, especially to the PM masses, as shown in the pie charts of Fig. 5. Resuspended road dust was a leading source in $PM_{2.5}$ but was much depleted in $PM_{1.0}$. Meanwhile, LRT aerosols were most abundant in $PM_{1.0}$ followed by coal fly ash and primary traffic emissions, suggesting the advantage of the characterization of these sources with little interference from road dust by studying $PM_{1.0}$, instead of $PM_{2.5}$.

Primary vehicular emissions moderately contributed to the PM masses, but particulate matter related to road traffic (primary emissions, secondary sulfate, and resuspended road dust) is overwhelming in $PM_{2.5}$. The primary vehicular emission and road dust contribute 16.2% to the $PM_{1.0}$ mass, but vehicular emissions are expected to be the largest *in situ* contributor to $PM_{1.0}$ if the missing sources related to the unmeasured organic carbon (OC) were included in the PMF modeling.

The seven sources extracted in the PMF models could explain approximately 78% of the PM mass loadings. The unexplained mass may come from unmeasured OC and water bound to particles. OC was not measured in the experiment, but the OC content can be roughly estimated at $5\text{--}9 \mu\text{g m}^{-3}$ using the OC-to-EC ratio (0.8–1.4) in the literature (Lee *et al.*, 2006; Tao *et al.*, 2012).

3.2.3 PMF model performance

A comparison between observed (input data) concentrations and model-predicted values shown the best fit for many species. The linear regression plots of modeled versus observed concentrations show that SO_4^{2-} , NH_4^+ , K^+ , K, Zn, and Si were well modeled with an R^2 greater than 0.95 and a slope well above 0.90. For Al, Fe, Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- , R^2 ranged from 0.8 to 0.9.

Fig. 5. Apportionment of sources to the PM mass concentrations.

The accuracy of the PMF model and its stability with regards to rotational ambiguity and input data uncertainties were checked by bootstrapping (Norris *et al.*, 2014). The relative uncertainties (standard deviation/mean) of factor profiles were ~5% for SO_4^{2-} and NH_4^+ in the LRT factor; ~10% for source fingerprints, such as Zn in traffic, K^+ in biomass burning, and Ca^{2+} in construction dust; 15–40% for other species; and ~20% for the PM masses (Fig. 5).

3.3 Air Mass Trajectories and LRT

The temporal variations in the contributions of LRT to the observed sulfate and ammonium reflect the variations in the trajectories and properties of air masses that arrive at Hanoi on the sampling days. The 4-day HYSPLIT backward trajectories of air masses (Stein *et al.*, 2015) that arrived in Hanoi in the middle of each sampling day (20:00 UTC) at 500 m above ground can be classified into four types, namely, 1) northerly (N) continental air masses originating from northern China, traveling through inland China and crossing the Vietnam-China border before arriving in Hanoi; 2) northwesterly (NW) continental dry air masses originating from India and traveling over Myanmar, northern Laos, and northwestern Vietnam; 3) southwesterly (SW) tropical humid air masses originating from the equatorial Pacific and traveling over Thailand, Cambodia, southern Laos, and central Vietnam; and 4) easterly (E) maritime air masses originating from western Pacific and passing over the East Sea before embarking on northern Vietnam via the Gulf of Tonkin (Fig. 6). The different abundances of SO_2 and NH_3 in the above regions could drive the trajectory dependence of the LRT impact at the receptor site. Thus, the northerly air mass may take up abundant SO_2 and BC as it travels over industrial areas and megacities in southern China. Intensive burning of agricultural residues and forest fires in the regions under the NW trajectories (Lasko *et al.*, 2018) may be significant sources of NH_3 , BC, and K. In contrast, the atmosphere beneath the East Sea may be polluted by emissions from ships and inland outflows associated with the northeast monsoon in the north and southeast monsoon in the south (Ding *et al.*, 2018; Fan *et al.*, 2015).

Fig. 6. 4-day HYSPLIT backward trajectories of air masses arriving in Hanoi on the sampling days from November 2015 to June 2016. Cluster 1 (N) in green, Cluster 2 (NW) in red, Cluster 3 (SW) in blue and Cluster 4 (E) in yellow.

The monthly distributions of trajectory types (Fig. 7) show that northerly and some easterly trajectories occurred mainly in winter in association with the northeast and southeast monsoons, southwesterly trajectories associated with the southwest monsoon occur mainly in summer, and northwesterly trajectories were found in the transition period (Hien *et al.*, 2004).

The N, NW, SW, and E trajectory types occurred on 15, 18, 35, and 17 sampling days, respectively. The modeled LRT sulfate concentrations for the sampling days were displayed in the box-and-whisker plots of Fig. 8. LRT ammonium concentrations follow similar patterns (not shown). The concentrations of LRT ammonium sulfate exhibited large variations within each trajectory type, reflecting the influence of meteorological factors on the formation and scavenging of secondary aerosols taking place during transport on the trajectory. The 2-tailed Kolmogorov-Smirnov test was used to compare the LRT sulfate contributions associated with different trajectory types. The easterly air masses passing over the East Sea were found to bring in the least sulfate and ammonium with $p < 0.04$ and $p < 0.05$ for $PM_{1.0}$ and $PM_{2.5}$, respectively. On the other hand, no statistically significant difference was found among the three remaining trajectory types.

Fig. 7. Monthly distributions of trajectory types; n is the total sampling days for each trajectory type.

Fig. 8. Box-and-whisker plots displaying LRT sulfate concentrations in the PM samples. The box represents the 25th, 50th (median), and 75th percentiles. Whiskers are the 10th and 90th percentiles.

4 DISCUSSION

Sulfate, ammonium, and BC were predominant constituents of PM_{1.0} and PM_{2.5}. Nitrate represented only a minor component in both particulate fractions. The PMF model resolved inorganic aerosols related to *in situ* emissions and those coming from LRT.

In situ sulfate and nitrate were formed mainly from uptake and reactions of gaseous sulfur and nitrogen species on the surface of mineral dust particles (Zhang and Carmichael, 1999; Perez *et al.*, 2008). The levels of SO₂ and NO₂ in the area under study were 30 µg m⁻³ and 40 µg m⁻³, respectively (Hien *et al.*, 2020). However, only small fractions of the aerosol precursor gases had been converted into *in situ* sulfate and nitrate. The ratio of molar sulfate/nitrate to total molar sulfur/nitrogen (Kaneyasu, 1995) was equal to 0.065 for SO₂ and even much smaller for NO₂—0.003. If the amounts of *in situ* sulfate and nitrate incorporated in the PM_{2.5–10} (coarse PM₁₀) fraction were added up using the data from our previous study (Hien *et al.*, 2005), these ratios would increase to 0.12 and 0.06, respectively. The loss of nitrate during sampling and the evaporation of ammonium nitrate due to high temperature may have reduced the nitrate level to some extent. However, the deficiency of NH₃ in the ambient condition may have been the main reason for the very low ammonium nitrate formation rate because NH₃ prefers to react with H₂SO₄ to form ammonium sulfate rather than react with HNO₃ to form NH₄NO₃. Ge *et al.* (2017) show that NH₄NO₃ starts to form when the molar ratio of NH₄⁺ to SO₄²⁻ is larger than 1.5 which is about one order of magnitude higher than the ratio in our case. Further studies are needed to elucidate the reasons for the observed low nitrate conversion rate.

LRT aerosols, comprising most of the observed sulfate and ammonium, were produced from SO₂ and NH₃ through reactions involving other gases in the atmosphere with subsequent gas-to-particle conversion processes. As a result, sulfate forms in the ultrafine nucleation mode with sizes less than 0.1 µm and the two modes in the submicron range, namely, the condensation and droplet modes with mass median aerodynamic diameters of ~0.2 µm and ~0.7 µm, respectively (John *et al.*, 1990; Meng and Seinfeld, 1994). Located mainly beyond the 1 µm cutoff, the droplet mode accounts for the difference between the properties of PM_{1.0} and PM_{2.5}. Sulfate in the condensation mode, formed by gas-phase homogeneous reactions of precursor gases, was acidic. Meanwhile, aerosols in the droplet mode, formed by heterogeneous reactions mainly in clouds after traveling far from the source location, were fully neutralized by ammonium (John *et al.*, 1990), which is consistent with the model-predicted molar ratio of LRT sulfate to ammonium in the two fractions (Section 3.2.1).

LRT secondary aerosols and their gas precursors come from far away so their impact largely reflected the pollution status of the region under their trajectory. Thus, the N air mass was expected to have a high impact as it traveled over highly urbanized southern China. Indeed, Pathak *et al.* (2003) found that 40% of the PM_{2.5} sulfate and ammonium measured in Hong Kong was brought in by the cold continental air masses that arrived in the area after passing over inland China in winter. In our PMF receptor modeling study of PM_{2.5} acquired from Hanoi in 2000–2001, the concentrations of LRT ammonium sulfate were also highest in the northeast monsoon's N air masses passing over inland China (Hien *et al.*, 2004).

5 CONCLUSIONS

The PMF models clearly differentiated the contribution of LRT aerosols, which accounted for more than two-thirds of the measured PM-bound sulfate and ammonium concentrations, from those of the six *in situ* sources, namely, resuspended road dust, primary vehicular emissions, coal fly ash, biomass burning emissions, construction dust, and sea salt. LRT aerosols, coal fly ash, and primary particulate vehicular emissions mainly occurred in the PM_{1.0}, whereas resuspended road dust and biomass-burning fly ash tended to appear in the PM_{1.0–2.5}; thus, we can characterize the anthropogenic emissions in this area by examining the profile of the PM_{1.0} rather than the PM_{2.5}. Furthermore, air masses with inland trajectories originating in northern China and nations northwest and southwest of Vietnam contained more ammonium, sulfate, and BC than those that had traveled over the East Sea. Also, the LRT aerosols displayed high acidity in the PM_{1.0} but neutrality in the PM_{2.5}.

Overall, our comparative analysis of PM_{1.0} and PM_{2.5} characterizes the sources of the former, which typically remain unaddressed in studies of the latter. This information is essential to developing effective pollution control measures for the airborne submicron PM in Hanoi.

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REFERENCES

- Acharja, P., Ali, K., Trivedi, D.K., Safai, P.D., Ghude, S., Prabhakaran, T., Rajeevan, M. (2020). Characterization of atmospheric trace gases and water soluble inorganic chemical ions of PM₁ and PM_{2.5} at Indira Gandhi International Airport, New Delhi during 2017–18 winter. *Sci. Total Environ.* 729, 138800. <https://doi.org/10.1016/j.scitotenv.2020.138800>
- Belis, C.A., Karagulian, F., Larsen, B.R., Hopke, P.K. (2013). Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. *Atmos. Environ.* 69, 94–108. <https://doi.org/10.1016/j.atmosenv.2012.11.009>
- Belis, C.A., Larsen, B.R., Amato, F., El Haddad, F., Favez, O., Harrison, R.M., Hopke, P.K., Nava, S., Paatero, P., Prévôt, A., UQuass, I., Vecchi, R., Viana, M. (2014). European Guide on Air Pollution Source Identification with Receptor Models. EUR 26080. Publications Office of the European
- Cabada, J.C., Rees, S., Takahama, S., Khlystov, A., Pandis, S.N., Davidson, C.I., Robinson, A.L. (2004). Mass size distributions and size-resolved chemical composition of fine particulate matter at the Pittsburgh supersite. *Atmos. Environ.* 38, 3127–3141. <https://doi.org/10.1016/j.atmosenv.2004.03.004>
- Chen, S., Zhao, Y., Zhang, R. (2018). Formation mechanism of atmospheric ammonium bisulfate: hydrogen-bond-promoted nearly barrierless reactions of SO₃ with NH₃ and H₂O. *ChemPhysChem* 19, 967–972. <https://doi.org/10.1002/cphc.201701333>
- Cheng, Y., Zou, S.C., Lee, S.C., Chow, J.C., Ho, K.F., Watson, J.G., Han, Y.M., Zhang, R.J., Zhang, F., Yau, P.S., Huang, Y., Bai, Y., Wu, W.J. (2011). Characteristics and source apportionment of PM₁ emission at a roadside station. *J. Hazard. Mater.* 195, 82–91. <https://doi.org/10.1016/j.jhazmat.2011.08.005>
- Crilley, L.R., Lucarelli, F., Bloss, W.J., Harrison, R.M., Beddows, D.C., Calzolari, G., Nava, S., Valli, G., Bernardoni, V., Vecchi, R. (2017). Source apportionment of fine and coarse particles at a roadside and urban background site in London during the 2012 summer ClearfLo campaign. *Environ. Pollut.* 220, 766–778. <https://doi.org/10.1016/j.envpol.2016.06.002>
- Deshmukh, D.K., Deb, M.K., Tsai, Y.I., Mkoma, S.L. (2011). Water-soluble ions in PM_{2.5} and PM₁ aerosols in Durg city, Chhattisgarh, India. *Aerosol Air Qual. Res.* 11, 696–708. <https://doi.org/10.4209/aaqr.2011.03.0023>
- Ding, J., van der A, R.J., Mijling, B., Jalkanen, J.P., Johansson, L., Levelt, P.F. (2018). Maritime NO_x emissions over Chinese seas derived from satellite observations. *Geophys. Res. Lett.* 45, 2031–2037. <https://doi.org/10.1002/2017GL076788>
- Fan, Q., Zhang, Y., Ma, W., Ma, H., Feng, J., Yu, Q., Yang, X., Ng, S.K.W., Fu, Q., Chen, L. (2016). Spatial and seasonal dynamics of ship emissions over the Yangtze River Delta and East China Sea and their potential environmental influence. *Environ. Sci. Technol.* 50, 1322–1329. <https://doi.org/10.1021/acs.est.5b03965>
- Faxon, C.B., Allen, D.T. (2013). Chlorine chemistry in urban atmospheres: A review. *Environ. Chem.* 10, 221–233. <https://doi.org/10.1071/EN13026>
- Ge, X., He, Y., Sun, Y., Xu, J., Wang, J., Shen, Y., Chen, M. (2017). Characteristics and formation mechanisms of fine particulate nitrate in typical urban areas in China. *Atmosphere* 8, 62. <https://doi.org/10.3390/atmos8030062>
- Gupta, T., Mandariya, A. (2013). Sources of submicron aerosol during fog-dominated wintertime at Kanpur. *Environ. Sci. Pollut. Res.* 20, 5615–5629. <https://doi.org/10.1007/s11356-013-1580-6>

- Hien, P.D., Bac, V.T., Lam, D.T., Thinh, N.T.H. (2004). PMF receptor modeling of fine and coarse PM₁₀ in air masses governing monsoon conditions in Hanoi, northern Vietnam. *Atmos. Environ.* 38, 189–201. <https://doi.org/10.1016/j.atmosenv.2003.09.064>
- Hien, P.D., Bac, V.T., Thinh, N.T.H. (2005). Investigation of sulfate and nitrate formation on mineral dust particles by receptor modeling. *Atmos. Environ.* 39, 7231–7239. <https://doi.org/10.1016/j.atmosenv.2005.09.003>
- Hien, P.D., Men, N.T., Tan, P.M., Hangartner, M. (2020). Impact of urban expansion on the air pollution landscape: A case study of Hanoi, Vietnam. *Sci. Total Environ.* 702, 134635. <https://doi.org/10.1016/j.scitotenv.2019.134635>
- Hildemann, L.M., Markowski, G.R., Jones, M.C., Cass, G.R. (1991). Submicrometer aerosol mass distributions of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. *Aerosol Sci. Technol.* 14, 138–152. <https://doi.org/10.1080/02786829108959478>
- Hopke, P.K., Cohen, D.D., Begum, B.A., Biswas, S.K., Ni, B., Pandit, G.G., Santoso, M., Chung, Y.S., Davy, P., Markwitz, A., Waheed, S., Siddique, N., Santos, F.L., Pabroa, P.C.B., Seneviratne, M.C.S., Wimolwattanapun, W., Bunprapob, S., Vuong, T.B., Duy Hien, P., Markowicz, A. (2008). Urban air quality in the Asian region. *Sci. Total Environ.* 404, 103–112. <https://doi.org/10.1016/j.scitotenv.2008.05.039>
- Hsu, C.Y., Chiang, H.C., Lin, S.L., Chen, M.J., Lin, T.Y., Chen, Y.C. (2016). Elemental characterization and source apportionment of PM₁₀ and PM_{2.5} in the western coastal area of central Taiwan. *Sci. Total Environ.* 541, 1139–1150. <https://doi.org/10.1016/j.scitotenv.2015.09.122>
- Hu, K., Guo, Y., Hu, D., Du, R., Yang, X., Zhong, J., Fei, F., Chen, F., Chen, G., Zhao, Q., Yang, J., Zhang, Y., Chen, Q., Ye, T., Li, S., Qi, J. (2018). Mortality burden attributable to PM₁ in Zhejiang province, China. *Environ. Int.* 121, 515–522. <https://doi.org/10.1016/j.envint.2018.09.033>
- Huang, S.L., Hsu, M.K., Chan, C.C. (2003). Effects of submicrometer particle compositions on cytokine production and lipid peroxidation of human bronchial epithelial cells. *Environ. Health Perspect.* 111, 478–482. <https://doi.org/10.1289/ehp.5519>
- Japan International Cooperation Agency (JICA) & People's Committee of Hanoi (2007). The comprehensive urban development program in Hanoi capital city of the Socialist Republic of Vietnam, March 2007. https://openjicareport.jica.go.jp/pdf/11856093_01.pdf
- John, W., Wall, S.M., Ondo, J.L., Winklmayr, W. (1990). Modes in the size distributions of atmospheric inorganic aerosol. *Atmos. Environ.* 24, 2349–2359. [https://doi.org/10.1016/0960-1686\(90\)90327-J](https://doi.org/10.1016/0960-1686(90)90327-J)
- Kaneyasu, N. (1995). Seasonal variation in the chemical composition of atmospheric aerosols and gaseous species in Sapporo, Japan. *Atmos. Environ.* 29, 1559–1568. [https://doi.org/10.1016/1352-2310\(94\)00356-P](https://doi.org/10.1016/1352-2310(94)00356-P)
- Lasko, K., Vadrevu, K.P., Nguyen, T.T.N. (2018). Analysis of air pollution over Hanoi, Vietnam using multi-satellite and MERRA reanalysis datasets. *PLoS One* 13, e0196629. <https://doi.org/10.1371/journal.pone.0196629>
- Lee, S.C., Cheng, Y., Ho, K.F., Cao, J.J., Louie, P.K.K., Chow, J.C., Watson, J.G. (2006). PM_{1.0} and PM_{2.5} Characteristics in the Roadside Environment of Hong Kong. *Aerosol Sci. Technol.* 40, 157–165. <https://doi.org/10.1080/02786820500494544>
- Lin, H., Tao, J., Du, Y., Liu, T., Qian, Z., Tian, L., Di, Q., Rutherford, S., Guo, L., Zeng, W., Xiao, J., Li, X., He, Z., Xu, Y., Ma, W. (2016). Particle size and chemical constituents of ambient particulate pollution associated with cardiovascular mortality in Guangzhou, China. *Environ. Pollut.* 208, 758–766. <https://doi.org/10.1016/j.envpol.2015.10.056>
- Lin, J.J., Lee, L.C. (2004). Characterization of the concentration and distribution of urban submicron (PM₁) aerosol particles. *Atmos. Environ.* 38, 469–475. <https://doi.org/10.1016/j.atmosenv.2003.09.056>
- Lundgren, D.A., Haing, D.N., Rich, T.A., Marple, V.A. (1996). PM₁₀/PM_{2.5}/PM₁ data from a trichotomous sampler. *Aerosol Sci. Technol.* 25, 353–357. <https://doi.org/10.1080/02786829608965401>
- Meng, Z., Seinfeld, J. (1994). On the source of the submicrometer droplet mode of urban and regional aerosols. *Aerosol Sci. Technol.* 20, 253–265. <https://doi.org/10.1080/02786829408959681>
- Norris, G., Brown, S. (2014). EPA positive matrix factorization (PMF) 5.0 fundamentals and user guide EPA/600/R-14/108 April 2014.

- Norris, G., Ram, V., Katie, W., Patrick, Z., Steve, B., Paatero, P., Eberly, S., Foley, C. (2009). Guidance document for PMF applications with the multilinear engine EPA 600/R-09/032 April 2009.
- Paatero, P., Tapper, U. (1994). Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5, 111–126. <https://doi.org/10.1002/ENV.3170050203>
- Pathak, R., Yao, X., Lau, A.K.H., Chan, C.K. (2003). Acidity and concentrations of ionic species of PM_{2.5} in Hong Kong. *Atmos. Environ.* 37, 1113–1124. [https://doi.org/10.1016/S1352-2310\(02\)00958-5](https://doi.org/10.1016/S1352-2310(02)00958-5)
- Perez, N., Pey, J., Querol, X., Alastuey, A., Lopez, J.M., Viana, M. (2008). Partitioning of major and trace components in PM₁₀–PM_{2.5}–PM₁ at an urban site in Southern Europe. *Atmos. Environ.* 42, 1677–1691. <https://doi.org/10.1016/j.atmosenv.2007.11.034>
- Prakash, J., Lohia, T., Mandariya, A.K., Habib, G., Gupta, T., Gupta, S.K. (2018). Chemical characterization and quantitative assessment of source-specific health risk of trace metals in PM_{1.0} at a road site of Delhi, India. *Environ. Sci. Pollut. Res.* 25, 8747–8764. <https://doi.org/10.1007/s11356-017-1174-9>
- Schmidt, M.W.I., Noack, A.G. (2000). Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochem. Cycles* 14, 777–793. <https://doi.org/10.1029/1999GB001208>
- Shao, P., Tian, H., Sun, Y., Liu, H., Wu, B., Liu, S., Liu, X., Wu, Y., Liang, W., Wang, Y., Gao, J., Xue, Y., Bai, X., Liu, W., Lin, S., Hu, G. (2018). Characterizing remarkable changes of severe haze events and chemical compositions in multi-size airborne particles (PM₁, PM_{2.5} and PM₁₀) from January 2013 to 2016–2017 winter in Beijing, China. *Atmos. Environ.* 189, 133–144. <https://doi.org/10.1016/j.atmosenv.2018.06.038>
- Shen, Z.X., Cao, J.J., Arimoto, R., Han, Y.M., Chu, C.S., Tian, J., Liu, S.X. (2010). Chemical characteristics of fine particles (PM₁) from Xi'an, China. *Aerosol Sci. Technol.* 44, 461–472. <https://doi.org/10.1080/02786821003738908>
- Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F. (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system, *Bull. Amer. Meteor. Soc.* 96, 2059–2077. <https://doi.org/10.1175/BAMS-D-14-00110.1>
- Tao, J., Shen, Z., Zhu, C., Yue, J., Cao, J., Liu, S., Zhu, L., Zhang, R. (2012). Seasonal variations and chemical characteristics of sub-micrometer particles (PM₁) in Guangzhou, China. *Atmos. Res.* 118, 222–231. <https://doi.org/10.1016/j.atmosres.2012.06.025>
- Watson, J., Chow, J.C., Chen, L.A., DuBois, D., Kohl, S., Trimble, D.L. (2008). Monitoring and data analysis for the Minnesota particulate matter 2.5 (PM_{2.5}) source apportionment study. Minnesota Pollution Control Agency. <https://www.researchgate.net/publication/235341852>
- Whitby, K.T. (1978). The physical characteristics of sulfur aerosols. *Atmos. Environ.* 12, 135–159. [https://doi.org/10.1016/0004-6981\(78\)90196-8](https://doi.org/10.1016/0004-6981(78)90196-8)
- World Bank (2011). Vietnam urbanization review: Technical assistance report. 611. Washington, DC. <https://openknowledge.worldbank.org/handle/10986/2826>
- Ye, Z., Liu, J., Gu, A., Feng, F., Liu, Y., Bi, C., Xu, J., Li, L., Chen, H., Chen, Y., Dai, L., Zhou, Q., Ge, X. (2017). Chemical characterization of fine particulate matter in Changzhou, China, and source apportionment with offline aerosol mass spectrometry. *Atmos. Chem. Phys.* 17, 2573–2592. <https://doi.org/10.5194/acp-17-2573-2017>
- Yin, P., Guo, J., Wang, L., Fan, W., Lu, F., Guo, M., Moreno, S.B.R., Wang, Y., Wang, H., Zhou, M., Dong, Z. (2020). Higher risk of cardiovascular disease associated with smaller size-fractioned particulate matter. *Environ. Sci. Technol. Lett.* 7, 95–101. <https://doi.org/10.1021/acs.estlett.9b00735>
- Zhang, Y., Carmichael, G.R. (1999). The role of mineral aerosol in tropospheric chemistry in East Asia—A model study. *J. Appl. Meteorol. Climatol.* 38, 353–366. [https://doi.org/10.1175/1520-0450\(1999\)038<0353:TROMAI>2.0.CO;2](https://doi.org/10.1175/1520-0450(1999)038<0353:TROMAI>2.0.CO;2)
- Zhang, Y., Lang, J., Cheng, S., Li, S., Zhou, Y., Chen, D., Zhang, H., Wang, H. (2018). Chemical composition and sources of PM₁ and PM_{2.5} in Beijing in autumn. *Sci. Total Environ.* 630, 72–82. <https://doi.org/10.1016/j.scitotenv.2018.02.151>