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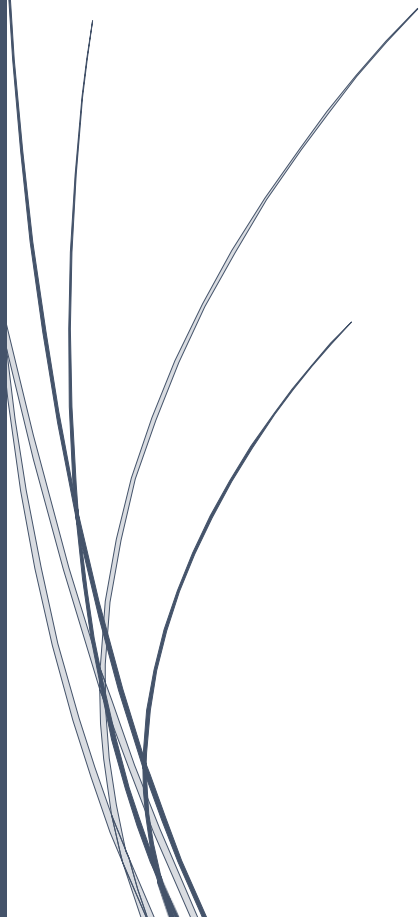
Doctoral Dissertation

Experimental and Numerical Investigation of PM_{2.5} Source Contribution in Hanoi, Vietnam

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December 2025

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Abstract

This dissertation investigates the sources, composition, and dynamics of fine particulate matter (PM_{2.5}) in Hanoi using a combination of field measurements, receptor modeling, and chemical transport modeling. Chapter 1 introduces the scientific background, highlighting the health and environmental impacts of PM_{2.5}, the specific challenges in Hanoi, and the research gaps motivating this study. Based on these challenges, the dissertation is structured to progressively link chemical characterization, source apportionment, and process-based modeling. The objectives were to characterize PM_{2.5} chemical composition, identify major sources through receptor modeling, and validate sector-specific contributions using Community Multiscale Air Quality - Integrated Source Apportionment Model (CMAQ-ISAM) simulations.

In Chapter 2, a comprehensive chemical characterization of PM_{2.5} was performed across three representative sites – Cau Giay (urban traffic), Pho Noi (industrial), and Tay Ho (agricultural), each reflecting a distinct emission regime within the Hanoi region. Using GC–MS and AIQS-DB, a total of 288 organic compounds across 19 classes were identified, including PAHs, solvents, industrial plasticizers, antioxidants, petroleum-related species, and pesticides. The results revealed site-specific chemical signatures, indicating diverse emission sources ranging from traffic and industry to agricultural and residential activities, thereby providing a chemical basis for subsequent receptor-based source apportionment. While Chapter 2 was initially designed with the expectation that trace organic species could serve as diagnostic markers for PMF source profiles, their relatively low abundance limited their applicability in the present receptor analysis; nevertheless, the detailed organic speciation established in this chapter provides a valuable foundation for future PMF studies incorporating organic tracers. Building on the compositional features identified in Chapter 2, Chapter 3 applied Positive Matrix Factorization (PMF) to apportion sources of PM_{2.5}. Six major factors were resolved: secondary sulfate, secondary nitrate, traffic, industry, biomass burning, and crustal dust. Secondary inorganic aerosols dominated, accounting for more than half of PM_{2.5} concentrations. Primary contributions from traffic (~15–20%), biomass burning (~10%), and industry (~10–12%) were also significant. Seasonal analysis highlighted stronger transboundary influences in winter and greater local contributions in summer, while spatial analysis showed roadside enrichment in traffic-related pollutants, demonstrating the sensitivity of PM_{2.5} sources to both temporal and spatial variability.

To extend the receptor-based findings beyond the monitoring locations and to resolve spatially explicit sectoral contributions, Chapter 4, the Weather Research and Forecasting (WRF)

–CMAQ model with ISAM was employed to trace contributions from specific sectors. Results showed household combustion as the largest contributor (~31%), followed by long-range transport (~23%), industry (~15–16%), and episodic open biomass burning (~5%). Traffic (~3–4%) and power plants (~2%) contributed smaller shares. The CMAQ-ISAM results emphasize the role of transboundary inflow as a baseline pollution source and complement the PMF analysis by providing process-resolved and sector-specific attribution across the modeling domain. Finally, Chapter 5 presents the general conclusions. By synthesizing observational evidence and model-based diagnostics, the integrated approach of combining detailed chemical speciation, PMF receptor modeling, and CMAQ-ISAM simulations provided a robust and cross-validated assessment of PM_{2.5} sources in Hanoi. Findings confirmed that secondary aerosols and combustion-related activities dominate fine particulate pollution, with strong seasonal and spatial variability. Beyond identifying priority emission sources, this dissertation discusses policy implications that focus not only on reducing specific sectoral emissions but also on how such reductions can be practically realized. These include promoting cleaner household energy use, improving regional coordination to mitigate transboundary pollution, refining emission inventories, and integrating scientific source apportionment results into adaptive air quality management strategies. This dissertation demonstrates the value of combining observational and modeling methods for air pollution source apportionment and establishes a scientific foundation for future studies of atmospheric composition in Southeast Asian megacities.

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List of abbreviations

PM	Particulate Matter
VOC	Volatile Organic Compounds
OC	Organic carbon
EC	Elemental carbon
SOA	Secondary Organic Aerosols
SIA	Secondary Inorganic Aerosols
POPs	Persistent Organic Pollutants
PCB	Polychlorinated biphenyls
ICP-MS	Inductively coupled plasma mass spectrometry
CMAQ	Community Multiscale Air Quality Model
WRF	Weather Research and Forecasting
ISAM	Integrated Source Apportionment Method
PMF	Positive Matrix Factorization
EPA	Environmental Protection Agency
MDL	Method Detection Limit
MQL	Method Quantification Limit
AOAC	Association of Official Analytical Chemists
Sd	standard deviation
RSD	Relative Standard Deviation
S/N	Signal-to-Noise Ratio
IA	Index of Agreement
MB	Mean Bias
RMSE	Root Mean Square Error
ICS	Ion Chromatography
WHO	World Health Organization
LRT	Long-Range Transport
CRM	Certified Reference Material
H.H	Household
LRT	Long-range transport
IND	Industry
OBB	Open biomass burning
OAN	Other anthropogenic
ROA	Road transport
POW	Power generation
OTR	Other transport
NAT	Natural

Research Achievements

1. **Le-Quang, H.**; Phuong, T.P.T.; Bui-Quang, M.; Nguyen-Tien, D.; Nguyen-Thanh, T.; Nguyen-Ha, M.; Shimadera, H.; Kondo, A.; Luong-Viet, M.; Nguyen-Quang, T. Comprehensive Analysis of Organic Micropollutants in Fine Particulate Matter in Hanoi Metropolitan Area, Vietnam. *Atmosphere* **2022**, *13*, 2088.
<https://doi.org/10.3390/atmos13122088>
2. **Quang Le, H.**, Phuong Pham, T. T., Minh Le, T., Bui, M. Q., Nguyen, D. T., Kondo, A., & Shimadera, H. (2025). Characteristics of fine particulate matter (PM_{2.5}) in Hanoi, Vietnam: source apportionment and pollution status. *International Journal of Environmental Analytical Chemistry*, 1–15.
<https://doi.org/10.1080/03067319.2025.2532592>
3. **Huong Quang Le**, Thao Thi Phuong Pham, Thuy Minh Le, Minh Quang Bui, Trung Quang Nguyen, Nanthapong Chantaraprachoom, Katsushige Uranishi, Tomohito Matsuo, Akira Kondo, Hikari Shimadera. *Source Apportionment of PM_{2.5} and Its Chemical Components in Hanoi, Vietnam: A Comparison of PMF and CMAQ-ISAM Approaches. (submitted in Enviroment Advance)*

Chapter 1 - Introduction

1.1. Research background

1.1.1. Introduction to PM_{2.5}

Particulate matter (PM_{2.5}) refers to a complex mixture of solid particles and liquid droplets suspended in the atmosphere (Chauhan, Corada et al. 2024). PM is typically classified according to its aerodynamic diameter. PM_{2.5}, also known as fine particulate matter, consists of particles with an aerodynamic diameter less than or equal to 2.5 micrometers (μm). Due to their extremely small size—approximately 30 times smaller than the width of a human hair—PM_{2.5} particles can remain airborne for extended periods and be transported over long distances.

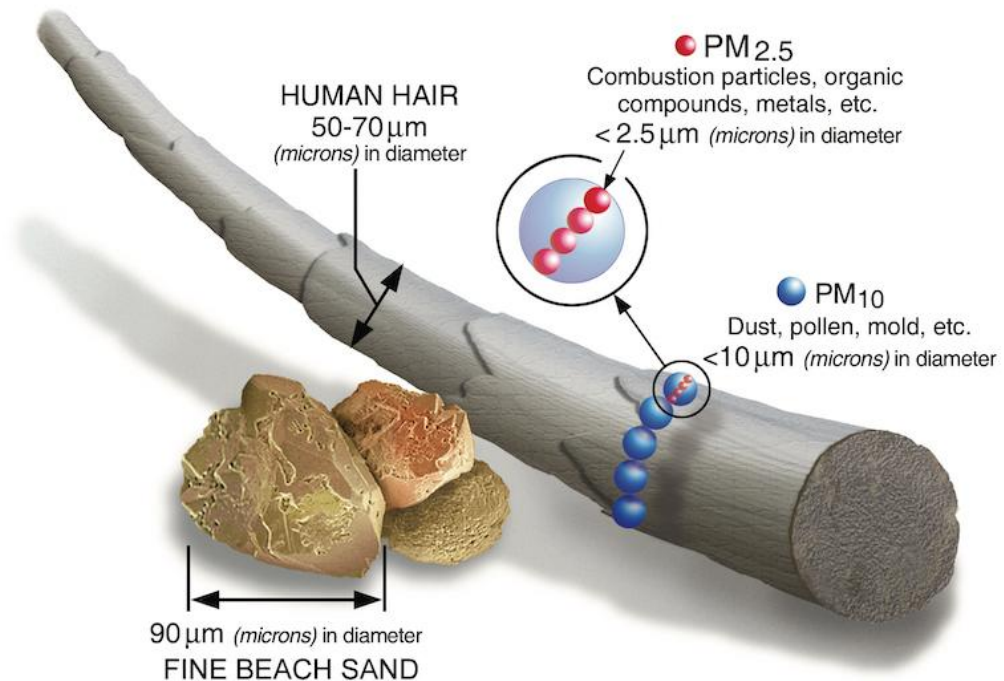


Figure 1. 1. Image description of PM_{2.5} (Tahir Bahadur, Rasool Shah et al. 2024)

The small size of PM_{2.5} allows it to penetrate deeply into the human respiratory system, reaching the alveolar region of the lungs, where gas exchange occurs. Unlike larger particles (such as PM₁₀), PM_{2.5} cannot be effectively filtered by the nose or upper respiratory tract, making it more hazardous to human health. Moreover, PM_{2.5} is not a single substance but rather a mixture of various chemical components, including inorganic ions (e.g., sulfates, nitrates, ammonium), carbonaceous materials (organic carbon and elemental carbon), trace metals, and organic compounds. Its chemical composition depends on emission sources, atmospheric conditions, and transformation processes.

From an environmental and public health perspective, PM_{2.5} is considered one of the most

harmful air pollutants. It contributes to visibility reduction (haze), influences climate by scattering and absorbing solar radiation, and serves as cloud condensation nuclei. More importantly, epidemiological evidence consistently links PM_{2.5} exposure to respiratory and cardiovascular diseases, premature mortality, and decreased life expectancy.

1.1.2. Source of PM_{2.5}

The sources of fine particulate matter (PM_{2.5}) are complex and multifaceted, comprising both natural and anthropogenic (human-induced) origins (Koçak, Mihalopoulos et al. 2007). These sources vary considerably across regions and seasons, and their relative importance depends on meteorological conditions, land use, and economic activities. Broadly, PM_{2.5} can originate from primary emissions (particles emitted directly into the atmosphere) and secondary formation (particles formed in the atmosphere from gaseous precursors).

- Natural Sources of PM_{2.5}
 - Although anthropogenic activities are often the dominant contributor in urban areas, natural processes still play an important role in shaping the background concentration of PM_{2.5}:
 - Windblown dust: Soil erosion, desertification, and agricultural activities release fine mineral particles into the air. Dust storms originating from arid regions (e.g., the Gobi Desert or Loess Plateau) can transport PM_{2.5} over thousands of kilometers, influencing air quality in downwind regions such as northern Vietnam during certain seasons.
 - Sea salt aerosols: Ocean waves and surf generate airborne salt particles. While coarse particles dominate, some fraction enters the PM_{2.5} range, particularly in coastal areas like Ha Long Bay or central Vietnam.
 - Volcanic activity: Eruptions emit ash, sulfur dioxide, and other gases that can transform into sulfate aerosols. Although sporadic, volcanic emissions can contribute significantly during eruptive events.
 - Wildfires and biomass burning (natural): Forest fires release large amounts of carbonaceous particles (organic carbon and elemental carbon) and trace gases that form secondary PM_{2.5}. In Southeast Asia, cross-border haze from large-scale forest fires in Indonesia has historically impacted regional air quality, including Vietnam.

- Biological particles: Natural biological matter, such as pollen fragments, fungal spores, bacteria, and plant debris, contributes to fine particle concentrations. These particles can also serve as nuclei for secondary aerosol formation.
- Overall, natural sources create a background level of PM_{2.5} and occasionally cause pollution episodes when combined with adverse meteorological conditions.
- Anthropogenic Sources of PM_{2.5} (Chen, Lin et al. 2023)
 - In rapidly developing countries like Vietnam, anthropogenic activities are the dominant sources of PM_{2.5} especially in urban centers such as Hanoi and Ho Chi Minh City. These sources include:
 - Transportation: Motorcycles, cars, trucks, and buses emit PM_{2.5} directly from fuel combustion (especially diesel engines) and indirectly through resuspension of road dust, brake wear, and tire abrasion. Given the high density of motorbikes in Vietnam, traffic-related emissions represent a critical contributor to urban PM_{2.5}.
 - Industrial activities: Power plants, steel production, cement factories, and other heavy industries release large amounts of PM_{2.5} through coal and fuel combustion. Industrial clusters surrounding major cities significantly influence local and regional air quality.
 - Residential combustion: Burning of coal, wood, and other biomass for cooking and heating is still common in rural and peri-urban areas. These activities emit organic carbon, black carbon, and trace metals, which directly contribute to PM_{2.5}.
 - Open burning of waste: The uncontrolled burning of municipal solid waste, agricultural residues (e.g., rice straw), and plastics produces PM_{2.5} rich in toxic organic compounds and heavy metals. In northern Vietnam, rice-straw burning after harvest seasons is a major episodic source.
 - Construction and road dust: Urban development activities such as construction, demolition, and land clearing generate large amounts of dust. While much of this is coarse material, finer particles also contribute to PM_{2.5} levels.
 - Secondary formation from precursor gases: A substantial fraction of PM_{2.5} is formed through atmospheric chemical reactions. The main precursors are: Sulfur dioxide (SO₂), primarily from coal combustion, which oxidizes to form sulfates. Nitrogen oxides (NO_x), largely from traffic and industry, which form nitrates. Ammonia (NH₃),

mainly from agriculture (livestock farming and fertilizer application), which neutralizes acidic species to produce ammonium sulfate and ammonium nitrate. Volatile organic compounds (VOCs), from traffic, industry, and biomass burning, which oxidize to form secondary organic aerosols (SOA).

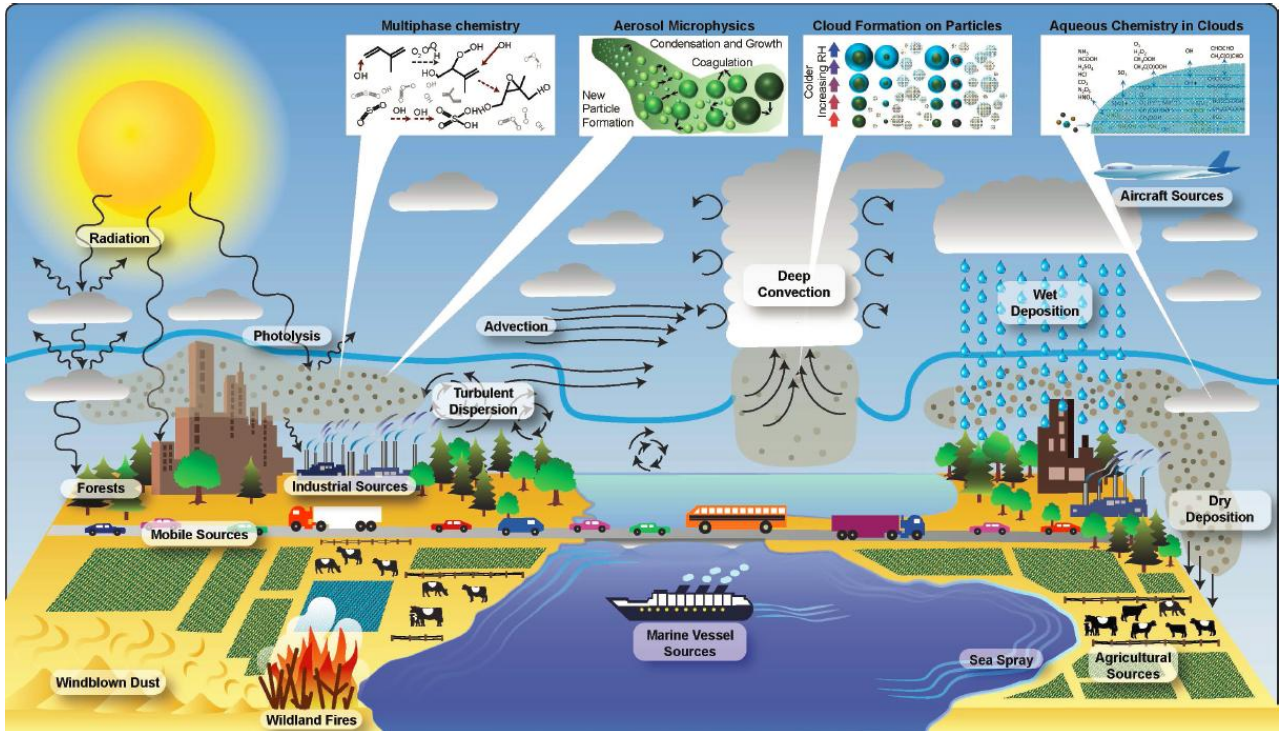


Figure 1. 2. Schematic of major emission sources and atmospheric processes leading to the formation, transformation, and removal of air pollutants (from <https://www.epa.gov/cmaq/overview-science-porcesses-cmaq>).

1.1.3. Impacts of PM_{2.5}

PM_{2.5} is widely recognized as one of the most harmful air pollutants due to its small size, complex chemical composition, and ability to persist in the atmosphere (Borgie, Dagher et al. 2015). Its impacts can be broadly categorized into public health effects, environmental consequences, and climate-related influences.

- Impacts on Human Health (Huang, Zhang et al. 2014) (Billet, Abbas et al. 2008)
 - Respiratory and cardiovascular diseases: PM_{2.5} particles penetrate deep into the lungs, reaching the alveolar region, and some ultrafine particles may even enter the bloodstream. Numerous epidemiological studies have shown strong associations between PM_{2.5} exposure and respiratory illnesses (asthma, chronic bronchitis, reduced lung function), as well as cardiovascular problems (ischemic heart disease, stroke, and hypertension).

- Increased morbidity and mortality: Long-term exposure to PM_{2.5} is linked to increased hospital admissions, reduced life expectancy, and premature deaths. According to the Global Burden of Disease (GBD) study, PM_{2.5} is among the leading environmental risk factors contributing to global mortality.
- Cancer risks: Certain chemical constituents of PM_{2.5}, such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals (e.g., arsenic, cadmium, nickel, lead), are carcinogenic and can increase the risk of lung cancer.
- Vulnerable populations: Children, the elderly, and individuals with pre-existing respiratory or cardiovascular conditions are particularly sensitive to PM_{2.5} exposure. In children, long-term exposure can impair lung development, while in the elderly, it increases the likelihood of chronic diseases.
- Environmental Impacts (Wolf, Emerson et al. 2022, Xu, Wang et al. 2022) (Jin, Guo et al. 2014, Zhou, Zhang et al. 2021)
 - Visibility reduction (haze): PM_{2.5} particles scatter and absorb solar radiation, reducing visibility and contributing to urban haze. This not only affects daily life but also undermines tourism and urban aesthetics in cities such as Hanoi.
 - Ecosystem degradation: When deposited on land and water surfaces, PM_{2.5} components such as sulfates, nitrates, and heavy metals can acidify soils and freshwater bodies, leading to biodiversity loss. Toxic metals and persistent organic pollutants contained in PM_{2.5} can accumulate in the food chain, posing long-term ecological risks.
 - Agricultural impacts: Deposition of PM_{2.5} and associated pollutants onto crops can impair photosynthesis, reduce crop yields, and affect food security, particularly in regions with intensive agriculture such as the Red River Delta.
- Climate Impacts (Onaiwu and Ayidu 2025)
 - Direct radiative forcing: PM_{2.5} influences the Earth's energy balance by scattering and absorbing solar and terrestrial radiation. Sulfate aerosols tend to cool the atmosphere by reflecting sunlight, whereas black carbon absorbs radiation, contributing to atmospheric warming.
 - Indirect climate effects: PM_{2.5} particles act as cloud condensation nuclei (CCN) and

ice nuclei (IN), modifying cloud microphysical properties. This affects cloud reflectivity, lifetime, and precipitation patterns, thereby influencing regional hydrological cycles.

- Regional climate variability: In Southeast Asia, seasonal haze events driven by biomass burning significantly alter radiative forcing, reduce solar radiation at the surface, and impact regional monsoon systems.
- Socioeconomic Implications (Jiang, Yang et al. 2018)
- Beyond its direct scientific and environmental dimensions, PM_{2.5} pollution carries heavy socioeconomic costs, including increased healthcare expenditures, productivity loss due to illness, and constraints on sustainable urban development. In Vietnam, frequent pollution episodes in major cities not only endanger public health but also challenge the country's long-term goals for green growth and climate resilience.

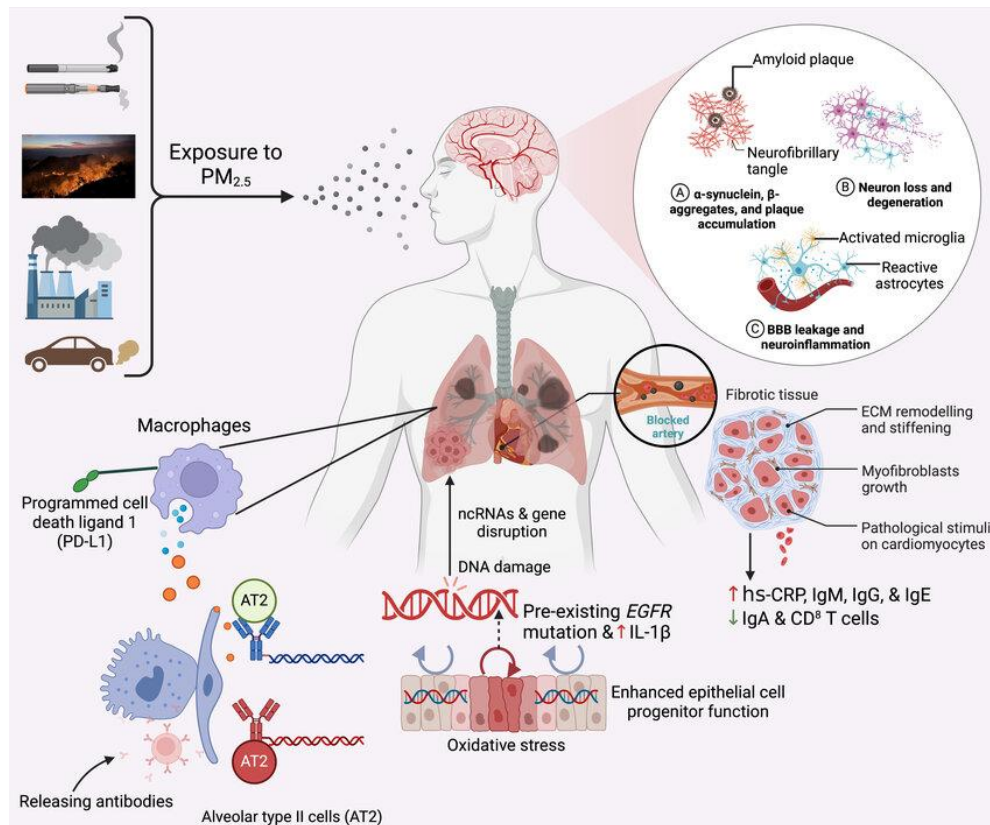


Figure 1. 3. Health impacts of PM_{2.5} on the eyes, skin, lungs, respiratory and cardiovascular systems (Sangkham, Phairuang et al. 2024) .

1.1.4. Overview of PM_{2.5} pollution

Air pollution has become one of the most pressing environmental challenges in rapidly developing countries, particularly in Southeast Asia. Among various air pollutants, PM_{2.5} has attracted increasing scientific and policy attention due to its adverse impacts on human health, atmospheric chemistry, and climate. PM_{2.5} particles are capable of penetrating deep into the human respiratory system, reaching the alveolar region, and have been strongly associated with respiratory and cardiovascular diseases, increased mortality, and reduced life expectancy (Nhung, Duc et al. 2022). Globally, the World Health Organization (WHO) has continuously revised its air quality guidelines to stricter levels, highlighting the urgent need to understand and control PM_{2.5} pollution.

Hanoi, the capital city of Vietnam, is a densely populated urban area with over eight million residents, characterized by rapid urbanization, industrialization, and significant increases in motor vehicle use. Geographically, Hanoi is situated in the Red River Delta and experiences a humid subtropical climate with distinct monsoon seasons. The combination of meteorological conditions, such as temperature inversions and low wind speeds during winter, with dense local emission sources, often results in elevated PM_{2.5} concentrations and prolonged pollution episodes. In fact, Hanoi has frequently been ranked among the cities with the poorest air quality in Southeast Asia, with annual PM_{2.5} levels far exceeding both national standards and WHO guidelines (Bui, Pham et al. 2025).

The major sources of PM_{2.5} in Hanoi are diverse and complex. They include traffic emissions from a rapidly growing number of motorbikes and cars, coal combustion from industrial and residential activities, biomass burning, and secondary aerosol formation from precursor gases such as SO₂, NO_x, and NH₃. Additionally, long-range transboundary transport of pollutants from surrounding industrial regions, combined with local emissions, further complicates source apportionment. Seasonal variations in meteorology also strongly influence PM_{2.5} concentrations, with higher levels often observed in the dry winter season compared to the wet summer season due to reduced atmospheric dispersion and scavenging (Hien, Bac et al. 2021).

The persistence of high PM_{2.5} levels in Hanoi poses substantial challenges to public health and sustainable urban development. Recent epidemiological studies have revealed strong associations between PM_{2.5} exposure and increased risks of respiratory symptoms, asthma incidence, and hospital admissions in Vietnamese populations. Moreover, the chemical

composition of PM_{2.5}, particularly its content of toxic heavy metals, organic compounds, and secondary inorganic aerosols, determines not only its toxicity but also its atmospheric reactivity and climate relevance (Zhou, Zhang et al. 2021). Therefore, comprehensive studies focusing on both the quantitative levels and the chemical characteristics of PM_{2.5} are essential to provide a scientific basis for air quality management in Hanoi.

Despite growing concerns, there remain significant gaps in understanding the sources, formation processes, and seasonal dynamics of PM_{2.5} in Hanoi. Previous monitoring efforts have been limited in spatial and temporal coverage, and many studies have focused primarily on mass concentrations without detailed chemical analysis. As Vietnam continues its rapid economic development, it is crucial to establish robust scientific evidence on the characteristics and drivers of PM_{2.5} pollution. Such knowledge will not only inform local policy and mitigation strategies but also contribute to the broader regional understanding of urban air pollution in Southeast Asia.

Against this backdrop, the present doctoral research aims to investigate the concentrations, chemical composition, and source contributions of PM_{2.5} in Hanoi. By combining field measurements, advanced chemical analyses, and receptor and forward modeling approaches, this study seeks to provide a comprehensive assessment of PM_{2.5} pollution in the city. The outcomes are expected to support evidence-based air quality management policies, improve public health protection, and enhance regional cooperation in air pollution mitigation.

1.1.5. Methods for source identification of PM_{2.5}

1.1.5.1. Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) (Paatero and Tapper 1994, Manousakas, Papaefthymiou et al. 2017) is a receptor modeling technique widely used for PM_{2.5} source apportionment. It is a form of multivariate factor analysis that decomposes a matrix of measured pollutant concentrations into two matrices – factor profiles and factor contributions – under the constraint that all contributions and species concentrations are non-negative. Formally, PMF models the observed data matrix X (of n samples by m chemical species) as the product of a G matrix ($n \times p$, representing the contribution of p factors to each sample) and an F matrix ($p \times m$, representing the composition profiles of the p factors), plus a residual matrix E (model error). The PMF algorithm iteratively adjusts the elements of G and F to minimize an objective function Q , which is essentially the weighted sum of squared residuals (Klitzke, Schroeder et al. 2015). Notably, each data point is weighted by its uncertainty in the fitting process, so that observations

with higher measurement uncertainty have less influence on the solution. This weighted least-squares approach with uncertainty estimates, combined with non-negativity constraints on G and F, yields physically meaningful factors that can be interpreted as actual pollution sources. A key assumption in PMF (and other receptor models) is mass conservation – the mass of each species in the aerosol is conserved and can be apportioned among the contributing sources. In contrast to source-oriented models, PMF does not use dispersion or emissions data; instead, it uses the statistical patterns in the observed chemical composition to infer source signatures and contributions (Wang, Zhu et al. 2024).

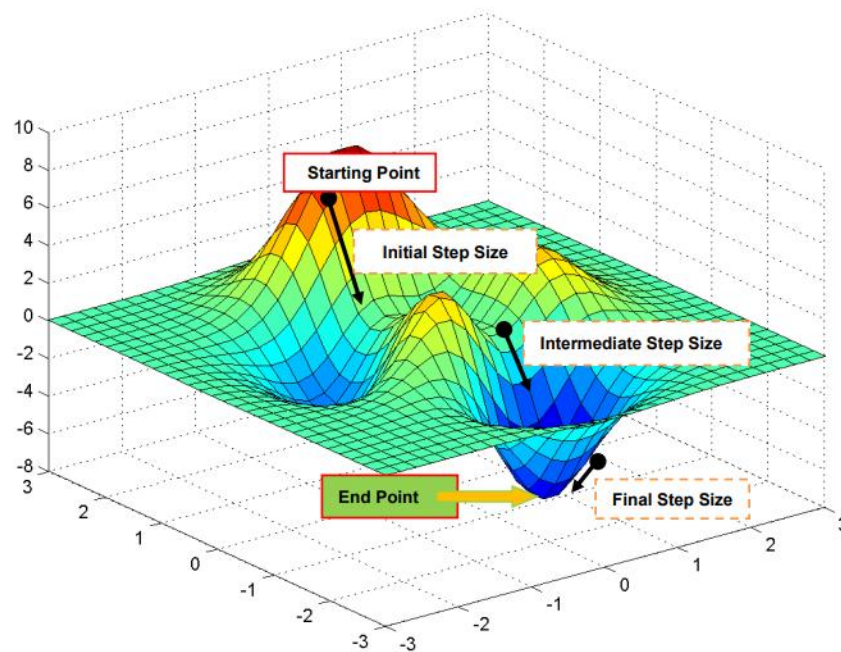


Figure 1. 4. Gradient-based optimization path showing step-size adjustments from the starting point to the final convergence point.

Advantages of PMF in Air Quality Research:

PMF offers several significant advantages for air quality and PM_{2.5} research, making it one of the most popular source apportionment methods worldwide:

Minimal *a priori* information required: Unlike chemical mass balance (CMB) models, PMF does not require the user to input known source profiles or assume the number of sources in advance. It can solve for both the source profiles and their contributions using only the ambient concentration data and estimated uncertainties. This is particularly valuable in regions where up-to-date local source composition profiles are not available, which is the case in much of the world.

Error-weighted robust modeling: PMF explicitly incorporates measurement uncertainties for each data point, down-weighting less reliable data. This yields a more statistically robust solution and helps distinguish true source signals from noise. The goodness-of-fit is evaluated through the Q value (based on weighted residuals), allowing the analyst to assess model performance and refine the number of factors.

Non-negativity constraints: By constraining source contributions and species fractions to be non-negative, PMF ensures all inferred source profiles and contributions are physically plausible (e.g. no “negative emissions”). This leads to more interpretable results compared to unconstrained factor analysis techniques.

Wide availability and validation: The PMF method has been extensively applied and validated in peer-reviewed studies globally, and it is supported by user-friendly software (e.g. EPA PMF). The U.S. Environmental Protection Agency provides PMF as a free tool (currently version 5.0) that has become a standard in the field. Consequently, PMF is now “*the most widely used source apportionment tool*” in particulate pollution studies, and its prevalence testifies to its reliability and relevance in atmospheric science.

Uncertainty in Positive Matrix Factorization (PMF) arises from both the quality of input measurement data and the intrinsic assumptions of the model. Measurement-related uncertainties include analytical errors, method detection limits, data completeness, and temporal representativeness of the measured chemical species, all of which directly affect the stability and interpretability of PMF solutions. In particular, species with low signal-to-noise ratios or high collinearity may lead to ambiguous factor separation and increased uncertainty in source identification. In addition to data-related issues, model-related uncertainties stem from the non-uniqueness of PMF solutions, subjective choices in the number of factors, and rotational ambiguity governed by parameters such as FPEAK. These factors can result in multiple mathematically acceptable solutions with differing physical interpretations. Consequently, PMF-derived source profiles and contribution estimates are sensitive to both data treatment and modeling decisions, underscoring the importance of careful uncertainty analysis and the use of complementary approaches to improve the robustness of PMF-based source apportionment.

Overall, these features make PMF a powerful and flexible receptor model for identifying pollution sources and quantifying their contributions to PM_{2.5} in a given location. The ability to resolve sources without detailed prior knowledge is especially advantageous in developing regions and complex urban environments.

1.1.5.2. Community Multiscale Air Quality (CMAQ) - Integrated Source Apportionment Method (ISAM)

The Community Multiscale Air Quality (CMAQ) model(Wang, Tong et al. 2023), developed by the U.S. Environmental Protection Agency (EPA), is a widely used chemical transport model designed to simulate the physical and chemical processes governing atmospheric pollutants. It integrates meteorological inputs (often from the WRF model) and detailed emission inventories to estimate pollutant concentrations, transport, transformation, and deposition across spatial and temporal scales.

CMAQ's multiscale framework allows simulations from urban to continental domains, enabling studies of both local pollution episodes and long-range transport. Its modular design supports advanced diagnostic tools, such as the Direct Decoupled Method (DDM) for sensitivity analysis and the Integrated Source Apportionment Method (ISAM) for direct source attribution. Owing to its open-source nature and extensive validation, CMAQ has become a cornerstone tool in air quality management and research worldwide.

While traditional CMAQ simulations provide total pollutant concentrations, they do not inherently distinguish contributions from individual sources. Historically, source contributions were estimated using “brute-force” sensitivity simulations, in which specific emission sources are removed or perturbed and differences in modeled concentrations are attributed to those sources. Although straightforward, this approach is computationally expensive and may produce biased results due to nonlinear atmospheric chemistry. For instance, removing NO_x emissions can paradoxically increase ozone concentrations under VOC-limited regimes.

The Integrated Source Apportionment Method (ISAM) (Kitagawa, Pedruzzi et al. 2021)was developed to overcome these limitations. ISAM employs a tagging approach that tracks emissions from specified sources (by sector, region, or pollutant class) throughout the transport and transformation processes in a single CMAQ simulation. Each source tag is propagated through chemical reactions, secondary formation, transport, and deposition, yielding source-resolved concentrations of pollutants, including PM_{2.5} and its components.

This methodology allows simultaneous quantification of contributions from multiple sources without altering the atmospheric chemical environment, thus avoiding biases inherent in zero-out approaches. Moreover, ISAM provides temporally and spatially resolved source apportionment results, making it particularly valuable for identifying dominant sources during

high-pollution episodes or across regions affected by transboundary pollution.

The primary purpose of the Integrated Source Apportionment Method (ISAM) is to quantify the contributions of specific emission sectors and source regions to ambient PM_{2.5} by explicitly simulating the transport, chemical transformation, and removal of tagged emissions within a chemical transport modeling framework. The fundamental difference between ISAM and receptor-based approaches arises from their methodological foundations: ISAM is source-oriented and relies on emission inventories and process-based atmospheric modeling, whereas receptor models infer source contributions statistically from observed concentration data at monitoring sites. As a result, ISAM can resolve spatially and temporally continuous source–receptor relationships and attribute secondary PM_{2.5} formation directly to precursor emissions, capabilities that are inherently beyond the scope of receptor models. However, uncertainties in emission inventories and model parameterizations may propagate into ISAM results. Therefore, combining ISAM with observation-based methods such as PMF provides a complementary advantage, in which PMF-derived source signatures and temporal patterns are used to evaluate and constrain ISAM-simulated source contributions. This integrated approach reduces methodological uncertainty, enhances confidence in source attribution, and enables a more comprehensive interpretation of PM_{2.5} sources for both scientific understanding and policy-relevant air quality management.

1.1.5.3. Chemical Mass Balance (CMB) Model

Chemical Mass Balance (CMB) is a classical receptor model that uses measured source profiles to solve linear “mass balance” equations for ambient PM_{2.5}. The EPA CMB model (e.g. EPA-CMB8.2) applies a least-squares fit of speciated ambient data to a set of known source composition profiles (Watson, Robinson et al. 1990). In practice, CMB requires that all major contributing sources have representative chemical signatures (profiles) and that species are conserved in the atmosphere. When these conditions hold, CMB can yield accurate estimates of source contributions for each sample. It has been used extensively in regulatory studies worldwide (e.g. in U.S. SIPs and urban air studies). For example, Begum et al applied EPA-CMB to apportion PM_{2.5} in Dhaka using locally derived profiles and found results comparable to PMF (Begum, Biswas et al. 2007)

- **Advantages:** CMB provides direct, quantitative source contributions on a per-sample basis. It is well-established in air quality management (EPA lists CMB in many SIP plans) and can leverage detailed local profiles to resolve sources. It can apportion daily or hourly

samples if high-resolution data are available.

- **Limitations:** CMB cannot resolve sources lacking profiles or with very similar chemistry. It assumes fixed source profiles and mass conservation, so errors in profiles or missing sources lead to “unportioned” mass. CMB also requires more a priori information than PMF: if profiles are outdated or incomplete, the results may be biased

1.1.5.4. UNMIX Model

UNMIX is another factor-analysis receptor model developed by the U.S. EPA. It performs a constrained principal component analysis on the ambient data and automatically determines how many source factors can be extracted (Henry 2000). In essence, UNMIX “unmixes” the observed concentrations into combinations of source types and their contributions. The model imposes non-negativity and mass-closure constraints, yielding physically realistic source profiles and time series. UNMIX does not require the user to pre-specify the number of sources or input source profiles; instead, it finds factors based solely on correlations in the data. For example, in a study of PM_{2.5} in Cincinnati, UNMIX successfully identified factors corresponding to soil dust, secondary aerosols, and biomass burning, which were confirmed by comparison with PMF (Liu and Liu 2016).

- **Advantages:** UNMIX automatically infers the number of source types and their profiles from the data. It uses a robust PCA-based algorithm with nonnegativity constraints to yield interpretable solutions. Like PMF, UNMIX is free and widely available (EPA provides the software). Its graphical interface helps visualize source contributions over time.
- **Limitations:** UNMIX can be sensitive to outliers and may require manual intervention (e.g. excluding outlier samples) to obtain stable solutions. It also relies on the variability in the data to separate sources – if two sources co-vary consistently, UNMIX may not distinguish them.

1.1.5.5. Principal Component / Factor Analysis (PCA/FA, APCS-MLR)

Traditional factor analysis methods (Principal Component Analysis [PCA] and Absolute Principal Component Scores [APCS]) were among the earliest receptor techniques. In PCA/APCS, the covariance matrix of speciated PM_{2.5} data is decomposed into orthogonal factors; these factors are interpreted as source types, and APCS (multiple linear regression) is then used to estimate their contributions. For example, Jain et al. (2017) applied PCA/APCS to Delhi

PM_{2.5} data and identified five major sources (secondary aerosol, vehicular, biomass burning, etc.) (Jain, Sharma et al. 2017). PCA/APCS has the advantage of being straightforward and requiring no a priori profiles, but it has several drawbacks: factor solutions can rotate arbitrarily, factors may be correlated, and negative loadings can occur if unconstrained. In practice, PCA factors often require subjective interpretation and may be complemented by other methods.

- **Usage:** PCA/FA methods have been applied in many studies worldwide (especially before PMF became widespread). They are useful for exploratory analysis. For instance, in Delhi, PCA/APCS identified five sources, whereas UNMIX and PMF identified four and seven sources, respectively.
- **Limitations:** Without non-negativity constraints, PCA factors may mix sources and be hard to interpret. Modern practice often favors PMF or UNMIX over raw PCA, because those impose physical constraints and error weighting.

1.1.5.6. Trajectory and Statistical Approaches (PSCF, CWT, Cluster)

Meteorological trajectory analysis is another class of “source identification” tools that link air masses to geographic source regions. Techniques like the Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT) use back-trajectory ensembles and pollutant concentrations to highlight likely source areas. These methods do not identify chemical sources by composition, but rather infer where air parcels originated when high PM_{2.5} levels were recorded. For example, multiday back-trajectory clustering and PSCF analysis in Beijing showed that long-range transport from upwind regions (e.g. Inner Mongolia, northwest China) contributed substantially to local PM_{2.5} during winter pollution episodes (Zhang, Jing et al. 2013).

- **Advantages:** These approaches require only PM_{2.5} concentration data and meteorological fields (e.g. HYSPLIT trajectories) and can pinpoint regional sources or transport pathways. They complement chemical receptor models by indicating whether pollution is local or transboundary.
- **Limitations:** They do not resolve specific emission sectors or chemical species – they only suggest spatial origins. They also require a large trajectory dataset and assume that “high-concentration” trajectories are dominated by a single region’s influence.

1.1.5.7. Source-Oriented CTMs with Tagging

Beyond CMAQ/ISAM, other full-chemistry air quality models incorporate internal

source-tagging methods to apportion PM_{2.5}. For instance, the CAMx model includes the Particulate Source Apportionment Technology (PSAT) module. PSAT uses “tagged” precursor species to follow emissions from specified sources (by sector or region) through chemical reactions (Koo, Wilson et al. 2009). In PSAT, each PM component (e.g. sulfate, nitrate, organic carbon) is apportioned to its precursor emissions (SO₂, NO_x, VOC, etc.) so that the contribution of each source can be tracked at the receptor. Similarly, CMAQ has an online Tagged Species Source Apportionment (TSSA) capability and WRF-Chem can be run with plume-in-grid tracers. These tagged-species methods have the advantage that multiple sources are resolved simultaneously in one model run, without perturbing the chemistry.

- **Advantages:** They account for full 3D transport and chemistry, so they capture secondary formation and nonlinear effects. They provide spatially and temporally resolved source contributions within the model grid. Unlike “zero-out” sensitivity runs, they do not suffer from altered chemistry when one source is removed.
- **Limitations:** Such CTM tagging is computationally intensive and dependent on the accuracy of the emission inventory. PSAT/TSSA will give different results if the number of categories changes or if precursor chemistry is highly nonlinear. For example, when limiting precursors (e.g. NO_x) interact, PSAT contributions may deviate from actual concentration changes as noted by Koo et al. (2009). In practice, results from CTM tagging should be interpreted alongside receptor-model estimates for validation.

1.1.5.8. Isotopic and Tracer-Based Methods

An emerging set of techniques uses chemical or isotopic “fingerprints” to trace sources. The most established example is radiocarbon (¹⁴C) analysis of carbonaceous PM. Since fossil fuels are depleted in ¹⁴C while contemporary biomass contains modern ¹⁴C, measuring ¹⁴C in organic carbon (OC) or black carbon (BC) uniquely partitions “fossil” vs. “modern” carbon in PM_{2.5} (Dasari and Widory 2022). This approach has been widely applied in Europe and North America – e.g. Szidat et al. (2006) used ¹⁴C to show that urban OC is roughly half biogenic in summer. Similarly, stable isotope ratios of other elements can fingerprint sources: for instance, Pb isotope measurements in PM_{2.5} have been used to distinguish coal combustion and vehicular sources. In Taiwan, Jung et al. (2022) showed that isotopic Pb in urban PM_{2.5} is dominated by coal-fired power plants (35–57 % of Pb) with a smaller contribution from vehicles (~12 %) (Jung, Chou et al. 2022).

- **Advantages:** Isotopic markers provide direct source attribution that is often independent of modeling assumptions. Radiocarbon gives a clear fossil vs. biomass split, and metal isotopes (e.g. Pb, Sr) can discriminate geological or industrial sources.
- **Limitations:** These methods usually require extensive sample preparation and expensive analyses (AMS for ¹⁴C, mass spectrometry for trace isotopes). They typically apply only to specific PM fractions (e.g. carbon, metals) rather than the total PM_{2.5}, and so are often used to complement bulk apportionment.

1.1.6. Previous Studies on PM_{2.5} in Hanoi

Air pollution in Hanoi has been extensively documented in the past decade, with particular focus on fine particulate matter (PM_{2.5}). Observational studies report annual mean concentrations in the range of 40–60 µg/m³, consistently exceeding the Vietnamese standard (25 µg/m³) and the WHO guideline (5 µg/m³). Seasonal variation is pronounced: concentrations peak in the dry winter monsoon, when stagnant meteorology and regional haze dominate, and are lowest during the summer wet season when rainfall enhances wet deposition (Makkonen, Vestenius et al. 2023). Severe pollution episodes have been reported with daily PM_{2.5} exceeding 300 µg/m³ in winter (Nguyen, Nagashima et al. 2020).

Positive Matrix Factorization (PMF) has been widely applied to identify sources of PM_{2.5} in Hanoi. A year-long PMF analysis reported that biomass burning (including crop residue burning and residential fuels) accounted for ~19–20% of PM_{2.5}, secondary inorganic aerosols (sulfate, nitrate, ammonium) for ~25–30%, and traffic-related emissions for ~10–12% (Kim, Pham et al. 2012, Makkonen, Vestenius et al. 2023). Industrial activities and coal combustion contributed an additional ~10%, while mineral dust explained 15–20% depending on season. Recent work combining PMF with oxidative potential (OP) measurements found that sources linked to fossil fuel combustion (residual oil, coal, and traffic) disproportionately drive aerosol toxicity, suggesting that not all PM_{2.5} sources have the same health relevance (Dominutti, Mari et al. 2024).

Chemical transport modeling with CMAQ has been employed to complement receptor-based studies. Nguyen et al. (2020) demonstrated that CMAQ reproduced daily PM_{2.5} variations with good correlation ($R \approx 0.77$) and found that ~50% of wintertime PM_{2.5} originated from regional transport. Local contributions were dominated by household and industrial combustion, which together explained nearly 80% of locally generated PM_{2.5}, whereas traffic and power

generation played relatively minor roles (Nguyen, Nagashima et al. 2020). More recent simulations for 2017–2018 confirmed that transboundary transport contributed 25–60% of PM_{2.5} depending on season, while agricultural burning accounted for up to 28% in post-harvest months. Future scenario analysis indicated that without additional emission controls, wintertime PM_{2.5} could increase by 1–2 $\mu\text{g}/\text{m}^3$ by 2030, leading to hundreds of excess premature deaths annually in Hanoi.

Overall, both PMF and CMAQ studies converge on the conclusion that Hanoi's PM_{2.5} pollution results from a combination of local combustion sources (biomass burning, household fuels, industry, and traffic) and transboundary inflow, with strong seasonal modulation. These findings provide a robust scientific foundation for policy, highlighting the need to reduce open burning and residential fuel use, strengthen industrial emission controls, and coordinate with neighboring regions to mitigate transported pollution.

1.2. Research gap and objectives

Despite a growing body of research on PM_{2.5} pollution in Vietnam, particularly in Hanoi, several critical gaps remain. First, most previous studies have primarily focused on bulk chemical characterization of PM_{2.5} (such as ions, carbonaceous components, and selected metals), whereas a comprehensive screening of organic compounds—including polycyclic aromatic hydrocarbons (PAHs), oxygenated organics, and other trace organics—remains limited. Such information is essential to better understand toxicity and source signatures.

Second, source apportionment studies in Hanoi have relied mainly on receptor models such as Positive Matrix Factorization (PMF) or PCA/APCS, which, although useful, are constrained by their dependence on chemical markers and local measurements. Very few studies have systematically compared receptor modeling results across multiple sites and seasons, which is necessary to capture spatial and temporal variability in emission sources.

Third, while chemical transport models such as WRF–CMAQ have been applied to selected case studies in Hanoi, the application of integrated source apportionment tools (e.g., CMAQ-ISAM) to quantitatively track precursor emissions and secondary formation remains scarce. Furthermore, no systematic effort has been made to validate and compare model-based source attribution with receptor-based methods, which is crucial for reducing uncertainties and guiding effective policy interventions.

Finally, existing studies often examine PM_{2.5} pollution in Hanoi in isolation, without

considering broader emission contexts across Vietnam. A coordinated experimental and modeling approach combining advanced chemical screening, receptor modeling, and chemical transport modeling has not yet been conducted. Addressing these gaps will provide a more comprehensive understanding of PM_{2.5} composition, its sources, and its seasonal dynamics, thereby contributing to both science and policy in air quality management.

The overarching aim of this research is to advance the scientific understanding of PM_{2.5} pollution in Vietnam by integrating experimental analyses with receptor and chemical transport modeling. Specifically, the study pursues three main objectives:

Screening and characterization of organic compounds in PM_{2.5} using AIQS-DB: To apply the Aerosol Inorganic and Organic Compound Screening Database (AIQS-DB) for the identification and quantification of organic species in PM_{2.5}. This approach enables comprehensive screening of polycyclic aromatic hydrocarbons (PAHs) and other organic tracers, providing insights into the chemical composition, atmospheric reactivity, and potential toxicity of organic matter associated with PM_{2.5}.

Source apportionment of PM_{2.5} using receptor modeling (PMF): To apply Positive Matrix Factorization (PMF) for source apportionment of PM_{2.5}, thereby identifying and quantifying contributions from major emission sectors (e.g., traffic, industry, biomass burning, residential activities, and secondary aerosols). Source contributions will be systematically compared across different locations and seasons, highlighting spatial and temporal variability in PM_{2.5} sources.

Simulation and source attribution using WRF–CMAQ–ISAM: To perform numerical simulations with the Weather Research and Forecasting (WRF) model coupled with the Community Multiscale Air Quality (CMAQ) model and its Integrated Source Apportionment Method (ISAM). This will enable the quantification of PM_{2.5} sources, evaluation of secondary aerosol formation, and analysis of long-range transport contributions. Model-derived source contributions will be compared with PMF receptor model results to assess consistency, identify discrepancies, and improve understanding of methodological uncertainties.

1.3. Research extent

This research is designed to provide a comprehensive investigation into the chemical composition and source contributions of PM_{2.5} in Vietnam, with a particular focus on the urban environments of Hanoi. Beyond local policy relevance, the study's scope is meticulously defined to yield significant contributions to the field of atmospheric science, especially concerning

complex urban-regional air pollution regimes in Southeast Asia. As shown in Table 1.1, each dimension of the study directly supports a core scientific objective, from enhancing chemical resolution to validating model consistency.

Table 1. 1. Definition and Scientific Rationale for the PM_{2.5} Source Apportionment Research Scope in Hanoi.

Dimension	Scope Definition	Scientific Implication
Geographical Extent	Field sampling and analysis were conducted primarily in Hanoi (urban traffic site, peri-urban site, industrial site).	Captures spatial heterogeneity and allows for the critical distinction between localized (e.g., traffic hotspots) and widely dispersed regional pollution components.
Temporal Extent	Sampling campaigns covered distinct dry and wet seasons (monsoonal influence).	Enables the assessment of seasonal shifts in source apportionment, particularly the dominant role of transboundary transport during the dry season vs. local emissions during the wet season.
Analytical Extent	Detailed characterization of PM _{2.5} components, including inorganic ions, carbonaceous fractions, trace elements, and 288 distinct organic compounds (PAHs, solvents, pesticides) via the AIQS-DB database.	Provides one of the most chemically comprehensive datasets for PM _{2.5} in Southeast Asia, essential for resolving specific and unexpected sources (e.g., agriculture-related pesticides).
Modeling Extent	Integration of Receptor Modeling (PMF) and Chemical Transport	Ensures a multi-dimensional perspective, using PMF for local empirical validation and CMAQ-ISAM for regional source attribution,

Dimension	Scope Definition	Scientific Implication
	Modeling (WRF–CMAQ–ISAM).	including secondary aerosol formation.
Comparative Extent	Systematic cross-validation and integration of results from PMF and CMAQ-ISAM.	Establishes the reliability and uncertainty bounds of the source apportionment conclusions, enhancing confidence in the policy recommendations derived from the synthesis.

This dissertation provides the following key contributions to the global atmospheric environment research community:

Establishing a Baseline for Complex Urban Organic Aerosols: This is the first study to conduct such an extensive screening and quantification of organic compounds in PM_{2.5} in a major Southeast Asian city. The identification of diverse sources like industrial solvents, plasticizers, and agricultural pesticides provides unique chemical fingerprints for urban environments influenced by rapid, unregulated development and intensive peri-urban agriculture. This advances the understanding of PM_{2.5} complexity beyond standard inorganic analysis.

Advancing Integrated Source Apportionment Methodology: By systematically comparing and synthesizing results from PMF (Observation-based) and CMAQ-ISAM (Physics-based), the research provides a robust template for validating source apportionment methods in environments where both local emissions (Household, Industry) and significant Long-Range Transport (LRT) are dominant. This integration is crucial for reconciling the inherent limitations of each model and setting a higher standard for accountability in air quality studies.

Informing Regional Air Pollution Control Policy: The quantification of Long-Range Transport (LRT) and the high contribution of Household combustion via the CMAQ-ISAM model offers actionable, sectoral data. The findings demonstrate that air quality solutions require a shift from focusing purely on traffic to controlling residential/small-scale combustion and coordinating regional emission controls across borders, which is highly relevant to other developing megacities facing similar transboundary challenges.

In summary, this research not only serves as a comprehensive tool for Hanoi's air quality

management but also provides a methodological blueprint and a unique chemical dataset for atmospheric scientists studying the challenging, hybrid pollution regimes common across rapidly industrializing regions.

1.4. Overview of Thesis Structure

This dissertation is systematically organized into five chapters, designed to address the stated research objectives through a comprehensive, integrated approach. The structure progresses logically from establishing the fundamental context to presenting a robust, cross-validated source apportionment assessment of in Hanoi.

The research follows a three-step integrated methodology based on the established objectives: Chemical Characterization (Chapter 2), Receptor Modeling (Chapter 3), and Chemical Transport Modeling (Chapter 4). This structure is built upon the foundational context of Chapter 1 and culminates in the synthesis of Chapter 5, as visualized in the Table 1.2.

Table 1. 2. Dissertation Structure: Focus, Methodology, and Key Outcome of Each Chapter.

Chapter	Focus	Primary Methodology	Key Outcome
Chapter 1	Introduction and Literature Review		Established the crisis in Hanoi, highlighted the lack of organic screening and model-to-model validation, and defined the necessity of the integrated approach.
Chapter 2	Chemical Characterization	Field Measurements; Advanced Chemical Analysis (e.g., AIQS-DB)	Revealed the exceptional complexity of Hanoi's aerosol, identifying 288 organic compounds (including solvents, plasticizers, and agricultural pesticides), establishing site-specific chemical fingerprints.
Chapter 3	Source Apportionment (PMF)	Positive Matrix Factorization (PMF)	Quantified the source factors based on mass. Concluded that Secondary Aerosols dominate the mass.

Chapter	Focus	Primary Methodology	Key Outcome
			Identified Traffic and showed strong seasonal variability driven by transboundary influence in winter.
Chapter 4	Source Attribution (WRF–CMAQ–ISAM)	WRF–CMAQ–ISAM (Numerical Model)	Attributed mass to specific sectors and regions. Identified Household combustion as the largest local source and Long-Range Transport as the largest imported fraction, providing the policy-specific origins of the pollution.
Chapter 5	Synthesis and Conclusions	Cross-Validation (PMF vs. CMAQ-ISAM)	Validated source findings (e.g., linking PMF factors to CMAQ-ISAM sectors). Provided a robust, evidence-based assessment and targeted policy recommendations for Hanoi's complex anthropogenic sources.

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Chapter 2 - Comprehensive Analysis of Organic Constituents in PM_{2.5}

2.1. Introduction

Due to the rapid urbanization, industrial development and population in big cities in Vietnam, air pollution has become the alarming environmental issue of Hanoi, the capital city. PM_{2.5} is a notable and widespread air pollutant in Hanoi (Cohen, Crawford et al. 2010, Cohen, Crawford et al. 2010, Hai and Oanh 2013, Bootdee, Chantara et al. 2016, Popovicheva, Shonija et al. 2017, Ngoc, Delbarre et al. 2021). The associated health risks, particularly long-term effects on the respiratory and cardiovascular systems, underscore the urgent need for accurate source identification (Baulig, Poirault et al. 2004). PM_{2.5} is a complex matrix, composed of inorganic ions, carbonaceous matter, trace elements, and a vast array of organic compounds. While previous studies have identified major emission sectors contributing to PM_{2.5} mass in Hanoi, including fossil fuel combustion, traffic, and industrial activities, significant knowledge gaps remain concerning the chemical nature and toxicity of the organic fraction.

Recent advances in analytical chemistry, particularly Gas Chromatography–Mass Spectrometry (GC–MS), have revolutionized the detailed screening of trace organic compounds. This study utilizes the Automated Identification and Quantification System Database (AIQS-DB), developed by Kadokami et al. (Kadokami, Tanada et al. 2004, Kadokami, Tanada et al. 2005, Kadokami, Pan et al. 2012, Duong, Kadokami et al. 2019). The AIQS-DB streamlines the identification and quantification of almost 1000 compounds by integrating retention times, calibration curves, and mass fragments based on an internal standard (IS)-based method. This significantly reduces the time, labor, and chemical costs associated with conventional GC-MS, enabling the simultaneous, large-scale screening required for complex environmental samples.

In the present study, such approaches were applied to PM_{2.5} samples collected across Hanoi. A total of 288 compounds from 19 chemical categories were identified, including industrial intermediates, solvents, antioxidants, plasticizers, PAHs, petroleum residues, and pesticides. This dataset represents one of the most comprehensive investigations of airborne organic micropollutants in Vietnam to date. The overarching goal of this chapter is to provide a comprehensive analysis of organic constituents in PM_{2.5} in Hanoi, bridging the knowledge gap between Vietnam and other Asian countries. The specific objectives are to: Characterize the chemical profile of organic micropollutants in PM_{2.5} at three representative sites: Cau Giay (urban traffic), Pho Noi (industrial), and Tay Ho (urban–agricultural).

2.2. Methods

2.2.1. Study site

The study was conducted in Hanoi, Vietnam, a megacity with over 8 million inhabitants and diverse emission sources. To capture the variability of pollution characteristics, three representative sites were selected:

Cau Giay (CG): an urban residential–traffic site located in central Hanoi. This area is characterized by dense road networks, heavy motorbike and car traffic, and limited industrial activities. It is representative of traffic-dominated emissions in the city.

Pho Noi (PN): an industrial zone situated approximately 30 km east of central Hanoi. PN is home to textile dyeing factories, metalworking industries, and chemical processing facilities. It was selected to represent industrial emissions, particularly solvents, intermediates, and plasticizers.

Tay Ho (TH): a mixed urban–agricultural site located around West Lake, one of the largest freshwater lakes in Hanoi. In addition to urban activities, the area is influenced by local horticulture, aquaculture, and small-scale agriculture. The presence of numerous restaurants and tourist boats also makes it a hotspot for agricultural and petroleum-related pollutants.

Thirty air fine particulate matter samples were collected at 3 locations in Hanoi in January 2021 (dry season). At each location, 10 samples were represented 10 consecutive days. Samples were collected for 10 hours from 8 am to 6 pm. Samples are coded in order of collection and sampling location, PN1–PN10 were collected at one location (20°57'04.6"N, 106°01'24.3"E) Pho Noi (PN) industrial zone, where was about 24 km from the center of Hanoi. TH1–TH10 (21°03'57.9"N, 105°49'22.1"E) were in Quang Ba ward, Tay Ho (TH) District, where had numerous agricultural activities including a big flower market. Meanwhile, CG1–CG10 (21°02'12.0"N, 105°47'01.6"E) were located Cau Giay (CG) District, an urban district of the city, where had excessive traffic and population density. A high-volume air sampler (Shibata HV-1000R, Japan) with cut-off PM_{2.5} was used for sample collection at an average flow rate of 15 m³/h (Nguyen, Bui *et al.* 2022). The quartz fiber filters were baked at 550°C for 6h and then stored in a desiccator (48h in desiccators with temperature 25 ± 2°C and relative humidity 50 ± 4 %) before use. The filters were weighed before and after sampling with the same conditions. After weighting, each filter was wrapped in aluminum foil, kept in a polypropylene bag and stored at –20°C until extraction.

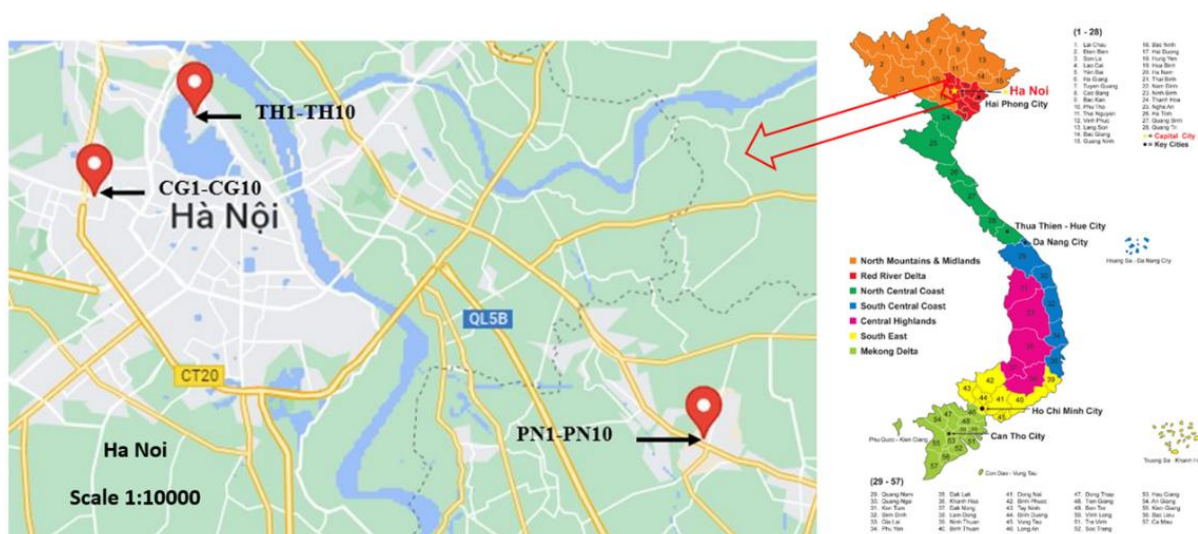


Figure 2. 1. Sampling sites in Hanoi (Cau Giay, Tay Ho, Pho Noi) with the city's location within Vietnam for trace organic analysis

2.2.2. Chemical analysis by GC–MS

Quantitation of the targeted compounds in each sample was conducted using a GC-MS-TQ8040 system (Shimadzu, Kyoto, Japan) in Full Scan Mode and Selected Ion Mode (SIM) equipped with an AIQS-DB which was described in the previous studies (*Kadokami, Tanada et al. 2005, Duong, Kadokami et al. 2015*). A column DB-5MS Ultra Inert (30 m length $\times$ 0.25 mm internal diameter $\times$ 0.25 μ m film thickness, Agilent Technologies) was used in this study. The injector temperature is 250 °C with helium carrier gas at a linear velocity of 40 cm/s. The temperature of interface between MS and GC was 300°C, ion source was setup at 200°C. Column oven temperature was set at 40°C (hold for 2 min) and then increased to 310°C (8°C/min, hold for 5 min). One microliter of each concentration was injected into the gas chromatograph in splitless mode. The method detection limits (MDL) for the substances were estimated from the instrument detection limit (IDL) in the full scan mode as shown in the previous studies (*Kadokami, Tanada et al. 2004, Kadokami, Tanada et al. 2005*). The organic compounds were validated if the retention times and mass fractions matched the data specified in the system and quantified using standard curve data in AIQS-DB.

2.2.3. Quality assurance and quality control (QA/QC)

Quality control was conducted by blank and surrogate recovery analysis. Blank samples were processed after every five samples for cross-verification. Blank concentrations were subtracted from the sample concentrations in the reported data. The accuracy of the method was confirmed by examining the recoveries of 21 surrogates (deuterium-labelled IS), which were spiked to the blank and PM_{2.5} samples and had the same range of broad physicochemical

properties as targeted compounds. Recoveries of 21 surrogates ranged from 80.5% to 121.5%. Relative standard deviations of 21 surrogates were below 20%, which clarified that sample analyses were acceptably precise.

2.3. Results and Discussion

2.3.1. Overview of Organic Micropollutants

The comprehensive GC–MS analysis identified a total of 288 organic compounds belonging to 19 chemical categories in PM_{2.5} samples collected across Hanoi, as shown in Tables 2.1. This broad spectrum demonstrates the chemical complexity of organic aerosols in the city, reflecting its diverse emission sources including traffic, industry, domestic combustion, and agriculture.

Among the identified groups, industrial intermediates and solvents accounted for the largest number of compounds (over 60 species), highlighting the influence of industrial activities such as textile dyeing and chemical manufacturing. Antioxidants and plasticizers, particularly bisphenol A (BPA) and phthalates, were frequently detected and contributed substantially to the total organic load, consistent with the widespread use of plastics and rubber materials.

Polycyclic aromatic hydrocarbons (PAHs) were also ubiquitous, with 23 species detected, including 11 classified as U.S. EPA priority pollutants. The presence of high molecular weight PAHs such as benzo[a]pyrene indicates strong contributions from combustion processes, notably traffic emissions and biomass burning.

A distinctive feature of Hanoi's organic aerosol profile was the significant presence of pesticide residues. More than 100 pesticides were identified, including fungicides, herbicides, and insecticides. Fungicides dominated in terms of both diversity and concentration, especially at the Tay Ho site, where horticultural activities are intensive. Importantly, certain banned or restricted pesticides such as captan and captafol were still detected, albeit at low levels, raising regulatory concerns.

Petroleum residues were another notable group, with concentrations particularly high at Tay Ho due to boat traffic and fuel-related activities on West Lake. This finding underlines the role of localized activities, beyond conventional sources, in shaping the organic PM_{2.5} burden in Hanoi.

Overall, the dataset reveals a hybrid pollution regime:

Pho Noi was dominated by industrial solvents, plasticizers, and intermediates.

Cau Giay showed strong signatures of traffic- and combustion-related compounds.

Tay Ho exhibited a unique combination of agricultural pesticides and petroleum residues.

This overview emphasizes that organic micropollutants in Hanoi's PM_{2.5} are not only diverse in composition but also highly site-specific, mirroring the coexistence of urban, industrial, and agricultural activities. Such chemical complexity differentiates Hanoi from many other Asian megacities and underscores the necessity of integrated air pollution control strategies.

Table 2. 1. Mean concentrations and ranges of PM_{2.5}-bound compounds measured at the three sampling sites in Hanoi: Tay Ho (agricultural), Pho Noi (industrial), and Cau Giay (urban traffic).

Site	Type	Mean Conc. (ng/m ³)	Range (ng/m ³)
Tay Ho (TH)	Agricultural	529.41	90.33 – 794.80
Pho Noi (PN)	Industrial	179.00	41.08 – 163.58
Cau Giay (CG)	Urban traffic	112.13	41.08 – 433.81

2.3.2. Distribution of organic micropollutants in PM_{2.5} by pollutant groups

Tables 2.2 and 2.3 summarize the concentrations of trace organic compounds detected in PM_{2.5}, classified into major pollutant groups in PM_{2.5}.

Table 2. 2. The concentration of trace-organic compounds derived from industry and agriculture (ng/m³)

Category	Intermediate for dyes	PAHs	Solvents	Reagents	Intermediates used in organic synthesis	Intermediates for resin	PCBs	Fungicides	Herbicides	Insecticides
PN1	2.18	1.85	25.72	59.52	0.90	1.27	0.39	27.28	0.34	21.18
PN2	1.38	4.40	22.05	20.91	2.83	1.63	0.29	18.88	0.06	18.98
PN3	1.84	1.94	38.16	48.47	0.91	1.79	0.42	29.87	0.37	10.34
PN4	0.94	0.29	11.56	31.31	0.64	2.16	-	13.39	0.13	15.94
PN5	1.88	0.47	13.00	22.90	0.82	1.40	-	13.43	0.10	8.66
PN6	0.87	0.54	20.95	22.06	0.96	1.77	-	15.61	0.10	3.84
PN7	1.61	0.68	20.51	13.04	0.69	1.35	-	13.13	0.20	6.91
PN8	1.15	0.45	20.75	11.52	0.68	1.05	-	20.11	0.16	9.83
PN9	0.80	0.57	12.62	10.93	0.55	2.07	-	9.92	0.09	8.03
PN10	1.86	0.68	12.55	10.25	0.56	1.87	-	8.43	0.13	3.31
TH1	0.01	0.95	9.26	3.99	1.77	0.02	-	102.40	-	202.45
TH2	0.00	0.75	6.21	2.78	1.08	0.02	0.04	63.65	-	149.34
TH3	0.02	2.88	4.42	1.82	1.52	0.04	0.04	58.41	-	133.33
TH4	-	-	4.36	1.15	0.98	0.22	-	63.02	-	132.30
TH5	-	-	3.22	0.54	0.49	0.19	-	46.41	-	107.17
TH6	-	-	3.72	1.78	2.06	0.17	-	33.28	-	87.06
TH7	-	-	1.93	0.96	1.82	0.11	-	43.68	-	122.55
TH8	-	-	5.66	0.71	0.38	0.21	-	38.70	-	96.12
TH9	-	-	3.17	0.27	0.82	0.09	-	45.17	-	77.37
TH10	-	-	4.06	1.58	1.27	0.05	-	52.15	-	83.81
CG1	1.08	1.26	16.63	32.72	0.54	0.06	0.23	29.65	4.72	9.36
CG2	1.30	1.20	16.74	31.58	0.56	0.83	0.24	32.18	0.12	27.29
CG3	1.00	1.24	13.82	28.99	0.37	0.12	0.20	8.97	0.89	4.83
CG4	1.10	1.87	14.81	21.38	0.36	0.62	0.26	17.11	3.87	22.38

Category	Intermediate for dyes	PAHs	Solvents	Reagents	Intermediates used in organic synthesis	Intermediates for resin	PCBs	Fungicides	Herbicides	Insecticides
CG5	1.32	1.01	22.93	34.60	0.47	0.06	0.23	28.37	0.96	16.19
CG6	0.93	0.66	14.54	20.27	0.51	-	0.22	15.86	0.02	6.19
CG7	1.09	1.49	12.99	25.13	2.07	0.02	0.23	14.73	0.28	8.98
CG8	0.56	1.45	3.27	17.16	0.08	-	0.11	3.46	0.88	2.11
CG9	0.71	0.67	9.24	13.38	0.24	0.03	0.24	10.59	0.06	11.05
CG10	0.44	0.23	5.12	5.67	0.11	0.08	0.00	5.33	-	3.31

Table 2. 3. The concentration of trace-organic compounds originated from business/household/traffic (ng/m³) and total trace organic compounds (ng/m³)

Category	Antioxidants	Cosmetics	Disinfectants	Fatty acid methyl ester	Fragrances	Leaching from tires	Petroleum	Plastics materials	PPCPs	Total trace organic compounds
PN1	2.5	0.1	0.3	4.2	1.5	4.2	158.7	21.9	35.7	163.6
PN2	4.1	0.5	0.1	9.5	1.2	2.8	21.0	35.5	3.2	158.9
PN3	2.2	0.2	0.2	4.6	0.8	5.0	149.3	17.3	32.2	72.5
PN4	2.1	-	0.1	2.3	0.1	0.2	32.6	2.5	22.8	132.2
PN5	2.8	0.1	0.1	2.3	0.2	0.4	33.5	2.2	12.0	142.9
PN6	1.6	-	0.2	2.9	0.2	0.2	35.7	2.4	22.7	86.6
PN7	1.7	-	0.0	3.1	0.3	0.3	34.2	2.2	23.7	114.9
PN8	1.9	0.2	0.2	2.6	0.3	0.3	32.3	3.0	13.0	41.1
PN9	3.2	-	0.1	2.3	0.2	0.3	26.6	2.3	13.6	96.7
PN10	0.6	-	0.1	3.3	0.3	0.4	30.3	1.9	13.9	45.2
TH1	0.7	5.6	1.9	26.7	1.8	2.8	419.7	11.2	3.4	369.7
TH2	2.4	0.1	0.3	24.3	1.3	1.2	460.3	16.1	27.3	170.7
TH3	2.4	-	0.5	30.4	0.9	0.7	456.1	25.4	27.3	346.0

Experimental and Numerical Investigation of PM_{2.5} Source Contribution in Hanoi, Vietnam

Le Huong Quang

Doctoral Dissertation

December 2025

Category	Antioxidants	Cosmetics	Disinfectants	Fatty acid methyl ester	Fragrances	Leaching from tires	Petroleum	Plastics materials	PPCPs	Total trace organic compounds
TH4	0.4	-	0.1	18.5	3.1	1.1	265.0	7.5	11.7	139.0
TH5	0.4	-	0.0	12.6	3.4	1.1	298.5	13.9	22.5	116.3
TH6	0.2	-	0.1	6.3	1.6	2.1	270.7	14.2	10.4	132.5
TH7	0.6	-	0.2	14.0	0.5	1.9	287.2	6.5	6.0	123.7
TH8	0.5	-	0.1	16.9	1.2	2.0	262.5	3.5	5.4	119.3
TH9	0.4	-	0.2	7.5	1.4	2.3	280.8	3.7	6.2	94.1
TH10	0.4	-	0.1	7.5	1.2	1.0	216.8	5.3	2.8	90.3
CG1	3.1	0.2	3.8	2.6	1.0	1.8	34.1	17.7	1.7	794.8
CG2	1.7	0.1	0.1	5.8	1.1	1.7	18.5	16.2	1.0	757.9
CG3	0.1	0.0	0.1	0.3	0.4	1.4	5.1	2.3	2.4	746.4
CG4	0.1	0.2	0.1	1.3	0.7	1.6	26.6	10.8	5.8	509.3
CG5	1.1	0.1	0.1	6.3	1.1	2.2	13.8	9.5	1.4	510.6
CG6	0.8	0.1	0.1	4.8	0.7	1.1	11.7	7.2	0.7	433.7
CG7	1.0	0.1	0.1	1.7	0.6	1.2	27.1	9.6	5.6	487.9
CG8	0.1	-	0.0	0.2	0.3	1.6	4.2	3.3	2.3	433.8
CG9	1.8	0.2	0.2	4.3	1.1	1.4	29.9	11.1	0.5	429.2
CG10	0.6	0.0	0.1	0.8	0.2	1.0	16.2	5.7	0.2	378.0

- Intermediates

Intermediates can be generated via industrial activities. In this study, 26 intermediates were found in 30 PM_{2.5} samples, which involved dyes, fibers, resins, and organic synthesis processing in Table 2.2. Chemicals for dyeing included one quinolone, one anthraquinone, and three aniline derivatives, all with concentrations less than 1.88 ng/m³. While 2,7-dimethyl quinolone was found in samples collected in CG and PN sites, benzanthrone was detected only in CG7 at a concentration of 0.05 ng/m³. Benzanthrone could be generated by military activities in the sampling area that can release trace amounts of this compound

Sixteen organic synthesizing by-products were detected in the samples. Total concentrations of these pollutants in samples ranged from 0.08 to 2.83 ng/m³ (Table 2.2), and the number of detected compounds per sample varied from 1 to 30. Hexachloroethane was detected in all samples at concentrations ranging from 0.04 to 0.64 ng/m³ whereas 2-naphthol was detected only in PN2 at 0.11 ng/m³. Hexachloroethane is a by-product of chemical production that may cause skin irritation and kidney damage (Smith-Simon, Donohue et al. 1997). Four compounds relating to resin processing and one by-product of fiber production were detected. Epsilon-Caprolactam, a material used to produce fiber, was detected at approximately 0.50 ng/m³ in PN2, TH2, and CG1 whereas concentrations were much lower in other samples. Among four resin intermediates, 4-tert-butylphenol was identified in 28 of 30 samples.

The highest concentration of 4-tert-butylphenol was 0.50 ng/m³ in PN2, whereas the concentrations were ≤ 0.05 ng/m³ in other samples. N-butyl acrylate was detected in 14 samples. The samples collected in PN contained the highest contents of this compound at up to 2.11 ng/m³. The detection of this compound in PN was reasonable, because several textile and garment development activities took place in this area. The concentrations in four other samples varied from 0.01 to 0.80 ng/m³. Similarly, 2,6-dimethylphenol was detected in only three samples at approximately 0.01 ng/m³. Whereas 3-methoxy-1-butyl acetate was detected only in CG3 at 0.08

- Solvents and reagents

Eight solvents and nine organic reagents were detected in the samples. Hexachlorobutadiene, a solvent for chlorinated compounds or protective coatings, was the highest content among solvent pollutants and detected in all 30 samples. Sixteen samples contained hexachlorobutadiene concentrations higher than 9 ng/m³. The highest concentrations were 34.08, 39.88, and 36.54 ng/m³ in PN1, PN2 and PN3, respectively (Table 2.3). Several waste-treatment facilities located in the PN industrial park, and the incineration of chlorinate-

containing products led to hexachlorobutadiene emissions (Wang, Bie et al. 2018). In contrast, TH1–TH3 samples showed the lowest hexachlorobutadiene concentrations at approximately 1 ng/m³.

Ethyl carbamate, a major reagent pollutant, showed trends similar to hexachlorobutadiene. PN1 had the highest contents of the compound at 59.02 ng/m³, followed by PN3 at 47.91 ng/m³; the lowest concentrations were found in TH and CG samples. Ethyl carbamate is used in the textile industry as a cross-linker for permanent pressing textile treatments to create “wash-and-wear” fabric, resulting in high concentrations in PN area.

Among other reagents, N-nitroso-di-n-butylamine and N-nitrosopiperidine were detected in 21 and 20 samples, respectively. Dibenzyl ether, 1-Acetoxy-2-methoxyethane, were also detected in about five samples.

- Antioxidants

Antioxidant contents ranged from 0.04 to 4.11 ng/m³ in the samples (Table 2.3). The concentrations of 2,6-di-tert-butyl-4-benzoquinone was detected ranged from 0.03 to 0.33 ng/m³ in all samples. In several samples, 2-tert-butyl-4-methoxyphenol, 4-methyl-2,6-di-t-butylphenol, 3,5-di-tert-butyl-4-hydroxybenzaldehyde, and N-phenyl-2-naphthylamine were detected at concentrations ≤ 0.65 ng/m³. These compounds are commonly generated by diesel combustion (Schuetzle, Lee et al. 1981). Significant differences in bisphenol A (BPA) concentrations were detected among samples. BPA was detected at concentrations ≥ 1.4 ng/m³ in 26 samples, reaching levels up to 3.03 ng/m³ in PN2; however, it was not found in TH1, CG3, CG4, and CG8. BPA is released into the atmosphere via the combustion of plastics and has potential hepatotoxicity, neurotoxicity, and immunotoxicity, even at low concentrations. Meanwhile, inhaling the other detected antioxidants, such as phenols, benzaldehyde, and benzoquinone derivatives, may cause headaches, nausea, or sore throat (Duong, Kadokami et al. 2019).

- Nonionic detergent metabolites and disinfectants

One non-ionic detergent metabolite and three disinfectants were detected in PM_{2.5} samples. The highest concentration of 4-tert-octylphenol, a non-ionic detergent, was detected in sample PN2 at 0.35 ng/m³, followed by CG9 and CG1 at 0.18 and 0.12 ng/m³, respectively. Among three aromatic disinfectants, the highest content was 3.78 ng.m-3 in CG1, followed by 1.91 ng/m³ in TH, whereas the lowest content was observed in CG8 at 0.03 ng/m³. The previous report did not detect these pollutants in atmospheric particulate matter in Hanoi (Duong, Kadokami et al. 2019). 98% of 4-tert-octylphenol is used in the manufacture of octyl phenol-

formaldehyde resins for tire rubber, insulation paint, printing inks, etc (Nyström 2018). This compound has the ability to bioaccumulate and is one of the compounds capable of causing hormonal disturbances, greatly affecting reproductive function (Calafat, Ye et al. 2008) .

- PAHs

Twenty-three constituents of PAH were detected in the samples. Phenanthrene and pyrene were detected in every sample, and 10 other PAHs were found in at least 10 samples. The total PAH concentrations ranged from 0.29 to 4.40 ng/m³ in Table 2.4. We detected 11 PAHs listed as high-priority PAH pollutants by the United States Environmental Protection Agency (EPA), namely, acenaphthylene, anthracene, benzo[a]pyrene, benzo[ghi]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, fluoranthene, indeno[1,2,3-cd]pyrene, perylene, phenanthrene, and pyrene.

Table 2. 4. Pyrogenic index values and methyl phenanthrene to phenanthrene (MP/P) ratios of polycyclic aromatic hydrocarbons detected in PM_{2.5} samples collected in Hanoi, Vietnam.

Location	PI index	MP/P
PN1	1.453	1.284
PN2	1.025	0.079
PN3	0.790	0.668
PN4	0.590	-
PN5	0.913	-
PN6	0.888	-
PN7	0.989	-
PN8	0.530	-
PN9	1.564	-
PN10	1.544	-
TH1	0.165	2.619
TH2	0.486	2.381
TH3	0.368	0.324
TH4 - TH10	-	-
CG1	1.164	0.810
CG2	0.392	1.001
CG3	0.197	0.000
CG4	1.110	0.403
CG5	1.979	1.902
CG6	1.116	1.417
CG7	2.124	0.776
CG8	0.130	-
CG9	0.838	-
CG10	-	-

Diagnostic ratios can be used to predict PAH sources. The Pyrogenic Index (PI) is an effective indicator to differentiate pyrogenic and petrogenic PAHs in Table 2.4. The PI index is defined as the ratio of total of three- to six-ring EPA priority PAHs to five alkylated PAHs, including homolog series of naphthalene, phenanthrene, dibenzothiophene, chrysene, and fluorene (Wang*, Yang et al. 2008). PI values less than 0.05 indicate petrogenic sources, whereas PI values between 0.13 and 2.12 indicate pyrolytic sources. The PI values and methyl phenanthrene to phenanthrene (MP/P) ratios of all samples are shown in Table 2.4. The MP/P ratios were ≤ 2 in most samples (excluding TH1 and TH2), suggesting the PAHs likely originated from the combustion of fossil fuels and other materials. Increases of traffic and industrial activities in Hanoi before the Lunar New Year may be contributing to high PAH levels, which have been reported to significantly increase during festivals (Bootdee, Chantara et al. 2016).

- Plastics

Thirteen pollutants originated from plastics were detected in the samples, at concentrations ranging from 2.31 to 35.45 ng/m³ in Table 2.4. Total plastic additives concentrations were higher in the industrial and agricultural areas (PN and TH) than CG, an urban area; PN2 had the highest content at 35.45 ng/m³. Phthalates were the major plastic additive pollutants in PM_{2.5} samples, and six phthalate derivatives were detected. Moreover, di-iso-butyl phthalate, di-n-butyl phthalate, and bis(2-ethylhexyl)phthalate were detected in all 30 samples, with concentrations ranging from 0.10 to 19.88 ng/m³ (median: 1.69 ng/m³). These compounds have been used in Vietnam to plasticize products commonly (Bekö, Weschler et al. 2013). The processing, use, and disposal of plastic products are the main source of phthalates in PM_{2.5}. Additionally, three alkylated phenols, two fatty acid esters, and two phosphate derivatives were identified.

- Petroleum

The concentrations of petroleum were particularly high in the TH samples. The concentrations in TH1–TH10 ranged from 216.8 to 460.3 ng/m³ in Table 2.2. In TH area, there is a big lake, namely West Lake (5.3 km²), where has a lot of tourist ships and floating restaurants. The commercial activities and vehicle parking lead to the release of petroleum compounds because fuel is not burned at suitable temperatures (Abbasi, Keshavarzi et al. 2019). Following TH, the total petroleum concentrations of PN samples were in a range of 21.00–158.70 ng/m³ (Table 2.3). There are two highways crossing this area. Petroleum transportation equipment, waste burning, and coal are the main contributors to pollution in this area. The vigorous operation

of industrial zones without emission regulations results in high levels of pollution. The total petroleum concentrations were lowest in CG with a range of 4.2–34.1 ng/m³ in Table 2.3. These petroleum emissions are mainly caused by traffic activities (Kao, Hsiang et al. 2018). The dust particles under the road accumulate these compounds, and air mixing caused by high traffic activities mixes these pollutants with the dust in the air.

- Agricultural pollutants

One hundred and four pesticides were detected in the PM_{2.5} samples. In a research report on pesticides within 10 years commented on the increase in pesticide use in Vietnam and show that many banned substances are still detected in agricultural products and have been found mixed into other pesticides (Anh Le and Quynh Linh 2020). Total pesticide concentrations in samples from agricultural zones (TH1–TH3) were significantly higher than in urban areas (CG1–CG9).

The highest total fungicide contents were found in TH, which varied in concentration from 33.3 to 102.4 ng/m³. PN1–PN3 and CG1; CG2; CG5 samples contained approximately 30 ng/m³, whereas the values in the other urban area samples (CG2–CG9) were less than 20 ng/m³. Similarly, insecticide and pesticide contents in TH1–TH3 samples were much higher than in the PN industrial area samples, and the urban areas had lower contents of these pollutants. Interestingly, herbicides were not detected in TH1–TH3 samples from agricultural areas and the highest herbicide content was detected in CG1 at 4.71 ng/m³. Six herbicides including mefenacet, etobenzanid, cafenstrole, pyridate, pyrazoxyfen and flumiclorac-pentyl were detected in at least one sample, all of which are permitted by Vietnam Ministry of Agriculture and Rural Development (VMARD) (Dung and Sharma 2017). The concentration of each herbicide was mostly < 1.00 ng/m³, except for flumiclorac-pentyl in CG1 (3.51 ng/m³) and pyrazoxyfen in CG4 (3.58 ng/m³).

Sixty-three insecticides were detected, includes many compounds banned by VMARD. The previous study detected 30 pesticide compounds in PM_{2.5} samples in Spain (Coscollà, Yusà et al. 2009). Dieldrin showed the highest contents at 202.5 ng/m³ in TH1, whereas those concentrations were ≥30 ng/m³ in TH2-TH9. Among permitted insecticides, fenprothrin and spiroticlofen were the most common, found in 28 and 30 samples, respectively. This finding differs from a previous report, in which propargite, imidacloprid, and omethoate were the most common insecticides (Duong, Doan et al. 2021). The difference may be attributed to different sampling periods and analytical methods.

Thirty-five fungicides were identified in the samples, among which captan and captafol were banned by VMARD. Captafol was found at 0.06 ng/m³ in only one sample (CG9), and captan was detected at 0.11–0.2 ng/m³ in four samples. Chloroneb and triadimenol II were the most common fungicides, observed in 21 of 30 samples. Oxpoconazole-fumalate was observed in the highest concentrations at 45.39, 43.43, and 44.80 ng/m³ in TH1, TH2, and TH3, respectively, and other samples contained the compound at ~30 ng/m³.

2.4. Conclusions

Utilizing GC-MS with the AIQS database, 288 compounds belonging to 19 pollutant groups were detected in PM_{2.5} samples collected in 3 areas of Hanoi. Furthermore, the differences in the types of pollutants among urban, agricultural, and industrial areas were apparent. Pesticides were specific to the pollution in the agricultural zone, whereas higher concentrations of chemicals used in manufacturing and other industrial processes comprised the majority of pollutants in the industrial zones. The pollution levels in the urban central district were lower than in other areas. The current study provides a more comprehensive picture of atmospheric PM_{2.5} pollutants in the capital city of Vietnam, demonstrating an advanced approach for analyzing a large number of compounds in environmental samples. The obtained results illustrate the first baseline data on the organic pollution in fine particulate matters in Hanoi. The variety of organic micropollutants found in this study implies further investigations to clarify their source apportionments

References – Chapter 2

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Chapter 3 - Source Apportionment of PM_{2.5} Using PMF: Seasonal and Spatial Comparison

3.1. Introduction

The persistently high levels of PM_{2.5} in Hanoi, reflected in the city's average concentration of 43.7 µg/m³ in 2023 (Nguyen, Fukuda et al. 2024) and Vietnam's low ranking on global environmental indices (Nguyen, Tran et al. 2023), underscore an urgent public health and regulatory crisis. The complex physicochemical diversity of PM_{2.5} attributed to a multitude of anthropogenic sources—including industrial zone operations, open combustion of crop residues (Truong 2024), heavy traffic, and domestic activities—makes tracing the origin of these particles exceptionally challenging (Mirakovski, Zendelska et al. 2024).

Effective air quality policy depends critically on source apportionment—the quantitative determination of mass contributions from specific emission sectors. To this end, the Vietnamese government has implemented numerous policies, such as the promotion of environmentally friendly technologies and the completion of public transportation networks, aiming to mitigate pollution (Dieu, Phuong et al. 2020). However, the success of these strategies hinges on accurate and updated source data.

Various analytical and modeling approaches have been employed globally to assess PM_{2.5} sources, ranging from simple source list methods to complex Chemical Transport Models (CTMs). Among the Receptor Models, the Positive Matrix Factorization (PMF) model stands out as the most widely accepted and recommended tool by regulatory bodies such as the U.S. Environmental Protection Agency (EPA). PMF mathematically decomposes the matrix of observed pollutant concentrations into two non-negative matrices—source contribution and source profile—allowing for the identification and quantification of pollution sources *without* requiring *a priori* knowledge of their chemical fingerprints (Howlett-Downing, Boman et al. 2024, Van der Westhuizen, Howlett-Downing et al. 2024)

Previous PMF studies in Hanoi have established a foundational understanding of PM_{2.5} sources, identifying contributions from traffic, dust, biomass burning, and both local and long-range transported secondary aerosols (Hien et al., 2021; Makkonen et al., 2023). However, these studies often lacked the chemical resolution needed to differentiate highly mixed urban sources, particularly the contribution of specific organic micropollutants.

3.2. Methodology

3.2.1. Description of Sampling Sites

Hanoi (Vietnam) is a highly populated city with the demand for transportation predominantly characterized by motorcycles and personal cars. In Hanoi, there are 13 types of vehicles, with a high traffic density of approximately 75 vehicles per minute passing through intersections.(Vu, Thai et al. 2025). Domestic activities, such as waste burning and coal combustion, are also prevalent. Most key industrial zones are located on the outskirts. Moreover, small and medium-sized agricultural areas, including rice and corn fields, have developed. The weather in Hanoi is characterized by a tropical monsoon climate with distinct seasons: the main winter (November to January), the main summer (May to July), and two transitional seasons, spring (February to April) and autumn (August to October). During the winter, the area is affected by high-pressure systems moving down from the north, resulting in a significant drop in temperature. Meteorological conditions , along with the diverse terrain and varied topography, contribute to the complexity of air pollution emission patterns in Hanoi (Geng, Hu et al. 2024).

Table 3. 1. The details of the geographical coordinates and precise time of outdoor dust samples.

No.	Sampling site	Location	Season	Sample ID	Note
1	HQV	21°02'54"N; 105°48'10"E	Spring Summer Autumn Winter	1-31 32-61 62-91 92-122	On the roof of the A28 building at the Vietnam Academy of Science and Technology building at a height of 30 meters and a distance of 100 meters from Hoang Quoc Viet Street.
2	NT	20°59'47"N; 105°48'30"E	Spring Summer Autumn Winter	123-153 154-183 184-213 214-244	On the roof of Hanoi University of Sciences building at a height of 15 meters and a distance of 50 meters from Nguyen Trai Street.

The high-volume air sampler (HV-1000, Sibata, Japan) was used for outdoor air sampling, with a pump rate of 1000 L/min. Table 3.1 provides details on the collecting of samples. PM_{2.5} samples were continuously collected on a daily basis during seasonally representative months in Hanoi in 2022, specifically March for spring, June for summer, August for autumn, and December for winter. Paired samples were simultaneously collected at the HQV and NT sites from 8 a.m. to 6 p.m., aligning with the typical working hours of local inhabitants. This timeframe coincides with the period when individuals are most susceptible to PM_{2.5} exposures, particularly those engaged in outdoor occupations(Chapter 2). The chemical

characterization presented in Chapter 2 indicates that organic components constituted a relatively minor fraction of PM_{2.5} mass during the study period, whereas inorganic species dominated the aerosol composition. In addition, the three sampling sites employed in Chapter 2 were selected to represent three characteristic emission regimes of the study area, providing a broad depiction of PM_{2.5} chemical variability under different source influences. Based on these findings, Chapter 3 moves from a descriptive compositional analysis to receptor-based source apportionment using Positive Matrix Factorization (PMF). To ensure sufficient data robustness for PMF analysis under conditions of low organic mass, the source apportionment in Chapter 3 focuses on two fixed receptor sites, HQV and NT, which capture contrasting urban traffic-influenced and background/suburban environments. This targeted site selection allows for a more reliable identification and comparison of PM_{2.5} sources under representative emission conditions identified in Chapter 2.

3.2.2. Methodology and Data Preparation

The water-soluble inorganic ions (Li^+ , Na^+ , K^+ , Mg^{2+} , NH_4^+ , Ca^{2+} , F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and PO_4^{3-}) were analyzed based on the standard EN 16913:2017b using ion chromatography with a conductivity detector (ICS-6000, Thermo Scientific, USA). The metal content was analyzed using the inductively coupled plasma mass spectrometry (iCAP-TQ system, Thermo Scientific, USA) under conventional conditions (Nishita-Hara, Nakano et al. 2024).

Quartz filter papers (20.3×25.4 cm, GB100R-810A, Advantec) used for collecting samples were pre-conditioned by being heated at 450°C in a furnace for 6 hours, followed by cooling and storage in a desiccator at 25°C with a humidity content less than 40% for at least 1 day. Subsequently, it was weighed on an analytical balance having a readability of 10 µg to determine weight before sampling as in EPA's 40 CFR Appendix O to Part 50 method (Gilliam and Hall 2016). The filter paper was stored in a zip-lock bag and placed in the dehumidifying cabinet (AD-50C, ANDBON, Taiwan). Samples were collected using these quartz filter papers installed in the HV-1000. The collected sample was stored in a desiccator under the same conditions for at least 2 hours and then weighed on a 6-digit analytical balance to determine the weight of PM_{2.5}. The filter paper after sample collection was divided into four parts for different purposes. The first one was placed in a 50-mL falcon tube containing 25 mL of deionized water and then sonicated for 2 hours. After sonication, the solution was filtered through a 0.45-µm membrane and analyzed by ion chromatography. The second one was placed in a Teflon vessel containing 5 mL of concentrated HNO₃, 2 mL of H₂O₂ and 1 µg internal standard (⁶Li, Bi, Ho,

In, Sc, Tb, Y, Rh) which was then digested for 40 min in a microwave digestion system (MAR SX 6, CEM, Matthews, NC). After that, the digestion solution was cooled to ambient, filtered, and rinsed through a quantitative filter with deionized water to a volume of 50-mL. Analysis was performed on the inductively coupled plasma mass spectrometry system. Blank samples are analyzed in each batch, and their values must be below the instrument's detection limit. The QA/QC of metal analysis is assessed through the recovery efficiency of the internal standard. The recovery efficiencies of eight internal standards in the samples ranged from 83.54% to 96.33%, meeting the required criteria for method accuracy. To ensure quality control in the analysis of water-soluble inorganic ions, each batch includes spiked samples (with known concentrations added) and repeat samples (duplicates of the same sample). The recovery of spike samples ranged from 86.7% to 104%, while the relative standard deviation (RSD%) of duplicate samples varied between 2.5% and 4.4%, all of which are within acceptable limits for analytical precision. (Paez, Barrett et al. 2016). The remaining two samples were sealed in zip-lock bags and stored in a deep freezer at approximately -20°C .

3.3. Results and Discussion

3.3.1. Overview of meteorological conditions and PM_{2.5} concentrations

The correlation between meteorological parameters and PM_{2.5} concentrations is illustrated in Figure 3.1. Hanoi's annual temperature most frequently ranged between 25–30 °C (35%). Elevated temperatures likely accelerated the reaction kinetics governing photochemical and secondary aerosol formation. Cooler temperatures (15–20°C), often observed at the onset of the monsoon, may have been associated with dust transport from external sources, while the lowest range (10–15°C) appeared under stable conditions. Humidity levels remained high throughout the year, exceeding 70% in approximately 68% of observations. While rainfall-related high humidity contributed to wet deposition and PM_{2.5} reduction (Cheng, He et al. 2015), moderate humidity (60–70%) was associated with increased PM_{2.5} concentrations due to reduced volatility (Wang, Zhang et al. 2019). Wind also influenced PM_{2.5} levels by enabling regional transport. Wind speeds were mainly in the range of 2.0–2.5 m/s, which supported pollutant dispersion and local concentration reduction (Li, Shi et al. 2023). Atmospheric pressure generally varied between 1000 and 1020 hPa, with low-pressure systems (21–23% occurrence) promoting vertical air movement and pollutant dispersion, thereby reducing PM_{2.5} concentrations.

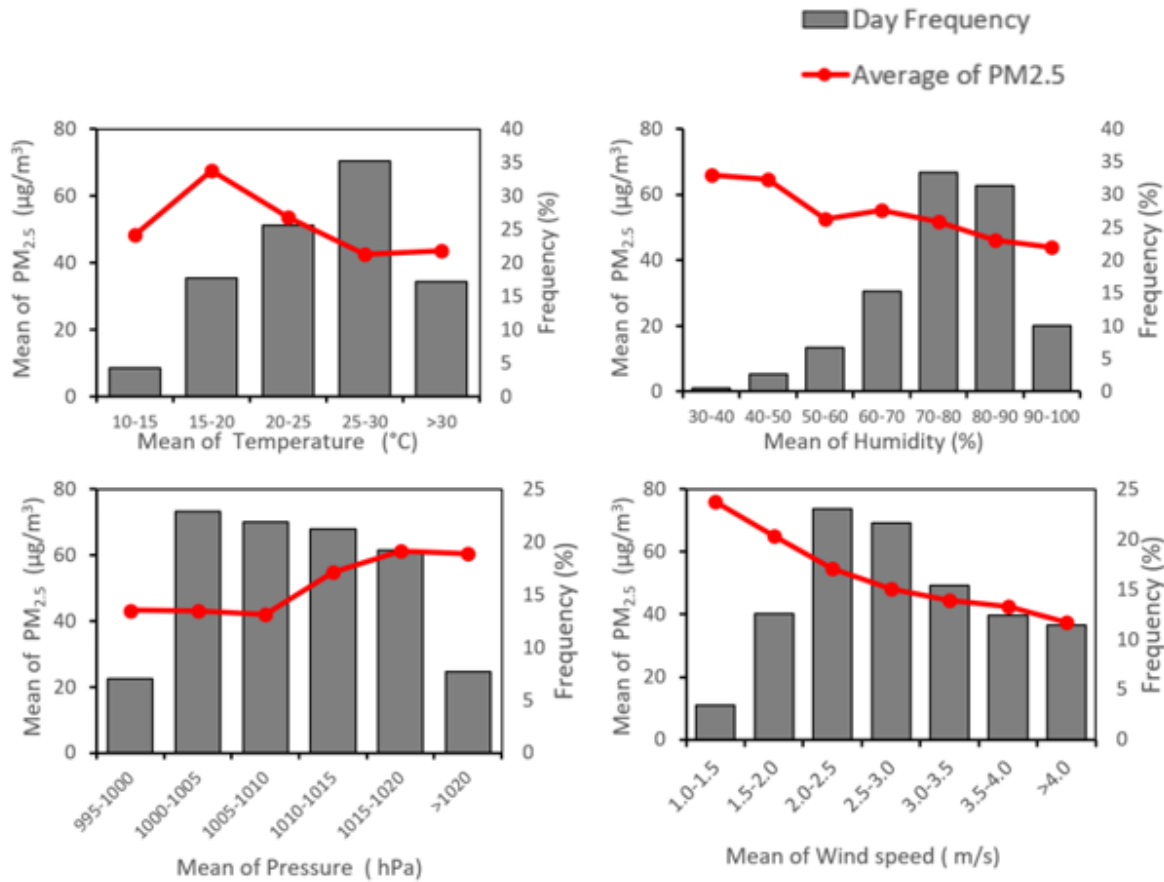


Figure 3. 1. Frequency Distribution and Correlation of PM_{2.5} Concentrations with Meteorological Parameters at the HQV and NT sites in Hanoi during 2022

The average PM_{2.5} concentration was approximately 60 μg/m³, which is more than twice the national limit defined in the "National Technical Regulation on Ambient Air Quality" (QCVN 05:2023/BTNMT, 25 μg/m³ and twelve times higher than the WHO guideline (5 μg/m³) (Organization 2021). In 2022, the average PM_{2.5} concentration was also higher than that recorded from February to March 2021 (41 μg/m³) (Bui, Nguyen et al. 2023), as well as levels at traffic sites (49 μg/m³) and the city center (46 μg/m³) from August 2019 to July 2020 (Makkonen, Vestenius et al. 2023). In this study, the total proportion of quantified compounds in PM_{2.5} samples ranged from 22% to 78% at HQV and from 18% to 82% at NT, indicating notable variability in chemical composition across sampling sites. As shown in the pairwise comparisons, despite the relatively short distance of 10 km between HQV and NT, statistically significant differences in annual PM_{2.5} levels were observed (p-value = 0.000). These results underscore the pivotal role of geographic location in shaping ambient PM_{2.5} distribution patterns.

3.3.2. The characteristics of chemical compositions in PM_{2.5}

3.3.2.1. Seasonal variation in chemical patterns

The average concentrations of PM_{2.5} compositions and their correlations with PM_{2.5} mass concentration by season are presented in Table 3.2. Overall, the concentrations of components tended to increase with a rise in PM_{2.5} concentration. The concentrations of chemical components are highest in the winter, followed by spring, summer, and autumn. The concentrations of SO₄²⁻ and NO₃⁻ were predominant in samples collected during winter and spring, with SO₄²⁻ concentrations slightly higher than those of NO₃⁻. This is because low humidity hinders NO₃⁻ condensation in PM_{2.5} (Li, Zhang et al. 2020). The chemical conversion of SO₄²⁻ in the atmosphere is faster than that of NO₃⁻, because (NH₄)₂SO₄ has better stability than NH₄NO₃ in atmosphere (Lai, Zou et al. 2007, Wang, Du et al. 2013).

Table 3. 2. The average composition and correlation with PM_{2.5} by season

Mean (μg/m³)

R: Correlation with PM_{2.5} concentration

Species	Year (n=244)		Spring (n=62)		Summer (n=60)		Autumn (n=60)		Winter (n=62)	
	Mean	R	Mean	R	Mean	R	Mean	R	Mean	R
PM_{2.5}	59.8 ± 22.5	1.0	55.5 ± 11.9	1.0	46.8 ± 6.8	1.0	48.4 ± 37.8	1.0	87.8 ± 28.4	1.0
Cl	1.4 ± 0.6	0.77	1.1 ± 0.2	0.84	0.5 ± 0.76	0.88	1.6 ± 1.8	0.92	2.3 ± 1.21	0.80
NO₃	6.8 ± 3.9	0.78	8.9 ± 1.01	0.90	4.3 ± 1.99	0.62	6.0 ± 4.2	0.88	8.00 ± 3.6	0.95
SO₄	8.3 ± 3.4	0.82	9.0 ± 1.76	0.89	7.5 ± 2.75	0.83	6.9 ± 5.9	0.86	9.7 ± 3.9	0.91
NH₄	4.6 ± 2.3	0.83	5.5 ± 0.83	0.89	3.7 ± 1.45	0.89	3.9 ± 3.13	0.89	5.5 ± 2.3	0.93
Na	1.1 ± 0.7	0.82	0.9 ± 0.38	0.80	1.0 ± 0.48	0.69	0.8 ± 1.10	0.83	1.8 ± 0.8	0.80
Mg	0.04 ± 0.02	0.70	0.03 ± 0.02	0.89	0.04 ± 0.02	0.83	0.04 ± 0.02	0.92	0.05 ± 0.02	0.95
Al	0.3 ± 0.1	0.40	0.2 ± 0.22	0.83	0.5 ± 0.2	0.68	0.3 ± 0.3	0.91	0.3 ± 0.2	0.66
K	1.0 ± 0.4	0.69	0.6 ± 0.76	0.89	1.0 ± 0.5	0.85	1.1 ± 0.7	0.84	1.2 ± 0.6	0.95
Ca	1.1 ± 1.3	0.33	1.4 ± 0.62	0.61	1.1 ± 0.5	0.75	1.2 ± 0.5	0.95	0.8 ± 0.8	0.94
Ti	0.05 ± 0.02	0.40	0.04 ± 0.03	0.85	0.07 ± 0.02	0.80	0.04 ± 0.03	0.91	0.04 ± 0.03	0.54
Mn	0.3 ± 0.2	0.75	0.3 ± 0.14	0.84	0.2 ± 0.2	0.85	0.3 ± 0.4	0.81	0.6 ± 0.3	0.65
Fe	1.9 ± 1.3	0.85	2.1 ± 0.72	0.88	1.3 ± 1.1	0.84	1.6 ± 1.7	0.84	2.6 ± 1.4	0.95
Cu	0.6 ± 0.5	0.75	0.7 ± 0.67	0.88	0.6 ± 0.3	0.79	0.2 ± 0.6	0.70	0.9 ± 0.6	0.83
Zn	0.5 ± 0.1	0.65	0.3 ± 0.60	0.95	0.8 ± 0.2	0.91	0.3 ± 0.5	0.86	0.8 ± 0.5	0.87
Pb	0.03 ± 0.01	0.54	0.02 ± 0.03	0.96	0.05 ± 0.02	0.88	0.02 ± 0.02	0.78	0.04 ± 0.03	0.90
ΣMetals	7.0 ± 4.0	0.86	6.5 ± 3.6	0.92	6.5 ± 3.3	0.93	6.0 ± 3.3	0.90	9.1 ± 4.2	0.99

The concentrations of SO₄²⁻ and NO₃⁻ were predominant in samples from autumn at the HQV location. The high temperatures during these months also hinder the formation of NO₃⁻ and SO₄²⁻ in the atmosphere (ChooChuay, Pongpiachan et al. 2020). Based on the results in Table 3.2, the comparison of paired values for HQV and NT in 2022 shows that only NO₃⁻ at the two sampling points exhibits a similar trend and results (p-value = 0.602), while Cl⁻, SO₄²⁻, Metals all have values close to zero, and NH₄⁺ shows p-value of 0.002 (Dahiru 2008). This indicates that

the atmospheric processes responsible for NO₃⁻ formation are likely analogous at the two locations. As a result, the temporal fluctuations in the concentrations of these compounds provide valuable insights into the variations in the emission sources of PM_{2.5} in Hanoi across different seasons, depending on the chemical compositions.

3.3.2.2. The correlation between components and PM_{2.5} concentrations

The correlation between the chemical compositions and PM_{2.5} concentration is ranged from 0.61 to 0.99 (Table 3.2). The correlation values for different seasons are as follows: Spring (0.61–0.96); Summer (0.62–0.93); Autumn (0.70–0.95); Winter (0.66–0.99) and the whole year (0.40–0.86). The mean concentration of NH₄⁺ in this study ($4.6 \pm 2.3 \mu\text{g}/\text{m}^3$) is higher than that in previous studies in Hanoi: $2.53 \mu\text{g}/\text{m}^3$ (Makkonen, Vestenius et al. 2023); $2.35 \mu\text{g}/\text{m}^3$ (Hien, Bac et al. 2021). This pattern is also observed in the level of SO₄²⁻ ($8.3 \pm 3.4 \mu\text{g}/\text{m}^3$), which is higher than those $6.11 \mu\text{g}/\text{m}^3$ (Makkonen, Vestenius et al. 2023), and approximately equal to the 2016 study in Hanoi ($8.66 \mu\text{g}/\text{m}^3$) (Hien, Bac et al. 2021). For NO₃⁻ ($6.8 \pm 3.9 \mu\text{g}/\text{m}^3$), the concentration is much higher than in previous studies in the same region ($1.62 \pm 2.92 \mu\text{g}/\text{m}^3$) in 2021 (Bui, Luong et al. 2025), at the traffic site ($2.91 \mu\text{g}/\text{m}^3$) and the city center site ($2.74 \mu\text{g}/\text{m}^3$) from August 2019–July 2020 (Makkonen, Vestenius et al. 2023)... The total metal concentration ($7.02 \pm 4.00 \mu\text{g}/\text{m}^3$) is approximately equal to the previous study in Hanoi ($7.10 \mu\text{g}/\text{m}^3$) (Makkonen, Vestenius et al. 2023). The highest metal concentration was observed for Fe ($1.93 \pm 1.33 \mu\text{g}/\text{m}^3$), which was significantly higher than values reported in a previous study conducted in Hanoi during the summer ($0.63 \pm 0.33 \mu\text{g}/\text{m}^3$) and autumn ($0.57 \pm 0.43 \mu\text{g}/\text{m}^3$) of 2020 (Bui, Nguyen et al. 2023), as well as during the dry ($0.72 \pm 0.74 \mu\text{g}/\text{m}^3$) and wet ($0.44 \pm 0.28 \mu\text{g}/\text{m}^3$) seasons in inner urban Hanoi in 2019 (Bui and Nguyen 2024). The second most abundant metal was Na ($1.12 \pm 0.68 \mu\text{g}/\text{m}^3$), followed by Ca ($1.11 \pm 1.33 \mu\text{g}/\text{m}^3$) and K ($0.96 \pm 0.41 \mu\text{g}/\text{m}^3$). The concentrations of the remaining metals ranged from 0.03 to $0.59 \mu\text{g}/\text{m}^3$. The generally higher chemical concentrations observed in this study compared to previous research may be attributed to the sampling period, which predominantly occurred during daytime hours, as well as differences in meteorological conditions that may have led to increased PM_{2.5}. (Ye, Li et al. 2017).

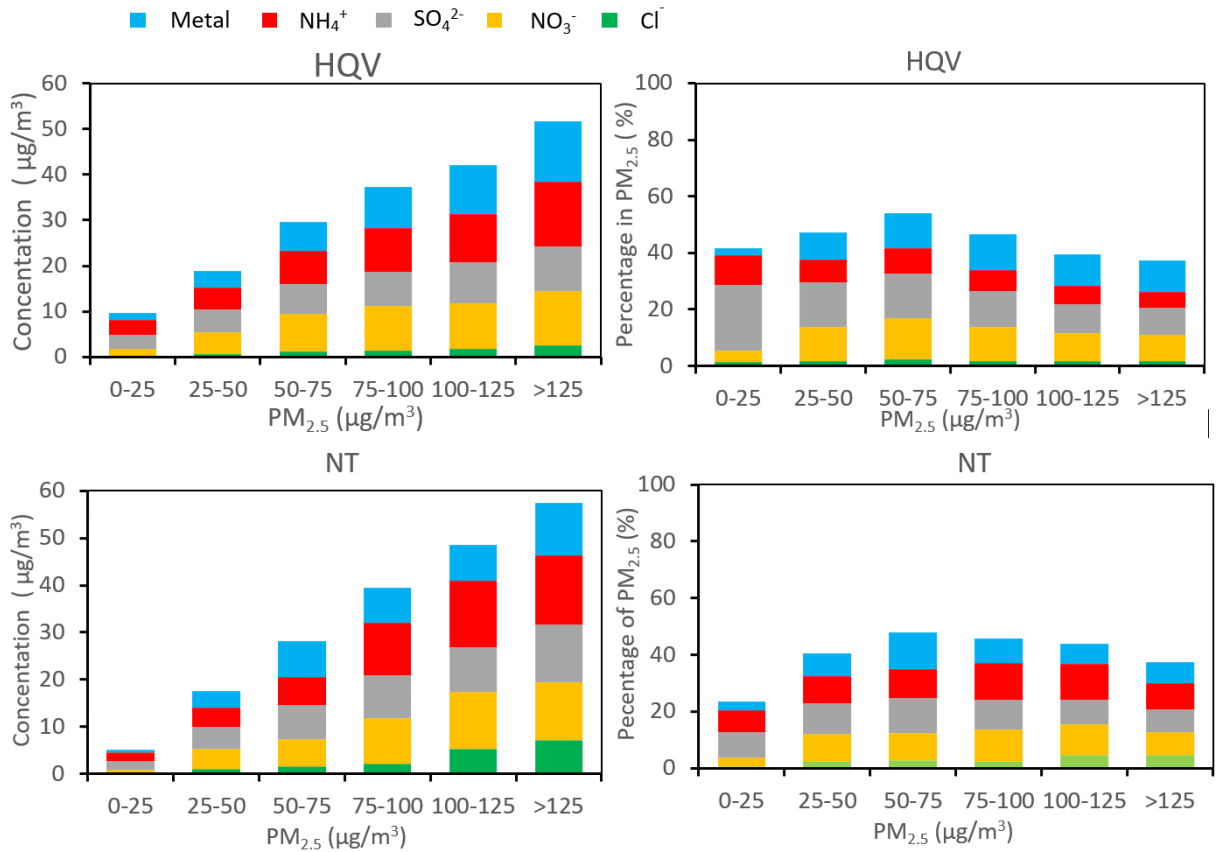


Figure 3. 2. Variation characteristic of WSIs and metals with different concentrations of $\text{PM}_{2.5}$ in two location samples.

Figure 3.2 illustrates the concentration and contribution of each component to each $\text{PM}_{2.5}$ concentration level. There were positive correlations between the levels of these components and the concentration of $\text{PM}_{2.5}$ when the $\text{PM}_{2.5}$ concentrations were below 75 $\mu\text{g}/\text{m}^3$. When the levels of $\text{PM}_{2.5}$ were higher than 75 $\mu\text{g}/\text{m}^3$, there was a reduction in the concentration of these components. These findings imply that, on heavily polluted days, $\text{PM}_{2.5}$ formation is influenced by a combination of sources, not limited to ionic contributors. The analysis of chemical species and their correlation with $\text{PM}_{2.5}$ concentrations serves as a useful tool for source apportionment.

3.3.2.3. The equilibrium of ions in $\text{PM}_{2.5}$

The ratios of NH_4^+ , NO_3^- , and SO_4^{2-} (mol/m^3) in the $\text{PM}_{2.5}$ samples are depicted in Figure 3.3. The main components of these ions in the atmosphere are in the form of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 (Meier, Wehner et al. 2009, Kong, Feng et al. 2020). Under idealized, ammonium-rich conditions, $(\text{NH}_4)_2\text{SO}_4$ is preferentially formed first due to the low volatility of sulfuric acid. The subsequent excess NH_4^+ then reacts with NO_3^- to form the more volatile. (Cheng, Zheng et al. 2016, Kong, Feng et al. 2020). However, in the heterogeneous atmosphere of Hanoi, the actual partitioning and formation pathways are subject to complex interactions. This sequential

formation process is strongly influenced by environmental factors such as temperature, relative humidity, and the local availability of NH₃ and precursor gases (SO₂ and NO_x). Therefore, the observed molar ratios must be interpreted within the context of these dynamic and site-specific atmospheric conditions. The mol ratios of NH₄⁺ and 2.SO₄²⁻ in this study were 1.63 in Spring; 1.29 in summer; 1.45 in autumn and 1.48 in winter (Figure 3.3a). This suggests that SO₄²⁻ in the air may be fully neutralized by forming (NH₄)₂SO₄. The ratio of excess NH₄⁺ (calculated as NH₄⁺ – 2.SO₄²⁻) to NO₃⁻ was less than 1 in all seasons (Figure 3.3b), indicating that NH₄⁺ has likely reacted to form other compounds such as NH₄NO₃, NH₄Cl and others. The annual average aggregate results from two locations also yield similar values, with K_{value} (NH₄⁺ and 2*SO₄²⁻) = 1.54 and K_{value} (NH₄⁺ - 2*SO₄²⁻ and NO₃⁻) = 0.88 (Figure 3.4). Based on these results, it is noticeable that in the spring and winter, these ratios are higher compared to the summer. Coupled with higher concentrations of PM_{2.5} in these months, this suggests that the origin of PM_{2.5} is closely related to NH₄⁺ emissions in the area. These results indicate that measures can be taken to reduce the emissions of SO₂, NO_x, and NH₃ in the environment, which in turn would reduce the formation of (NH₄)₂SO₄ and NH₄NO₃, and thereby the PM_{2.5} concentration (Kong, Feng et al. 2020).

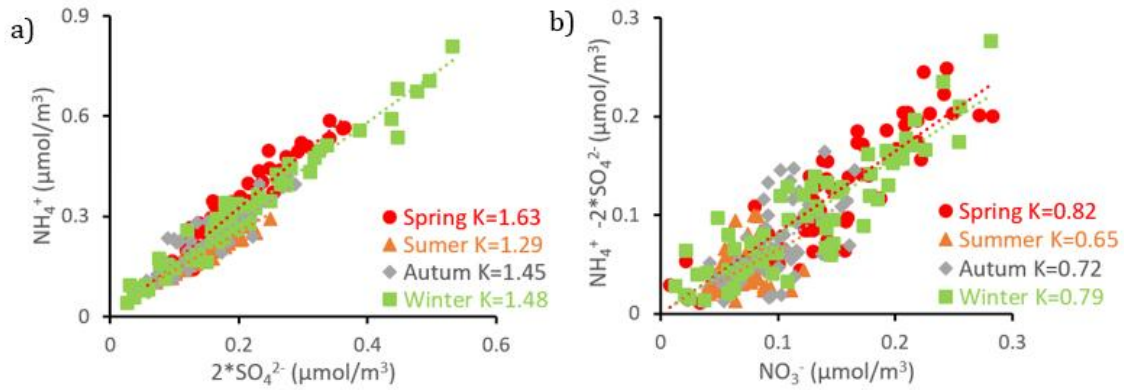


Figure 3. 3. Molar ratio analysis of ammonium, sulfate, nitrate in PM_{2.5} by season. (a) The mol ratios of NH₄⁺ and 2.SO₄²⁻. (b) The mol ratios of (NH₄⁺-2.SO₄²⁻) and NO₃⁻.

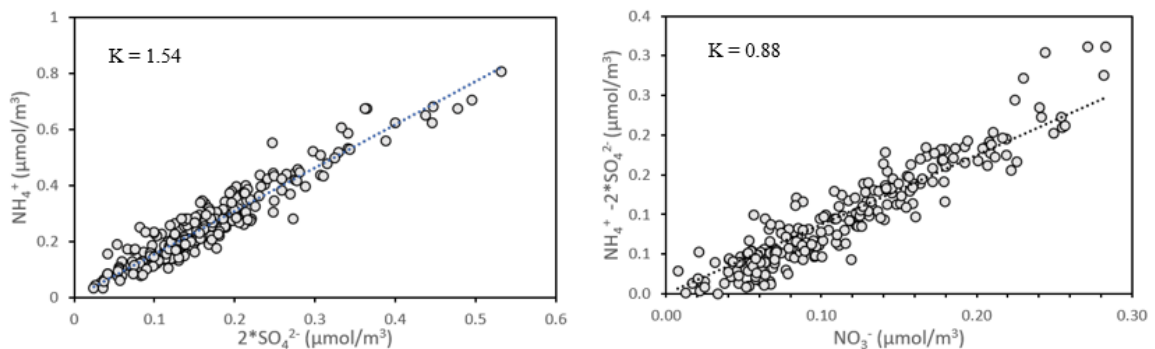


Figure 3. 4. Molar ratio analysis of ammonium, sulfate, nitrate in PM_{2.5} by the year

3.3.3. Source contribution by PMF

3.3.3.1. The profile of source apportionment

After 20 basic runs, PMF analysis yielded a Q_{robust} value of 223,301. the Q_{robust} to Q_{true} was 0.85, which is generally considered acceptable for a robust solution (Baumann, Jayanty et al. 2008). This acceptable ratio suggests that the weighted residuals were well-described by the model's solution. To further evaluate the stability and reliability of the PMF solution, three key diagnostic analyses were performed: the Bootstrap (BS) method, Displacement (DIS) analysis, and a combined BS-DIS approach. These advanced runs were conducted after applying specific constraints to assess the rotational ambiguity and uncertainty associated with the resolved source factors (Figure A1.1, A1.2).

Table 3. 3. Percent of bootstrap factors mapped back to the original PMF factors from the six factor PMF solution in PM_{2.5}

Factor	% Bootstrap factors mapped to original PMF factors
B.B	89
Secondary Nitrate	92
Soil	85
Secondary Sulfate	87
Traffic	88
Industry	91

Specifically, 100 bootstrap runs were performed for each dataset (with a default minimum correlation R value of 0.6), and the results were deemed reliable as more than 85% of the factors were successfully mapped (Table 3.3). The six sources were identified based on the results obtained from the PMF software. Figure 3.5 and Table 3.4 present comprehensive data on the characteristics of each emission source, derived from the PMF model's discoveries. Secondary nitrate is characterized by significant contributions of NO_3^- (50%) and NH_4^+ (22%), indicating notable influences across both regions. Traffic emissions encompass both exhaust sources, such as vehicle tailpipe emissions (Fang, Wang et al. 2023) and non-exhaust contributions, including brake wear, tire abrasion, road surface erosion, and the re-suspension of road dust (Dai, Bi et al. 2015, Zhang, Zhou et al. 2018, Liu, Yang et al. 2021). Combustion processes involving sulfur-containing gasoline yield SO_2 , which subsequently forms SO_4^{2-} (21.7%). Additionally, engine abrasion processes are identified as significant contributors to Cu (81.5%), Zn (45.8%), and Fe (50.6%) emissions. Secondary sulfate formation is attributed to the atmospheric conversion of SO_2 and long-range dust transport. This category is characterized by elevated levels of SO_4^{2-}

(53%) and NH_4^+ (45%), predominantly forming $(\text{NH}_4)_2\text{SO}_4$. The B.B in HQV-NT is marked by significant contributions of K (50%) and Cl (31%). Key sources include post-harvest crop residue combustion (Le, Khoi et al. 2022) (Hien, Bac et al. 2021) and burning household waste (Chakraborty, Heydon et al. 2020, Wang, Wang et al. 2022, Mardones 2023). Pb (58%), Ti (51%), Zn (47%), Mg (43%) are known as key indicators of industrial emissions - transportation of industrial dust in industrial zones (Khiem, Sera et al. 2020, Makkonen, Vestenius et al. 2023, Vuong, Bac et al. 2023). The re-suspension of dust from the soil's natural activities (Jain, Sharma et al. 2020, Liu, Wang et al. 2022, Tang, Yang et al. 2022) constitutes the primary factor of the soil source, characterized by Al (61%) and Ca (80%)

Table 3. 4. Species composition percentage within each factor

Name	Percent of species (%)					
	Soil	Biomass Burning	Traffic	Secondary Sulfate	Industry	Secondary Nitrate
PM _{2.5}	1.1	10	27	41	4.0	16
Cl	24	31.	7.7	23	0.0	15
NO ₃	0.0	10.	19	19	1.4	50
SO ₄	12.7	0.0	22	53	11	1.6
NH ₄	2.1	5.4	15	45	10	22
Na	38	4.2	5.8	9.6	28	15
Mg	40	4.7	5.1	1.0	43	7.0
Al	61	0.00	16	1.0	22	0.0
K	33.	50	6.2	0.0	10	0.7
Ca	80	7.9	0.0	0.0	12	0.0
Ti	17	0.9	30	0.0	51	0.6
Mn	20	27	18	2.5	31	2.0
Fe	18	0.0	51	3.0.	29	0.0
Cu	5.7	0.0	81	0.0	13	0.0
Zn	0.7	0.0	45.	2.7	47	3.9
Pb	10	4.4	25	1.1	58	0.0

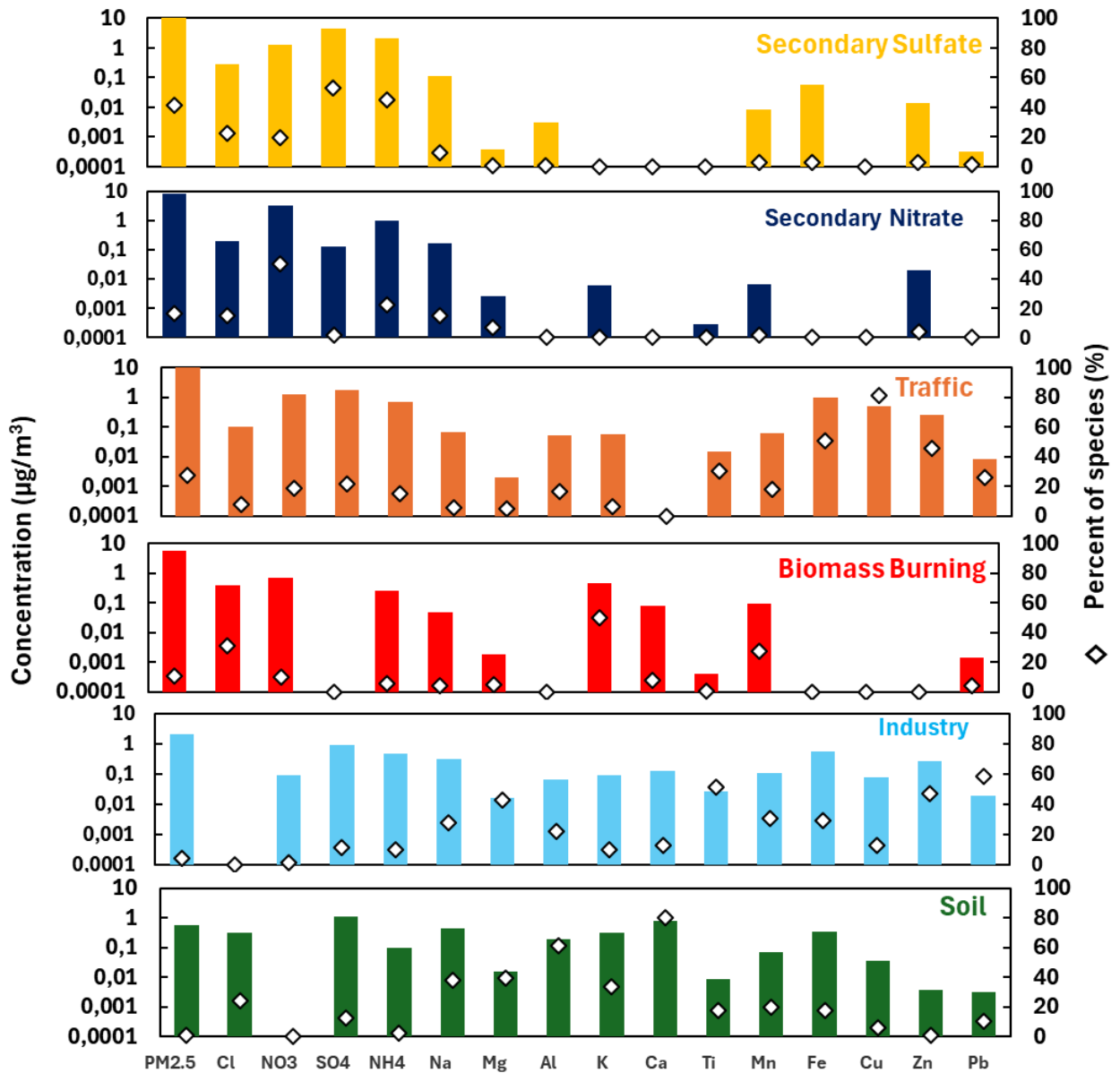


Figure 3. 5. Source profile derived from PMF modeling at the study sites in 2022

3.3.3.2. The performance of PMF model

The performance of the PMF model, evaluated with observed and predicted PM_{2.5} concentrations, is $r=0.92$ (Figure 3.6), indicating excellent PM_{2.5} source identification. The concentrations in 244 samples are depicted in Figure 3.8. The residuals of PM_{2.5} show higher concentration errors at the NT site compared to HQV, with the highest values observed in both sites during winter (Figure 3.9). This can be explained by the tropical monsoon climate of Vietnam, where secondary sulfate primarily originates from monsoon winds. Meanwhile, Hanoi's high population density and consistent activity patterns contribute to the relatively stable levels of secondary nitrate sources.

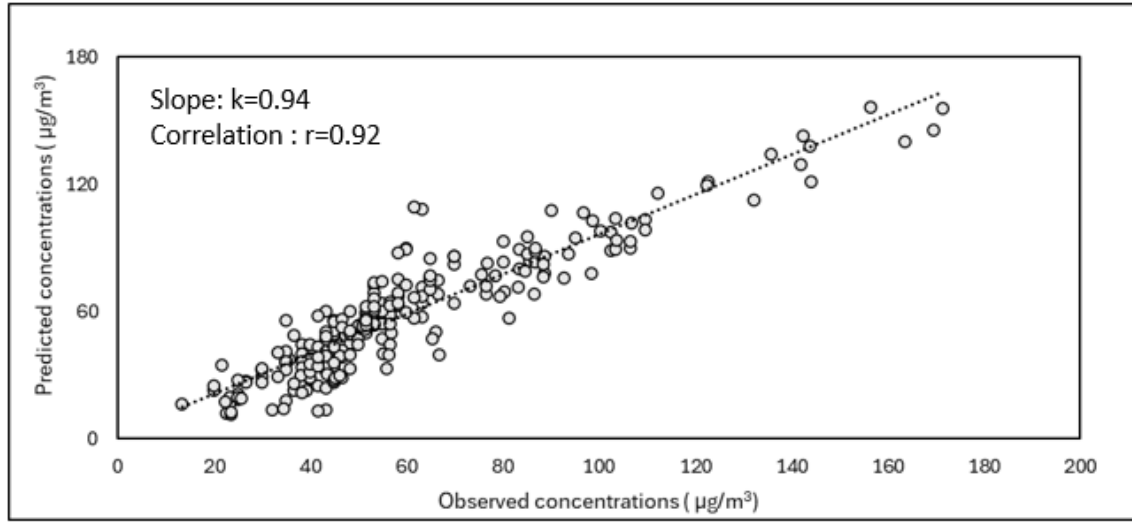


Figure 3. 6. The scatter plot displays the performance of PMF modeling during the study period.

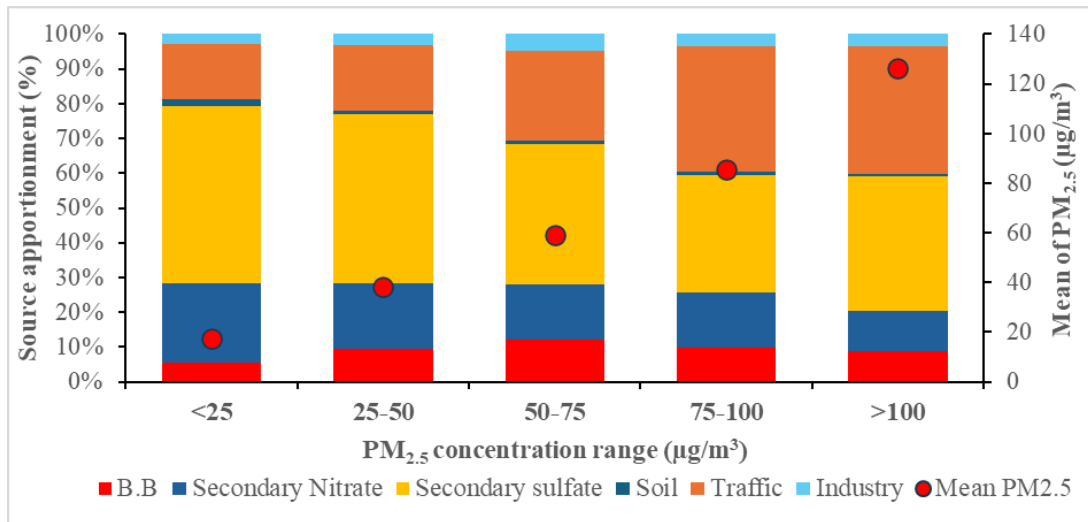


Figure 3. 7. The correlation between source apportionment and PM_{2.5} resolved by PMF

The contribution of different sources to each PM_{2.5} concentration level is illustrated in Figure 3.8. It can be observed that on days with low pollution levels, secondary sulfate source was the predominant source. Sources such as traffic emissions, industry, and B.B gradually increase as the PM_{2.5} concentration increases, indicating their significant contribution to pollution in Hanoi. When the PM_{2.5} concentration in Hanoi exceeds 75 µg/m³, the contribution of secondary sulfate slightly increases, implying the transportation of dust by seasonal winds. This trend aligns with the reduction in the proportion of ion components (NH₄⁺, NO₃⁻, and SO₄²⁻) when PM_{2.5} concentration exceeds 75 µg/m³. While other sources' contribution increases, their contribution to ion mass, such as metals, Cl⁻, and WSIs, is smaller compared to NH₄⁺, NO₃⁻, and SO₄²⁻ from the secondary sulfate source.

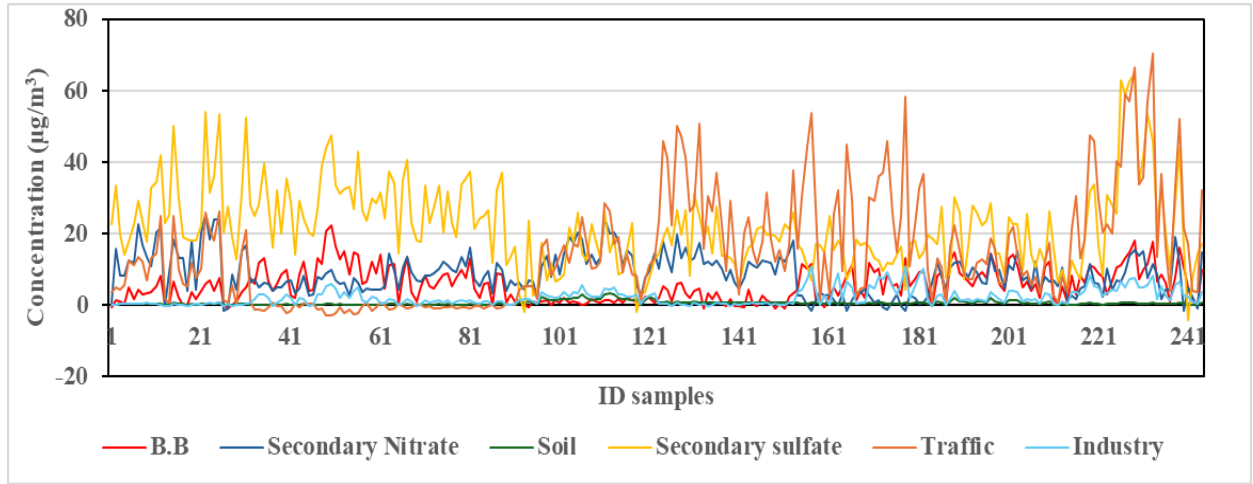


Figure 3. 8. The graph of source apportionment concentrations in 244 ID samples

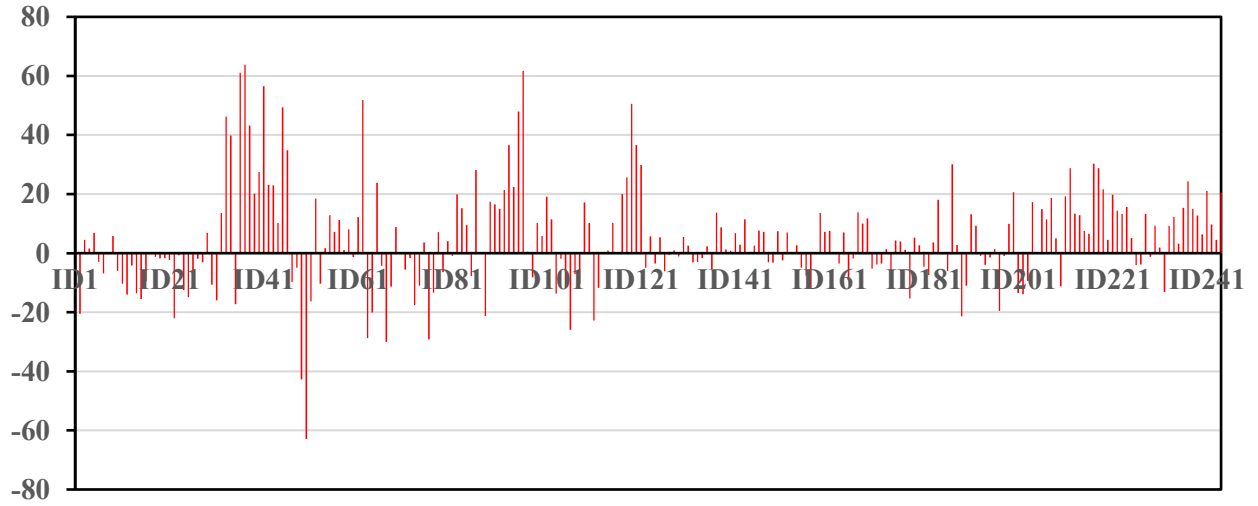


Figure 3. 9. The residuals of PM_{2.5} for 244 ID samples analyzed using PMF

3.3.3.3. Sources of PM_{2.5} by season

Based on the results of the PMF model, six sources were identified for PM_{2.5} in HQV and NT. For instance, the primary sources including secondary sulfate (41%), followed by traffic emissions (21%), secondary nitrate (16%), B.B (10%), Industry (4%), and Soil (1%) in Figure 3.10. Overall, while certain differences in source contribution levels exist, the identified sources are broadly in agreement with previous studies (Makkonen, Vestenius et al. 2023, Dominutti, Mari et al. 2024), highlighting the reliability of the PMF results and the importance of local context in source apportionment. The seasonal source distribution at the two sampling sites is summarized with detailed seasonal values for each location provided in Table 3.5. At both HQV and NT, the seasonal average contributions from secondary sulfate sources consistently dominated the PM_{2.5} composition, ranging from 37.53% to 44.16%. These results suggest that

the primary source of PM_{2.5} at these sites is associated with the transport and transformation of SO₄²⁻ precursors.

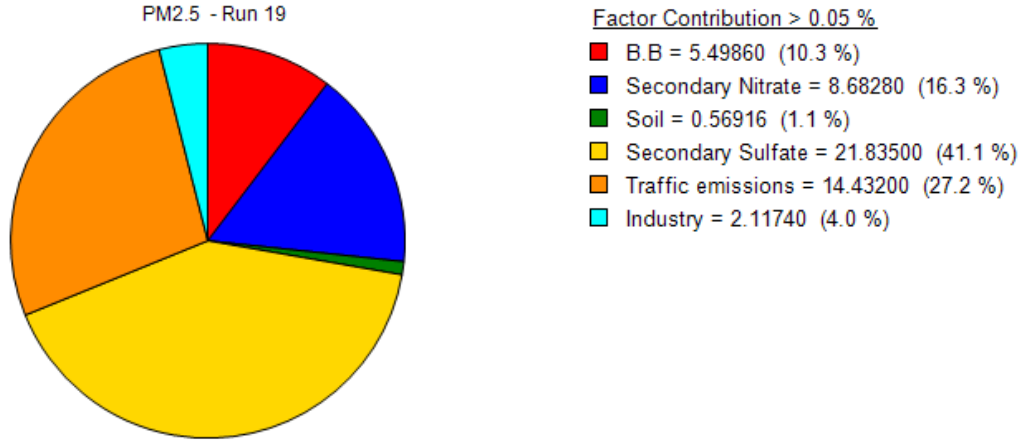


Figure 3. 10. Source of PM_{2.5} in both HQV and NT

Table 3. 5. Source profile results for aggregated data at both HQV and NT

Time	Source Contribution of HQV-NT					
	B.B	Secondary Nitrate	Soil	Secondary Sulfate	Traffic	Industry
Spring	4.5	23.3	0.9	44.2	26.2	0.9
Summer	15.4	10.7	0.6	41.5	25.2	6.7
Autumn	12.9	20.6	0.9	41.5	22.0	2.2
Winter	8.9	10.5	1.9	37.5	35.1	6.1
All year	10.4	16.3	1.1	41.2	27.1	4.0

The secondary nitrate sources showed higher contributions in spring (23%) and autumn (21%) compared to summer (11%) and winter (10%). This pattern may be attributed to the moderate temperature and humidity in spring and autumn, which likely facilitate the conversion of NO_x to NO₃⁻, leading to elevated PM_{2.5} levels from this process. In contrast, the elevated temperature in summer, and the reduced humidity in winter, may inhibit this conversion process, resulting in lower contributions during these seasons. The contribution of traffic emissions at both HQV and NT sites remained relatively stable throughout the year, ranging from 22% to 26% during spring, summer, and autumn. This indicates that the increased traffic activity on weekdays contributes to higher PM_{2.5} levels. However, during winter, traffic emissions increased significantly to 35%. This spike can likely be attributed to the impact of thermal inversions, which frequently occur in winter, trapping pollutants near the ground and preventing their dispersion.

The contribution from B.B sources was notably higher in summer and autumn. This trend is likely due to the widespread practice of straw burning in Hanoi during harvest periods, combined with dry weather conditions that facilitate forest fires in areas surrounding the city

(Xu, Liu et al. 2024). The industrial source contribution was higher during summer (6.73%) and winter (6.09%) compared to spring (0.90%) and autumn (2.20%). This seasonal variation mirrors the trend observed for secondary nitrate, with increased NO₃⁻ concentrations leading to reduced pH levels (Jiang, Liu et al. 2019). The resulting acidic environment facilitates the chemical transformation of metallic components within PM_{2.5} into more soluble ionic forms. This process enhances the hygroscopicity of the existing particles, altering their physical properties and increasing their toxicity and atmospheric lifetime, rather than solely contributing to their initial formation. The contribution from soil sources was minimal, ranging from 0.55% to 1.92% at both locations. This is likely due to the limited resuspension of dust from soil and rock surfaces, driven by wind and human activities.

3.3.3.4. Sources of PM_{2.5} by location

In the context of PMF analysis, grouping samples by location and season enables identification of season-specific PM_{2.5} sources at each site. The seasonal and site-specific origins of PM_{2.5} are presented in Table 3.6. Traffic emissions and secondary sulfate were the most noticeable differences between the two locations. This occurred because NT had a much higher traffic density compared to HQV. For secondary sulfate, HQV exhibited higher values than NT, partly due to the significant contribution of traffic emissions in NT. The northern part of HQV was adjacent to West Lake, facilitating the transport of dust from the north (secondary sulfate mainly originated from the northeast monsoon) (Makkonen, Vestenius et al. 2023). On the other hand, NT was an urban area with high-rise buildings that obstructed this transport (Li, Zheng et al. 2023). Soil sources accounted for a minimal portion of the PM_{2.5} composition; the regeneration of dust from soil might only have increased the amount of dust larger than PM_{2.5} (Park, Gong et al. 2010).

The industrial source at NT (5%) exhibited a higher annual average contribution compared to HQV (3%). This difference is likely attributed to the proximity of major industrial facilities in urban Hanoi, including the Thang Long Tobacco Company and Thuong Dinh Industrial Zone (approximately 200 meters from NT), a military materials production plant (150 meters from HQV), and the Cau Dien incinerator (2 kilometers from HQV). Furthermore, emissions may have originated from the transportation of industrial dust from suburban regions, such as Bac Tu Liem, Sai Dong, Thang Long, and Dai Tu industrial zones (Kim, Pham et al. 2012). The secondary nitrate source was more significant at HQV (19%) compared to NT (14%). This finding suggests that the open landscape and fewer high-rise buildings at HQV provide favorable conditions for the dispersion of atmospheric emissions (Huang, Gao et al. 2021)

Biomass burning (B.B) contributed more substantially at NT (11%) than at HQV (9%). The elevated proportion at NT is associated with higher population density, indicating that biomass burning in Hanoi primarily originates from household waste combustion (Kicińska, Caba et al. 2024). Seasonal spikes, such as the notable contribution of 19% at HQV during the summer, may result from rice straw burning following the harvest season (Xu, Liu et al. 2024).

Table 3. 6. Source PM_{2.5} by location in HQV and NT

Time	Source Contribution of HQV (%)					
	B.B	Secondary Nitrate	Soil	Secondary Sulfate	Traffic	Industry
Spring	5.3	24	0.6	53	17	0.3
Summer	19	11	0.2	56	10	4.1
Autumn	12	27	0.3	49	11	1.2
Winter	1.9	13	3.1	53	24	5.3
All year	9.5	19	1.0	53	16	2.8
	Source Contribution of NT (%)					
	B.B	Secondary Nitrate	Soil	Secondary Sulfate	Traffic	Industry
Spring	3.7	23	1.3	36	35	1.5
Summer	12	11	0.9	27	40	9.4
Autumn	14	14	1.4	34	33	3.1
Winter	15	7.7	0.8	22	47	6.7
All year	11	14	1.1	30	39	5.2

3.4. Conclusions

This study examines seasonal variations in PM_{2.5} concentrations at two sites in Hanoi and their correlations with meteorological conditions. The annual average PM_{2.5} concentration was 59.8 µg/m³, with seasonal values highest in winter (87.8 µg/m³), exceeding both Vietnam's QCVN 05:2023/BTNMT standard (25 µg/m³) and WHO guideline (5 µg/m³), indicating severe air pollution. Positive Matrix Factorization (PMF) identified six PM_{2.5} sources: biomass burning, industrial emissions, traffic, soil, secondary sulfate, and secondary nitrate. Winter showed the highest levels of chemical components, particularly water-soluble ions (WSIs), while metals dominated in summer and autumn. Major ions included NH₄⁺, NO₃⁻, and SO₄²⁻, with their contributions declining at PM_{2.5} concentrations above 75 µg/m³. PMF model performance was strong ($r=0.92$). In HQV-NT, secondary sulfate (41%) was the dominant source, followed by traffic (27%) and secondary nitrate (19%). A key difference between sites was traffic contribution: 10.4–23.6% at HQV and 33.2–47.4% at NT.

References – Chapter 3

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Chapter 4 - Source Apportionment of PM_{2.5} Using WRF–CMAQ–ISAM: A Comparative Assessment with PMF

4.1. Introduction

Source apportionment models are essential for quantifying the contributions of different emission sources to ambient PM_{2.5}. Two widely applied approaches are receptor-based statistical models, such as PMF, and chemical transport models (CTMs) equipped with source apportionment techniques, such as the ISAM - CMAQ model. PMF resolves source profiles and contributions directly from observed chemical speciation data, making it effective for extracting secondary aerosol factors; however, it is subject to uncertainty due to rotational ambiguity and the limited number of chemical tracers available (Paatero et al., 2014; Brown et al., 2015).

By contrast, CMAQ-ISAM is a model-based tagging technique that links source contributions to predefined emission sectors and boundary inflows. It allows quantification of both primary and secondary components while accounting for chemical transformations and transport processes in a process-based framework (Kwok et al., 2013; Ying & Li, 2011). Recent applications of CMAQ-ISAM in Asia have demonstrated its ability to capture household combustion, industrial emissions, biomass burning, and especially long-range transport (LRT) as major contributors to PM_{2.5} (Li et al., 2020; Thunis et al., 2019). Compared with PMF, CMAQ-ISAM provides a more detailed sectoral and regional attribution, although its performance strongly depends on the accuracy of emission inventories and meteorological fields.

This study applies both PMF and WRF-CMAQ-ISAM to a full year (2023) of observations in Hanoi, Vietnam, to investigate PM_{2.5} sources. PMF is expected to identify secondary sulfate and nitrate, traffic, industry, biomass burning, and soil dust as dominant factors, whereas CMAQ-ISAM is expected to attribute the largest contributions to household emissions and long-range transport, alongside industry, biomass burning, and other anthropogenic sectors. By comparing the results of these two complementary approaches, this work provides a robust assessment of source contributions and highlights method-dependent uncertainties relevant for developing targeted air quality management strategies in northern Vietnam.

4.2. Methodology

4.2.1. Study area

Ambient PM_{2.5} samples were collected at a fixed monitoring site located in the urban core of Hanoi. Outdoor air sampling was conducted using a high-volume air sampler (HV-1000, Sibata, Japan) operating at a flow rate of 1000 L/min. Samples were collected over 24-hour

periods at the HQV site (21°02'54"N, 105°48'10"E) (Figure 4.1) on 2–3 days per week throughout the year 2023, resulting in a total of 112 samples. The sampling site at HQV, northern Hanoi, is located near West Lake, providing an open area suitable for capturing both local and long-range transported (Makkonen, Vestenius et al. 2023). The site is located in an urban area close to a major road with high traffic density, surrounded by residential and commercial areas, reflecting contributions from traffic, secondary sulfate, secondary nitrate, soil dust, and biomass burning, with limited influence from distant industrial sources (Kim, Pham et al. 2012). Its location away from major construction ensures that collected samples represent a typical mix of local and transported pollutants. Among the receptor sites used in this study, the HQV site provides favorable geographical and spatial conditions for comparison with CMAQ–ISAM simulation results. The site is located in proximity to West Lake, within an open area characterized by relatively good ventilation and limited influence from immediate local emission sources. The surrounding environment does not include any dominant point sources or major industrial activities that could exert strong, localized impacts on PM_{2.5} concentrations. As a result, ambient PM_{2.5} levels at HQV are more representative of the grid-scale atmospheric conditions resolved by the CMAQ model. This geographical setting reduces the mismatch between point-scale observations and grid-averaged model outputs, thereby enhancing the reliability of model–observation comparison. In contrast, the NT site is subject to more heterogeneous and localized emission influences at sub-grid scales, making it less suitable for direct comparison with CMAQ–ISAM results given the spatial resolution of the model.

Surface meteorological observations from the Lang station (weather monitoring station, WMS) (21°01'13.3"N, 105°48'24.2"E) via Weather Underground provided hourly measurements of wind speed (W), relative humidity (H), temperature (T), from January to December 2023. Air quality monitoring data were collected from the World Air Quality Project and the U.S. EPA at a nearby air quality monitoring station (AMS) (21°01'58"N, 105°48'51"E), located ~500 m from the sampling site, which provides hourly real-time PM_{2.5} and co-pollutant measurements.

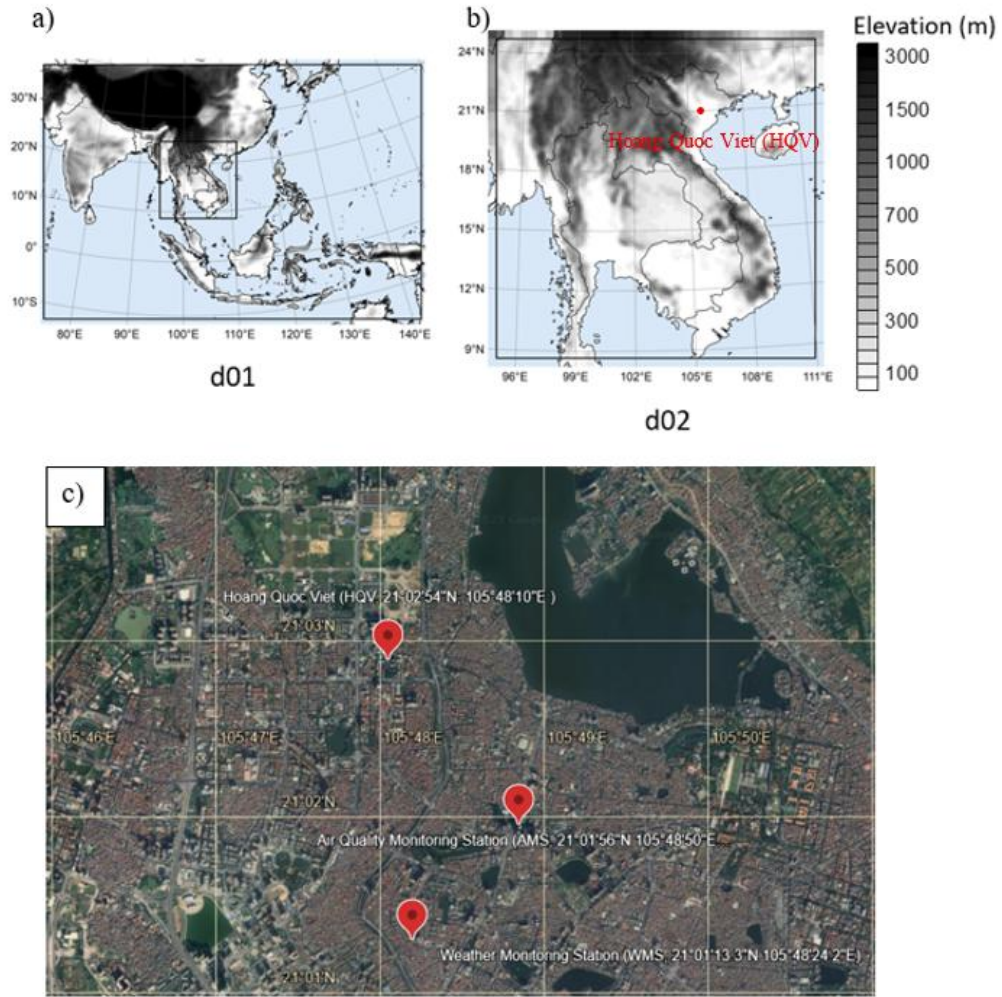


Figure 4. 1. Study area: (a) Outer simulation domain (d01) covering Southeast Asia. (b) Nested domain (d02) covering Indochinese Peninsula (d02). (c) Sampling location (HQV) and experimental monitoring sites in Hanoi (AMS and WMS)

4.2.2. Sample preparation and measurement

The 112 samples were analyzed for water-soluble inorganic ions (Li^+ , Na^+ , K^+ , Mg^{2+} , NH_4^+ , Ca^{2+} , F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) were determined by ion chromatography following the EN 16913:2017b method, while trace elements were quantified by ICP-MS under standard conditions. PM_{2.5} sampling was conducted on pre-baked quartz fiber filters, prepared and weighed according to U.S. EPA (40 CFR Part 50, Appendix O) procedures. After collection, each filter was divided into subsamples for ion and elemental analyses as described in chapter 3

4.2.3. Model Configuration

4.2.3.1. Source Apportionment Using Positive Matrix Factorization (PMF)

The input species for PMF analysis were selected according to their signal-to-noise (S/N) ratios. Major inorganic ions (Na^+ , K^+ , Mg^{2+} , NH_4^+ , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) and trace metals

(Al, Ti, Mn, Fe, Cu, Zn, Pb) with S/N values above 3 were treated as “strong” variables and retained in the model. Species with S/N values lower than 0.5 or concentrations consistently below the method detection limits (e.g., As, Hg, Cr, Cd, Co, Mo, Ag, Li⁺, F⁻, NO₂⁻, PO₄³⁻) were excluded from further analysis to ensure robustness and stability of the solution, 20 runs with different seed values and bootstrapping procedures were performed. The extracted source profiles were interpreted based on characteristic chemical markers and cross-referenced with existing literature (Paatero and Tapper 1994). Typical sources identified included secondary inorganic aerosol, vehicular emissions, industrial processes, biomass burning, and resuspended soil dust.

4.2.3.2. WRF–CMAQ Model Configuration and Source Apportionment Setup

The Weather Research and Forecasting model (WRF v4.3) (Skamarock, Klemp et al. 2019) was employed to generate meteorological fields using geographic inputs from GMTED2010 and MODIS (30-sec resolution) and initial and boundary conditions from ERA5 reanalysis data (0.25°, 3-hour). The WRF model configuration comprised the Grell 3D cumulus parameterization, Morrison microphysics scheme, RRTMG radiation, MYNN3 planetary boundary-layer scheme, and Noah land surface model. Analysis nudging was applied, with coefficients for temperature and water vapor of $5.0 \times 10^{-5} \text{ s}^{-1}$ (d01) and $3.0 \times 10^{-5} \text{ s}^{-1}$ (d02), and for horizontal winds of $1.0 \times 10^{-4} \text{ s}^{-1}$ across domains in the same way as Chatani et al. (Chatani, Shimadera et al. 2020). The chemical transport simulations were conducted using CMAQ v5.3.3) coupled with ISAM (applied for d02 only). Boundary conditions were derived from the Whole Atmosphere Community Climate Model (WACCM) (Gettelman, Mills et al. 2019). Emission inputs included anthropogenic sources from the Regional Emission inventory in *Asia* version 3.2.1 (REAS v3.2.1, base year 2015) (Kurokawa and Ohara 2019) and the Hemispheric Transport of Air Pollution version 2.2 (HTAP v2.2, base year 2010) (Janssens-Maenhout, Crippa et al. 2015). Open biomass burning emissions were obtained from the Global Fire Assimilation System (GFAS) (Kaiser, Heil et al. 2012), while biogenic emissions were estimated using the Model of Emissions of Gases and Aerosols from Nature version 2.04 (MEGAN v2.04) (Guenther, Karl et al. 2006), and volcanic emissions from the Carn database (Carn, Fioletov et al. 2017). The atmospheric chemistry was simulated using SAPRC07tc and AERO6 with aqueous-phase reactions. The simulation period covered the entire year of 2023, with December 2022 used as a spin-up period. Two nested domains were configured: the parent domain (d01) encompassed South and Southeast Asia with a 192×129 grid at 45 km horizontal resolution, while the nested domain (d02) focused on the Indochinese Peninsula with a 117×117 grid at 15 km resolution.

Both domains were vertically resolved from the surface up to 50 hPa with 30 layers, where the first model layer represented approximately 30 m above ground level.

The ISAM in CMAQ was employed to quantify the contributions of different source categories to PM_{2.5} and its major components. Emission sources were tracked with nine tags: household (H.H), long-range transport (LRT), industry (IND), open biomass burning (OBB), other anthropogenic (OAN), road transport (ROA), power generation (POW), other transport (OTR), and natural sources (NAT). In this configuration, LRT represents inflow from outside the modeling domain (boundary conditions). All tags were defined in d02. Because ISAM of CMAQ v5.3.3 does not track secondary organic aerosol (SOA), SOA simulated by CMAQ was additionally incorporated as an independent component in the source apportionment results. This approach allows an assessment of total PM_{2.5} contributions.

4.3. Results and Discussion

4.3.1. Chemical Composition of observed PM_{2.5}

The chemical composition of PM_{2.5} was characterized based on major water-soluble ions and selected elemental species as shown in Table 4.1. The average PM_{2.5} concentration in Hanoi during 2023 was 49.2 µg/m³, with a median of 41.3 µg/m³ and a maximum value reaching 157 µg/m³, demonstrating substantial temporal variability in PM_{2.5} (standard deviation = 27 µg/m³) (standard deviation = 27 µg/m³). A total of 16 water-soluble ions and elemental species were quantified to characterize the chemical composition of PM_{2.5}.

The sulfate (SO₄²⁻) and nitrate (NO₃⁻) were the most abundant components, with mean concentrations of 7.8 µg/m³ and 7.9 µg/m³, respectively. These levels are comparable to values reported for high pollution episodes in Hanoi (SO₄²⁻ = 8.7 µg/m³, NO₃⁻ = 2.7 µg/m³) (Vuong, Ha et al. 2023). Their relatively high levels suggest a strong contribution from secondary formation processes, likely driven by SO₂ and NO_x emissions associated with fossil fuel combustion (Guerra, Olsen et al. 2014, Colombo, Marongiu et al. 2024). Ammonium (NH₄⁺), which serves as a neutralizing ion in aerosol systems, exhibited a mean concentration of 5.5 µg/m³ in this study. This value is slightly higher than the level reported for Hanoi in 2025 (4.6 ± 2.3 µg/m³) (Quang Le, Phuong Pham et al. 2025), and substantially exceeds those measured in 2021 (2.53 µg/m³) (Le Ha, Hien et al. 2023) and 2019 (2.35 µg/m³) (Hien, Bac et al. 2021). The upward trend in NH₄⁺ concentrations across studies suggests a growing role of ammonia emissions—primarily from agriculture and traffic that drives secondary aerosol formation in the urban

environment of Hanoi (Colombo, Marongiu et al. 2024). The concentration of chloride (Cl^-) was relatively low (mean = $0.2 \mu\text{g}/\text{m}^3$), suggesting limited influence from fresh sea spray or waste burning (Pedersen, Frandsen et al. 2009, Peng, Suzuki et al. 2021).

The crustal elements such as aluminum (Al), calcium (Ca), iron (Fe), and titanium (Ti) were observed, with Fe being the most abundant (mean = $1.7 \mu\text{g}/\text{m}^3$), followed by Ca ($1.0 \mu\text{g}/\text{m}^3$) and Al ($0.3 \mu\text{g}/\text{m}^3$), indicating contributions from soil dust (Zhang, Shen et al. 2014) and mechanical processes such as road wear (Panko, Hitchcock et al. 2019) and construction activities (Thammasaroj and Jinsart 2019). Several trace metals including copper (Cu), zinc (Zn), manganese (Mn), and lead (Pb) were measured at lower concentrations (mean = $0.06 \mu\text{g}/\text{m}^3$) but are key tracers of anthropogenic pollution. These elements likely originate from anthropogenic sources such as vehicular abrasion (Matthaios, Lawrence et al. 2022), industrial emissions (Dai, Bi et al. 2015, Wu, Vu et al. 2018), or residual combustion (Ni, Tian et al. 2017, Zhang, Hu et al. 2017).

In addition, potassium (K) was found at a mean level of $1.00 \mu\text{g}/\text{m}^3$, which may originate from both soil dust and biomass burning (Ni, Tian et al. 2017, Ravindra, Singh et al. 2021). The presence of sodium (Na) and magnesium (Mg) at moderate concentrations may indicate contributions from non-sea-salt sources such as resuspended road dust or mineral matter, rather than direct sea salt influence, given the relatively weak chloride (Cl^-) signal (Zhang, Shen et al. 2014, Bui, Nguyen et al. 2023, Makkonen, Vestenius et al. 2023).

Table 4. 1. Descriptive statistics of PM_{2.5} concentrations and major chemical components measured in Hanoi, Vietnam during 2023

	Concentration ($\mu\text{g}/\text{m}^3$)				Sd
	Mean	Median	Maximum	Minimum	
PM _{2.5}	49.2	41.3	157	17.0	27.4
SO_4^{2-}	7.8	6.1	26	1.03	5.2
NO_3^-	7.9	5.6	34	1.10	7.1
NH_4^+	5.5	4.1	22	0.26	4.7
Cl^-	0.2	0.08	0.9	0.001	0.2
Na	1.0	0.9	3.6	0.28	0.6
Mg	0.2	0.2	0.6	0.04	0.1
Al	0.3	0.3	1.0	0.09	0.2
K	1.0	0.9	2.9	0.21	0.5
Ca	1.0	0.9	3.1	0.28	0.6

	Concentration ($\mu\text{g}/\text{m}^3$)				Sd
	Mean	Median	Maximum	Minimum	
Ti	0.03	0.02	0.2	0.01	0.03
Mn	0.6	0.5	2.3	0.06	0.5
Fe	1.7	1.5	5.2	0.39	1.1
Cu	0.3	0.3	1.1	0.08	0.2
Zn	0.4	0.3	1.2	0.11	0.2
Pb	0.06	0.05	0.2	0.001	0.04

Overall, the PM_{2.5} composition data highlight the combined effects of secondary aerosol formation, crustal material, and anthropogenic emissions. The dominance of SO_4^{2-} , NO_3^- , and NH_4^+ implies that regional atmospheric chemistry plays a central role in shaping fine particulate matter levels, while the presence of trace metals points to localized anthropogenic contributions (Chyzhykov, Baumann, Jayanty et al. 2008, Bui, Luong et al. 2025).

4.3.2. Model Performance

4.3.2.1. The WRF-CMAQ Model Performance

The WRF - CMAQ system was evaluated against observed data at the AMS site. The model performance was assessed for four variables: temperature (T), wind speed (W), relative humidity (H), and PM_{2.5} concentrations (Table 4.2 ; Figure 4.2). Statistical methods that have been applied include the Pearson's correlation coefficient (R), mean bias (MB), root mean square error (RMSE), and the index of agreement (IA) (Willmott 1981, Uranishi, Ikemori et al. 2017). The model demonstrated strong performance in simulating meteorological parameters, particularly temperature and wind speed, while showing moderate performance for PM_{2.5}.

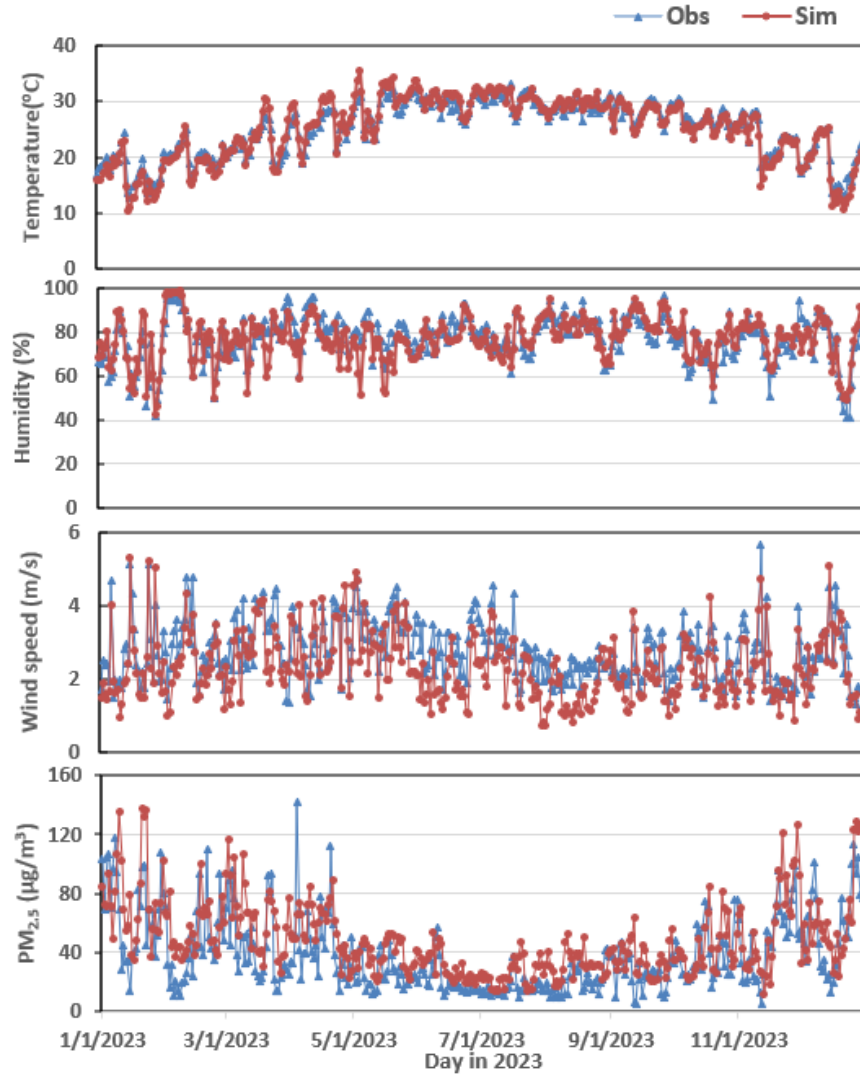


Figure 4. 2. Observed vs. Simulated Daily Meteorological Parameters in Hanoi (2023)

The WRF–CMAQ system slightly underestimated PM_{2.5} concentrations, with a simulated annual mean of 42.7 $\mu\text{g}/\text{m}^3$ compared to the observed mean of 48.3 $\mu\text{g}/\text{m}^3$, yielding a mean bias (MB) of $-5.5 \mu\text{g}/\text{m}^3$. Nevertheless, the model reproduced temporal variability well, as reflected by a correlation coefficient (R) of 0.80 and an index of agreement (IA) of 0.87, although the RMSE of 19.2 $\mu\text{g}/\text{m}^3$ remains considerable relative to the observed mean. CMAQ outputs further indicated that SOA contributed substantially to PM_{2.5}, with an annual mean of $\sim 5.8 \mu\text{g}/\text{m}^3$ (Table A2.1), equivalent to $\sim 13.6\%$ of the simulated mean and $\sim 12.0\%$ of the observed mean. Monthly averages revealed distinct seasonality: during winter (January–February and November–December (Table A2.1), PM_{2.5} levels exceeded 50–70 $\mu\text{g}/\text{m}^3$ while the SOA fraction remained modest (9–12%), suggesting dominance of primary emissions and long-range transport. In spring (March–April), SOA concentrations rose to 7.1–11.7 $\mu\text{g}/\text{m}^3$, accounting for 14–20% of total

PM_{2.5}, and peaked in May at 25.8% despite relatively low PM_{2.5} (33.8 $\mu\text{g}/\text{m}^3$). During summer (June–August), PM_{2.5} concentrations were lowest (16–23 $\mu\text{g}/\text{m}^3$), yet SOA still contributed 14–18%, consistent with enhanced photochemistry and biogenic VOC emissions. In autumn (September–October), SOA contributed ~13–14% as PM_{2.5} concentrations increased again. This seasonal pattern highlights the key role of SOA during warm months and emphasizes that while wintertime PM_{2.5} is dominated by primary sources, secondary organic aerosol formation is an important contributor in spring and summer, consistent with previous studies on seasonal SOA variability.(Matthias, Arndt et al. 2018). Such discrepancies are consistent with previous findings in Hanoi, where regional-scale modeling approaches tend to underestimate PM_{2.5} due to uncertainties in emission inventories, meteorological inputs, and the representation of secondary aerosol processes(Nguyen, Nagashima et al. 2020).

Table 4. 2. Statistical evaluation of WRF-CMAQ model performance for daily mean temperature (T), wind speed (W), relative humidity (H), and PM_{2.5} at AMS in Hanoi during 2023

	T (°C)	W (m/s)	H (%)	PM _{2.5} ($\mu\text{g}/\text{m}^3$)
Sample number	365	365	365	365
Mean Obs	25.1	2.8	77.1	48.3
Mean Sim	25.0	2.3	77.1	42.7
R	0.97	0.79	0.84	0.80
MB	- 0.09	-0.43	0.03	-5.50
RMSE	1.43	0.71	5.81	19.2
IA	0.98	0.83	0.91	0.87

4.3.2.2. Evaluation of CMAQ for Simulating PM_{2.5} and Secondary Inorganic Aerosols

The performance of the CMAQ-ISAM model in simulating PM_{2.5} and its major secondary inorganic components sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) was evaluated by comparing simulated and observed concentrations at 112 matched sampling points in Table 4.3. The model reproduces PM_{2.5} concentrations with a reasonably strong correlation ($R = 0.84$) and a high index of agreement ($IA = 0.81$), indicating that it captures the overall temporal variability well. However, the simulated mean concentration of 112 matched sampling points (40.1 $\mu\text{g}/\text{m}^3$) is substantially lower than the sample mean (49.2 $\mu\text{g}/\text{m}^3$), resulting in a negative mean bias (MB) of -9.2 $\mu\text{g}/\text{m}^3$ and an RMSE of 18.5 $\mu\text{g}/\text{m}^3$.

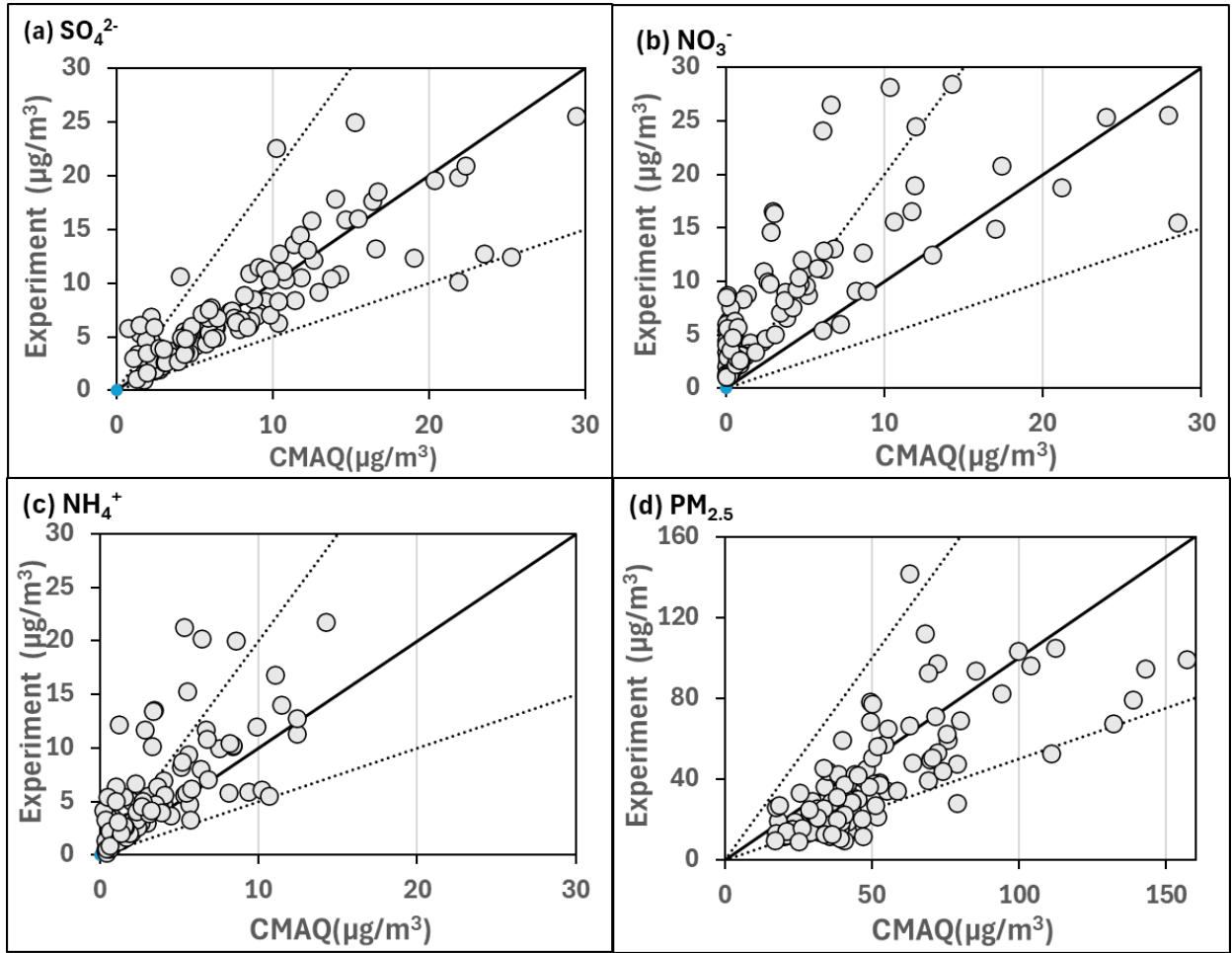


Figure 4.3. Comparison between observed and CMAQ simulated concentrations of major PM_{2.5} components in Hanoi, 2023

Figure 4.3 and Table 4.3 present a comprehensive comparison between simulated and observed concentrations of PM_{2.5} and its major ionic components (SO₄²⁻, NO₃⁻, and NH₄⁺). The scatter plots illustrate the capability of the CMAQ model to reproduce observed concentrations and provide insight into both the level of agreement and remaining systematic discrepancies. Model performance is evaluated using multiple statistical metrics, including correlation coefficient (R), index of agreement (IA), mean bias (MB), normalized mean bias (NMB), and root mean square error (RMSE), following commonly adopted benchmarks for chemical transport model evaluation (Emery et al., 2017).

For SO₄²⁻, the model demonstrates excellent performance. The simulated and observed mean concentrations are nearly identical (7.87 vs. 7.84 µg/m³), corresponding to an almost negligible bias (MB = 0.03 µg/m³; NMB ≈ 0.4%). The strong correlation (R = 0.84) and high IA (0.91), together with a relatively low RMSE (3.16 µg/m³), indicate that CMAQ reliably captures both the magnitude and temporal variability of sulfate. This strong agreement is consistent with

the dominant influence of long-range transport and the relatively well-characterized oxidation pathways of SO₂ in regional models (Guerra and Olsen et al., 2014).

In contrast, NO₃⁻ is substantially underestimated. The simulated mean concentration (3.7 µg/m³) is less than half of the observed mean (7.9 µg/m³), resulting in a pronounced negative bias (MB = -4.2 µg/m³; NMB ≈ -53%). Although the temporal correlation remains relatively high (R = 0.77), the lower IA (0.78) and larger RMSE (6.2 µg/m³) indicate reduced model skill in reproducing both the magnitude and variability of nitrate. Such underestimation is commonly reported in CMAQ applications and may be attributed to uncertainties in NO_x emissions, as well as limitations in the representation of gas-particle partitioning under varying temperature and relative humidity conditions (Wang, Sun et al., 2023).

Similarly, NH₄⁺ concentrations are underestimated by the model, with a simulated mean of 3.48 µg/m³ compared to an observed mean of 5.49 µg/m³ (MB = -2.03 µg/m³; NMB ≈ -37%). While the correlation (R = 0.73) and IA (0.76) suggest acceptable temporal consistency, the negative bias indicates that CMAQ may underrepresent ammonium formation and neutralization processes, particularly during episodes characterized by elevated sulfate and nitrate levels. This behavior is consistent with the coupled underestimation of nitrate and highlights the sensitivity of NH₄⁺ predictions to uncertainties in precursor emissions and aerosol thermodynamics.

Table 4. 3. Performance statistics for simulated versus experimental PM_{2.5} and secondary inorganic aerosol (SIA) components

	PM _{2.5} (µg/m ³)	SO ₄ ²⁻ (µg/m ³)	NO ₃ ⁻ (µg/m ³)	NH ₄ ⁺ (µg/m ³)
Sample number	112	112	112	112
Mean Exp	49.2	7.8	7.9	5.5
Mean Sim	40.1	7.9	3.7	3.5
R	0.84	0.84	0.77	0.73
MB	-9.2	0.03	-4.2	-2.0
RMSE	18.5	3.2	6.2	3.8
IA	0.87	0.91	0.78	0.76

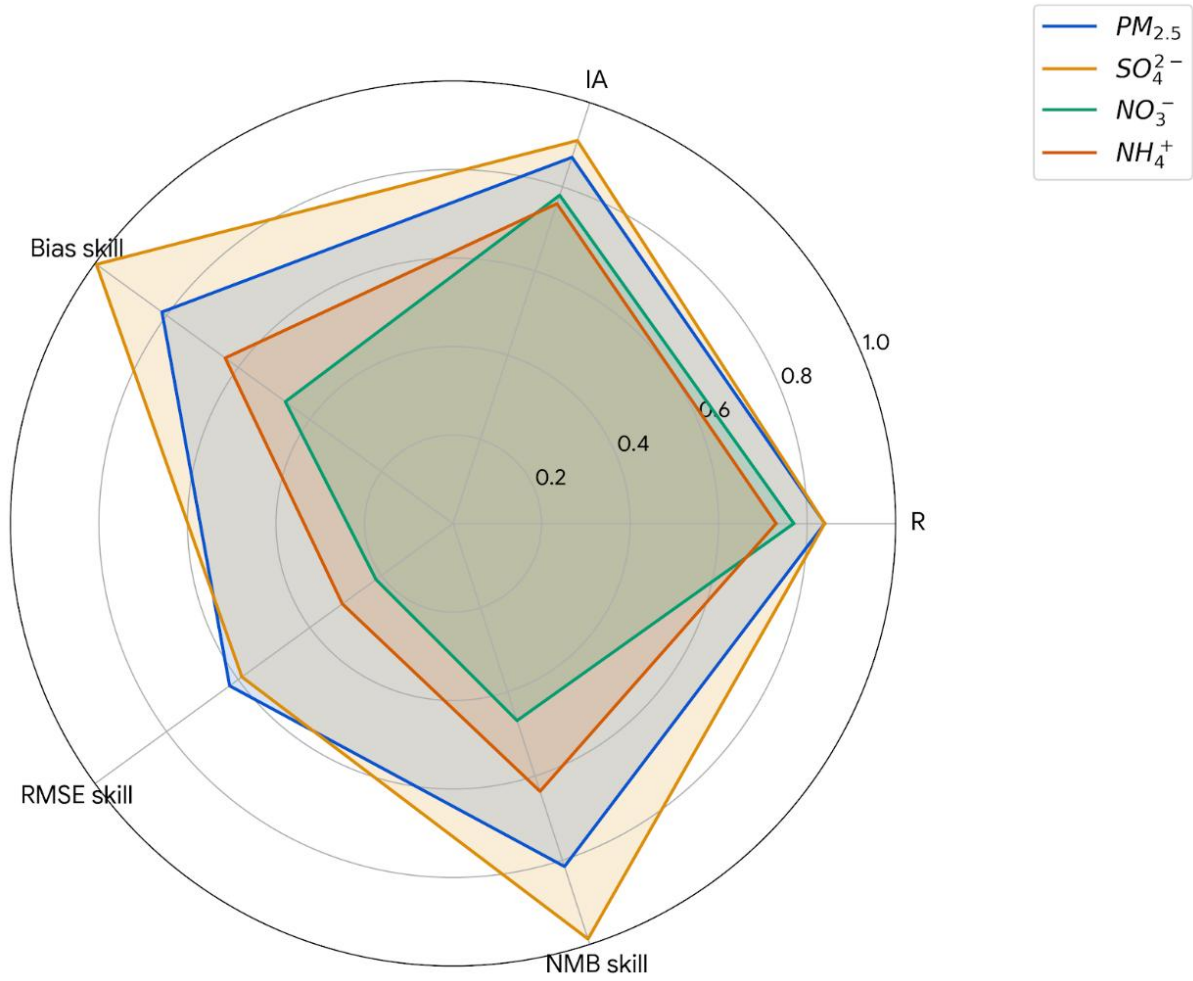


Figure 4. 4. CMAQ model performance for PM_{2.5} and inorganic aerosol species evaluated using multi-metric skill radar (R, IA, RMSE, MB, and NMB)

In addition to individual statistical metrics and scatter plots, the overall model performance is further synthesized using a multi-metric skill radar plot (Figure 4.4), which integrates R, IA, RMSE-based skill, and normalized mean bias (NMB) into a unified framework following Emery et al. (2017). The radar visualization highlights the strong and consistent performance of CMAQ for SO₄²⁻, characterized by high correlation, high agreement, and minimal systematic bias, while clearly revealing the comparatively lower skill for NO₃⁻ and NH₄⁺ driven by pronounced negative NMB values. By emphasizing systematic rather than random errors, the NMB-based radar plot provides a concise and robust assessment of model bias patterns across aerosol components.

Despite these limitations in reproducing absolute concentrations of nitrate and ammonium, the overall model performance for PM_{2.5} and secondary inorganic aerosols remains within acceptable ranges for regional-scale source attribution. This level of performance supports

the subsequent application of CMAQ-ISAM to investigate sector-specific and regional contributions, where relative source signals and transport pathways are of primary interest rather than exact concentration matching. Consequently, the ISAM results presented in the following section are interpreted in the context of the identified systematic biases, allowing a more physically consistent linkage between model evaluation and source apportionment.

4.3.2.3. The PMF Model Performance

The PMF model successfully resolved six distinct emission sources: Soil, Biomass Burning Traffic, Secondary Sulfate, Industry, and Secondary Nitrate. The PMF solution demonstrated strong fidelity to the ambient observations:

- **Residual Analysis:** The residuals of PM_{2.5} concentrations (Figure 4.5) were generally small and randomly distributed, with a maximum deviation of 11.5 µg/m³ indicating that the model effectively reproduced the observed time series.
- **Correlation:** A high correlation ($r = 0.98$) and slope ($k = 0.96$) between the observed and predicted PM_{2.5} concentrations (Figure A2.5) further attest to the overall robustness of the source contribution estimates.
- **Uncertainty Estimation:** Error estimation methods, including classical Bootstrap (BS), displacement (DISP), and BS-DISP configurations (Figures A2.2 – A2.4), confirmed the stability of the solution by showing that the factors primarily mapped to themselves (BS analysis) and that the Q_{value} did not change drastically under rotational perturbation (DISP analysis)

The identified source profiles (Figure 4.6 and Table 4.5) exhibit distinct chemical signatures, demonstrating strong consistency with the enhanced chemical characterization presented in Chapter 3:

- **Soil:** Highly enriched in crustal elements such as Ca (62.8%), Al (49.3%), and Na, validating the inclusion of these elements as tracers for resuspended dust.
- **Biomass Burning:** Strongly dominated by K (56.0 %) a classic tracer for burning processes (e.g., crop residue, wood).
- **Secondary Aerosols (Sulfate and Nitrate):** These factors exhibit the most stable chemical profiles across uncertainty runs.
 - **Secondary Sulfate (30.7% of total PM_{2.5})** is characterized by high contributions from SO₄²⁻ (40.3%) and Cl⁻ (58.2%). The strong presence of Cl suggests a potential influence from coal combustion or specific industrial sources contributing to the secondary pool.

○ **Secondary Nitrate** (23.1% of total PM_{2.5}) is overwhelmingly dominated by NO₃⁻ confirming the dominant role of traffic NO_x and regional NO_x emissions in forming secondary fine particles.

- **Traffic and Industry:** These two factors showed greater compositional variability across uncertainty runs (e.g., fluctuating trace metal signatures), suggesting potential factor overlap or high heterogeneity in local emissions.

- **Traffic:** Characterized by Fe (49.4%), Ti (54.5%), Mn and Zn consistent with vehicular abrasion (tire/brake wear) and oil combustion.
- **Industry:** Distinguished by high contributions from Pb (53.1%), Zn (44.0%) and Mg (56.4%), which are typical signatures of local metallurgy, smelting, and manufacturing activities in the surrounding industrial zones.

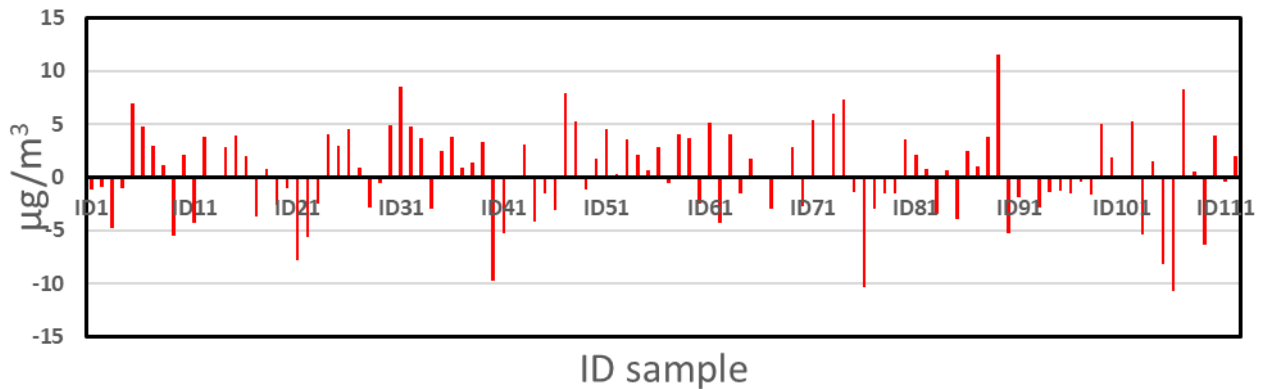


Figure 4. 5. The residuals of PM_{2.5} for 112 ID samples analyzed using PMF

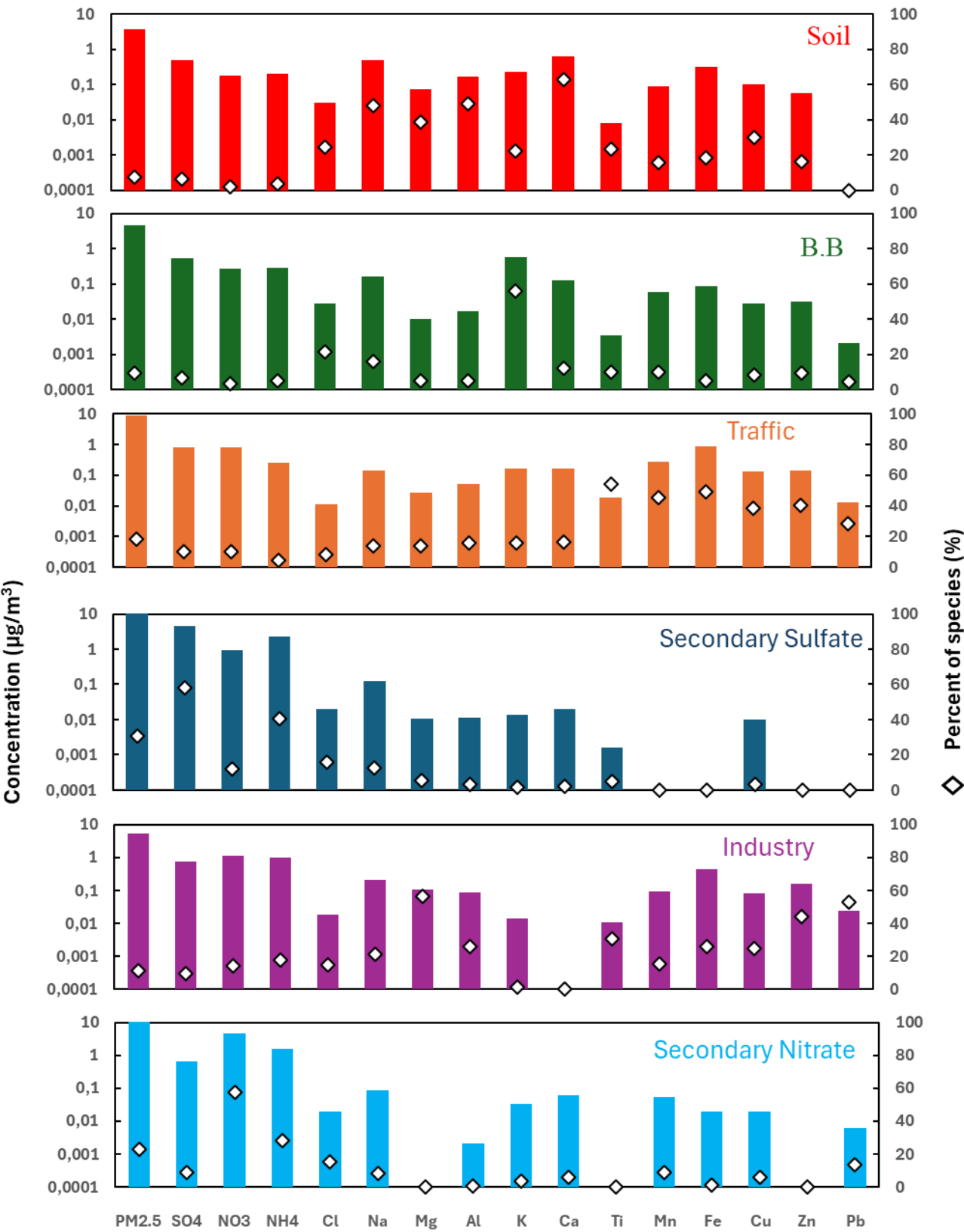


Figure 4. 6. Source profile derived from PMF modeling at the study sites in 2023

Table 4. 4. Species composition percentage within each factor

Name	Percent of species (%)					
	Soil	Biomass Burning	Traffic	Secondary Sulfate	Industry	Secondary Nitrate
PM _{2.5}	7.4	9.7	18.1	30.7	11.1	23.1
Cl	6.3	6.7	10.4	58.2	9.7	8.6
NO ₃	2.3	3.5	10.2	12.2	14.4	57.4
SO ₄	3.8	5.3	4.7	40.3	17.9	28.0
NH ₄	24.3	21.4	8.5	15.9	14.7	15.1
Na	28.1	16.1	13.7	12.4	21.2	8.4
Mg	18.8	5.1	14.0	5.6	56.4	0.0
Al	49.3	4.9	15.8	3.4	26.0	0.6
K	22.2	56.0	15.7	1.4	1.3	3.3
Ca	62.8	12.2	16.8	2.0	0.0	6.1
Ti	0.0	10.2	54.5	4.7	30.5	0.0
Mn	19.5	10.4	45.5	0.0	15.6	9.0
Fe	18.2	5.2	49.4	0.0	26.0	1.1
Cu	19.9	8.4	38.3	3.1	24.6	5.8
Zn	6.4	9.3	40.3	0.0	44.0	0.0
Pb	0.0	4.8	28.5	0.0	53.1	13.6

4.3.3. Source apportionment of PM_{2.5} by the PMF model

Figure 4.7 presents the source contributions to PM_{2.5} mass resolved by the PMF model, indicating six major sources including secondary sulfate, secondary nitrate, traffic, industry, biomass burning, and soil. The soil source is dominated by crustal elements such as Al (49.3%), Ca (62.8%), and Na (28.1%), indicative of resuspended mineral dust (Song, Zhang et al. 2006, Howlett-Downing, Boman et al. 2024), contributing 7.4% to PM_{2.5}, likely due to construction and agricultural activities. The B.B source, accounting for 9.7%, is characterized by high K (56.0%), along with Cl, Zn, and Pb, consistent with biomass combustion and linked to residential solid fuel use and open burning (Hien, Bac et al. 2021, Le, Khoi et al. 2022). Traffic emissions contributed 18.1%, marked by elevated Mn, Fe, Zn, and Cu, reflecting non-exhaust (Dai, Bi et al. 2015, Liu, Yang et al. 2021) and exhaust sources (Fang, Wang et al. 2023), including brake and tire wear and road dust resuspension. Moderate levels of SO₄²⁻ and NO₃⁻ in this factor indicate both primary and secondary processes (Liu, Sun et al. 2015, Wang, Wei et al. 2019). The Secondary sulfate factor contributed the largest share (30.7%) and is characterized by high SO₄²⁻ (58.2%) and NH₄⁺ (40.3%), representing aged, regionally transported aerosols formed from SO₂ oxidation, primarily from fossil fuel combustion and industrial activities (Liu, Chan et al. 2021).

The industry profile, contributing 11.1%, includes various metals (Fe, Cu, Zn, Pb) and moderate secondary components, suggesting mixed emissions from manufacturing and combustion processes (Makkonen, Vestenius et al. 2023, Vuong, Bac et al. 2023). The Secondary nitrate source, dominated by NO_3^- (57.4%) and NH_4^+ (28.0%), accounted for 23.1%, associated with ammonium nitrate formation under favorable atmospheric conditions and linked to NO_x emissions from mobile and stationary sources (Zhao, Su et al. 2025). These findings highlight the diverse origins of PM_{2.5}, with secondary aerosols (sulfate and nitrate) comprising over half of the total PM_{2.5}, underscoring the need for integrated regional and local control strategies targeting both primary and secondary pollutants to effectively mitigate urban air pollution.

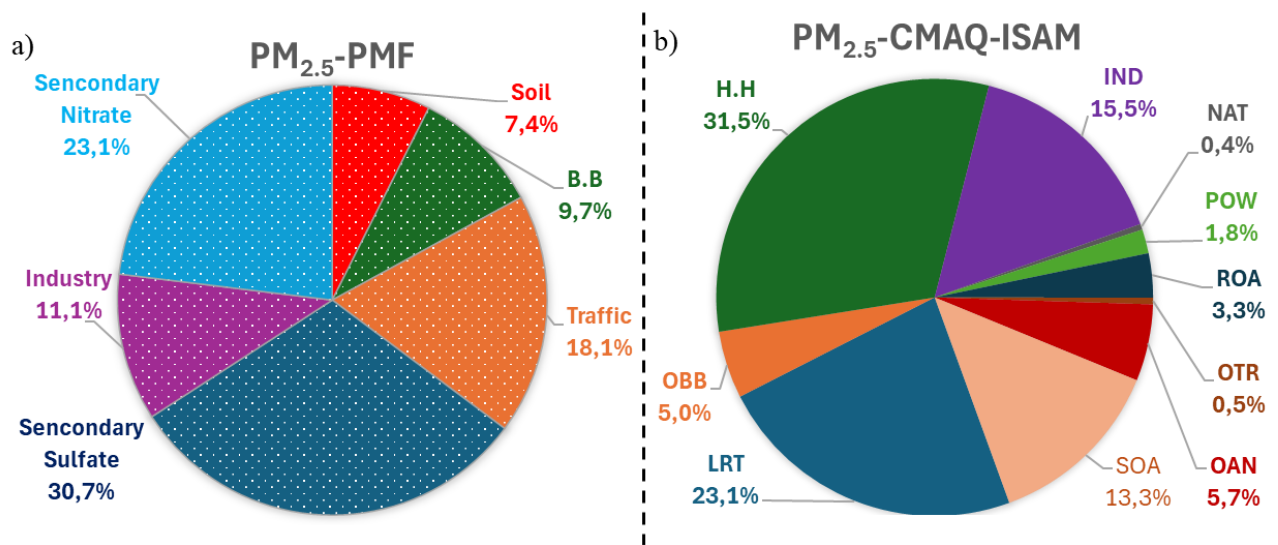


Figure 4. 7. Source contributions to PM_{2.5} in Hanoi identified by PMF receptor modeling in 2023(a), by WRF-CMAQ-ISAM modeling (including SOA) (b).

4.3.4. Source apportionment of PM_{2.5} by CMAQ-ISAM

Figure 4.7 presents the source apportionment results obtained from CMAQ-ISAM v5.3.3. SOA formation is attributed back to precursor VOC emissions from their respective sectors (e.g., residential combustion, traffic, industry, biomass burning, and biogenic sources). This limitation reflects the capabilities of ISAM in the version applied here although independent SOA source apportionment has already been incorporated in the latest CMAQ release. Future studies should therefore take advantage of these updated features, which allow direct quantification of SOA contributions by source category, thereby improving the accuracy and completeness of PM_{2.5} source apportionment.

The source apportionment results based on the CMAQ-ISAM model indicate that H.H are the dominant contributor to ambient PM_{2.5} concentrations, accounting for 31.4% of the total. This highlights the significant influence of residential activities, such as cooking and household combustion, on air quality in the study region (Chan, Xia et al. 2023). The LRT source, representing the influx of pollutants transported from outside the modeling domain, also contribute substantially (23.0%), suggesting a notable impact of transboundary pollution. The IND source account for 15.5%, reflecting the role of industrial activities in local PM_{2.5}. Emissions from OBB source based on the GFAS contribute 5.0%, indicating the influence of open burning events such as agricultural residue burning and forest fires detected via satellite data. The OAN category accounts for approximately 5.7% of total contributions. Critically, the OAN category is dominated by agricultural ammonia (NH₃) emissions, primarily from fertilizer application and livestock manure management, which represent the largest sources of NH₃ in most regions (Kurokawa and Ohara 2019). Although OAN emissions include fugitive VOCs in the inventory, their contributions to PM_{2.5} are not represented in ISAM v5.3.3 because SOA formation from VOC oxidation is not tracked. Therefore, VOC emissions in this category do not directly contribute to the modeled PM_{2.5} apportionment. ROA source contributes a smaller fraction (3.7%), along with POW (2.0%) and OTR (0.6%). In this simulation, natural (NAT) sources, including biogenic emissions, wind-blown dust, and sea-salt aerosols, contributed negligibly (<1% in total) to PM_{2.5}, indicating a minimal influence of natural processes compared to anthropogenic sources. This is consistent with the geographical characteristics of Hanoi, an inland urban area located far from the coastline, where marine aerosol input is minimal, and with limited arid or desert like surfaces, which reduces the influence of wind-blown mineral dust. These results underscore the need for targeted mitigation strategies focusing on household and industrial sectors, while also emphasizing the importance of regional collaboration to address cross-border pollution transport.

4.3.5. Comparison of PMF and CMAQ-ISAM

4.3.5.1. Comparison of Source apportionment of PM_{2.5} derived from CMAQ-ISAM and the PMF model

Figures 4.8a and 4.8b present the source apportionment of PM_{2.5} by concentration range derived from CMAQ-ISAM and PMF, respectively. In CMAQ-ISAM (Figure 4.8b), PM_{2.5} at lower concentrations (0–25 µg/m³) is dominated by H.H and OAN with smaller contributions from LRT and IND. As concentrations increase, the relative importance of LRT and OAN becomes more pronounced, indicating the increasing role of regional transport and secondary

formation at higher pollution levels. In contrast, the PMF results (Figure 4.8a) show that low concentrations are associated with a mixture of soil, traffic, and B.B, while secondary sulfate and nitrate already account for a substantial fraction. With rising PM_{2.5} levels, PMF reveals sharp increases in secondary sulfate and nitrate contributions, whereas primary sources such as traffic and biomass burning remain relatively stable. At the highest concentration ($>100 \mu\text{g}/\text{m}^3$), secondary aerosols (sulfate and nitrate) clearly dominate in PMF, while CMAQ-ISAM emphasizes LRT and OAN contributions.

The comparison of CMAQ-ISAM and PMF results reveals both consistencies and systematic differences rooted in the assumptions of each approach. Both methods consistently attribute substantial fractions of PM_{2.5} to combustion-related activities and atmospheric transformation products; however, their representations diverge. PMF identifies ‘secondary sulfate’ and ‘secondary nitrate’ factors directly from receptor measurements, but these factors inherently conflate contributions from both primary emissions and secondary formation. By contrast, ISAM, when appropriately configured, can separate primary and secondary components and distribute sulfate and nitrate among specific emission sectors (e.g., industry, households, or long-range transport). Additional distinctions arise in the treatment of biomass burning and regional transport. In ISAM, the OBB category exclusively represents open biomass burning, whereas the PMF ‘biomass burning’ factor may also encompass household combustion. Similarly, LRT emerges as major contributor in ISAM, cannot be explicitly resolved by PMF due to its reliance on receptor-site observations. The two methods provide complementary methodological perspectives: PMF yields observation-based source profiles that capture integrated local and secondary influences, while CMAQ-ISAM offers process-level attribution linking emissions, atmospheric transformations, and regional transport. Their combined application therefore enables a more comprehensive and policy-relevant understanding of PM_{2.5} pollutions episodes in Hanoi than either approach could achieve independently.

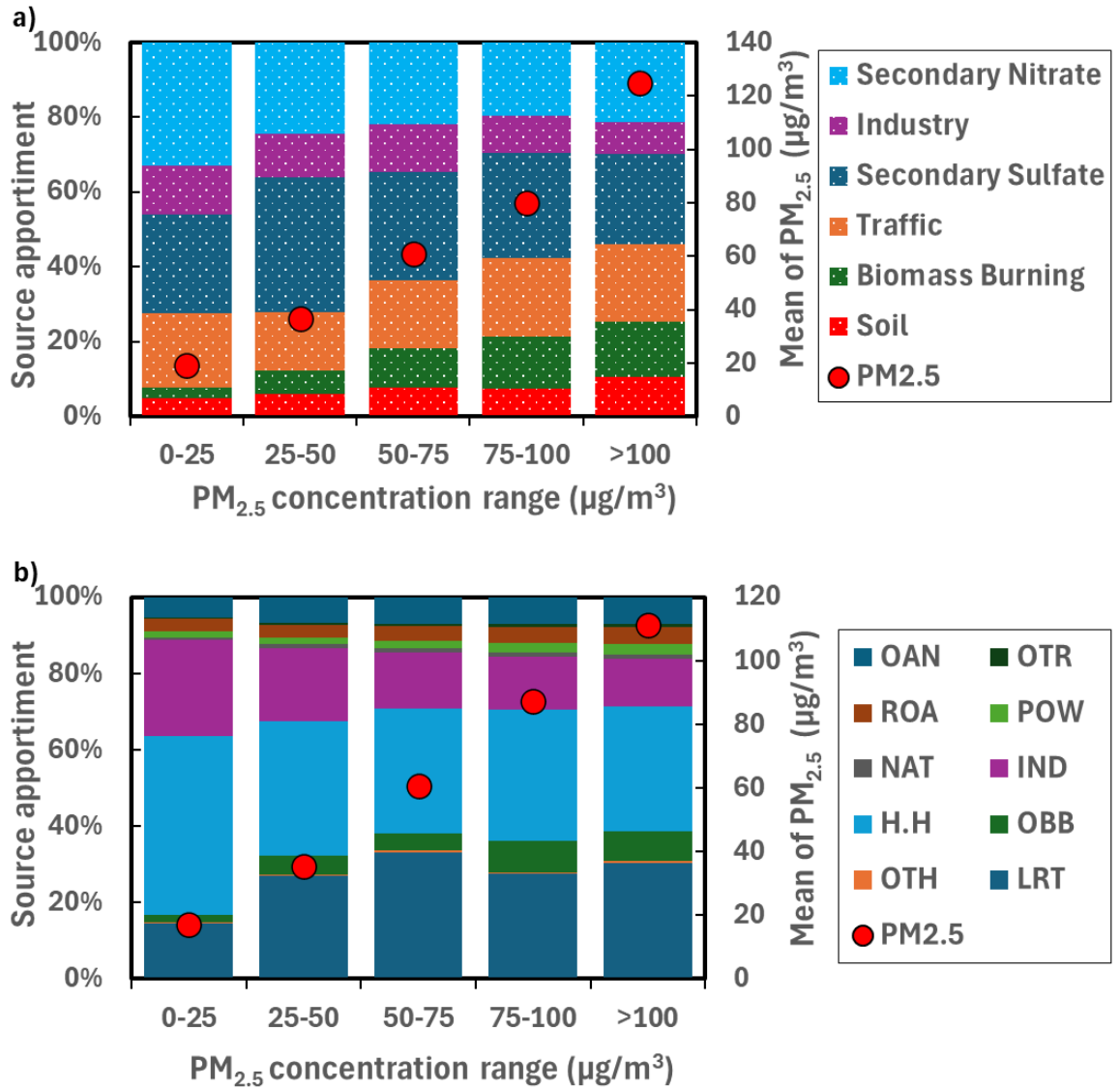


Figure 4.7. Relative contributions of PM_{2.5} sources by concentration range in Hanoi based on PMF (a) and CMAQ-ISAM (b) results

4.3.5.2. Source of ion in PM_{2.5}

The source apportionment of major inorganic ions in PM_{2.5}, including SO₄²⁻, NO₃⁻ and NH₄⁺, as shown in Figure 4.9, reveals significant discrepancies between the CMAQ-ISAM and PMF results. These three ions represent the dominant fraction of water-soluble inorganic species in PM_{2.5} and thus provide a robust basis for comparing the two approaches

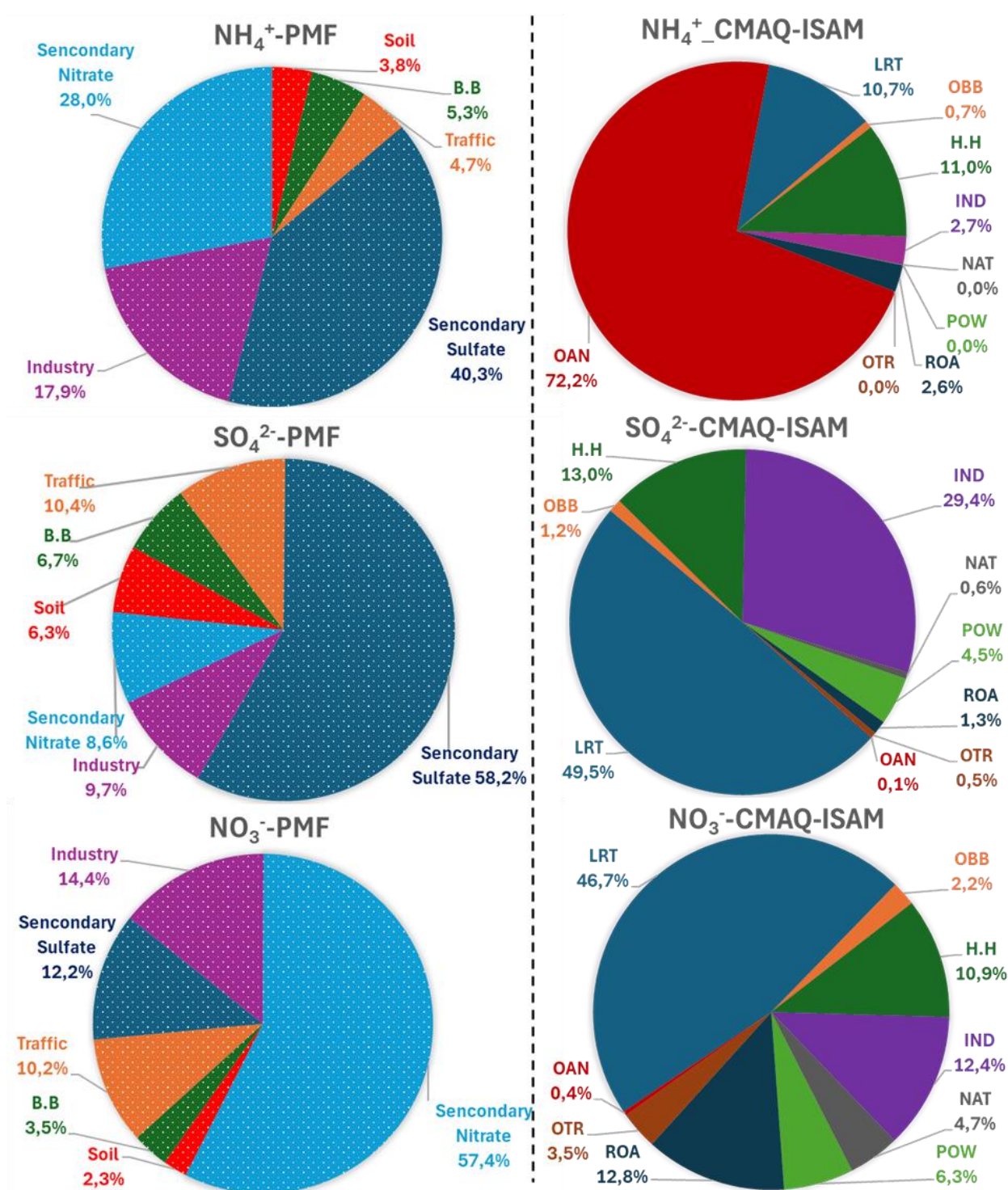


Figure 4. 8. Comparison of source contributions to major inorganic ions in PM_{2.5} between PMF receptor modeling and CMAQ-ISAM simulations in Hanoi, 2023

The SO₄²⁻ source by the CMAQ-ISAM results indicate that LRT contributes the largest fraction (49.5%), followed by IND (29.4%) and H.H (13.0%). In contrast, the PMF results are dominated by secondary sulfate (58.2%), with smaller contributions from industry (9.7%), traffic

(10.4%), biomass burning (6.7%), and soil (6.3%). This divergence highlights that PMF, as a receptor-based statistical model, does not explicitly resolve the atmospheric pathways of secondary aerosol formation but instead captures their aggregate influence within factor profiles. In contrast, CMAQ-ISAM, when appropriately configured, offers greater capability to attribute sulfate, nitrate, and ammonium to their precursor emissions and to distinguish between primary and secondary formation processes. (Kitagawa, Pedruzzi et al. 2021).

For NO₃⁻, CMAQ-ISAM attributes nearly half of the mass to LRT (46.7%), with additional contributions from ROA (12.8%), IND (12.4%), and POW (6.3%). It is important to note that in CMAQ-ISAM nearly all nitrate is formed secondarily in the atmosphere; the reported contributions therefore represent the distribution of precursor emissions across sectors and regions rather than direct primary emissions. By contrast, PMF resolves a dominant ‘secondary nitrate’ factor (57.4%) alongside industry (14.4%) and traffic (10.2%), indicating that the receptor model encapsulates atmospheric processing within explicit factors rather than attributing it back to individual precursor sources.

Regarding NH₄⁺, CMAQ-ISAM identifies OAN (72.2%) as the dominant contributor, followed by LRT (10.7%) and H.H (11.0%). In contrast, PMF attributes ammonium primarily to secondary sulfate (40.3%), secondary nitrate (28.0%), and industrial sources (17.9%), reflecting its formation as ammonium sulfate and ammonium nitrate in the atmosphere. The dominant contribution of the OAN source, representing other anthropogenic sources primarily associated with agricultural NH₃ emissions, to ambient NH₄⁺ concentrations can be attributed to both the magnitude of NH₃ emissions and the chemical transformation processes in the atmosphere. Agricultural activities, including fertilizer application and livestock farming, release substantial amounts of NH₃, which readily reacts with acidic species such as sulfuric acid (H₂SO₄) and nitric acid (HNO₃) to form secondary inorganic aerosols, notably ammonium sulfate ((NH₄)₂SO₄) and ammonium nitrate (NH₄NO₃). These reactions are rapid and efficient under typical atmospheric conditions, resulting in a high conversion rate of emitted NH₃ to particulate NH₄⁺. In contrast, other NH₃ sources, including domestic and traffic-related emissions, contribute comparatively less, both in terms of total emission mass and local accumulation. Consequently, CMAQ-ISAM simulations indicate that OAN accounts for approximately 70% of the ambient NH₄⁺, underscoring the pivotal role of agricultural emissions in secondary aerosol formation and PM_{2.5} pollution as indicated by the PMF.

Overall, CMAQ-ISAM provides a sector-resolved attribution of both primary emissions and secondary products derived from their precursors, whereas PMF extracts statistical factors

that represent the combined influence of local sources and atmospheric processing, often aggregating sulfate, nitrate, and ammonium into explicit secondary components. These distinctions underscore the conceptual complementarity of the two approaches: ISAM explicitly links secondary formation to emission sectors, while PMF reflects observation-based chemical signatures at the receptor site. A comparative application of both frameworks therefore affords a more comprehensive characterization of PM_{2.5} sources contributions than either method in isolation

4.4. Conclusions

This study provided an integrated analysis of PM_{2.5} characteristics and source contributions in Hanoi, Vietnam, during 2023 by combining chemical measurements, receptor modeling (PMF), and regional chemical transport modeling (WRF-CMAQ-ISAM). PM_{2.5} concentrations were moderately captured ($R = 0.80$; $MB = -5.5 \mu\text{g}/\text{m}^3$), indicating that while temporal patterns were well represented, absolute values were underestimated. The average PM_{2.5} concentration was $49.2 \mu\text{g}/\text{m}^3$, with secondary inorganic aerosols—sulfate ($7.84 \mu\text{g}/\text{m}^3$), nitrate ($7.90 \mu\text{g}/\text{m}^3$), and ammonium ($5.49 \mu\text{g}/\text{m}^3$) as dominant components, accounting for a substantial portion of total mass. Trace metals such as Fe ($1.72 \mu\text{g}/\text{m}^3$), Ca ($1.03 \mu\text{g}/\text{m}^3$), and Zn ($0.35 \mu\text{g}/\text{m}^3$) were also present, indicating contributions from crustal dust and anthropogenic activities. PMF source apportionment identified six major contributors: secondary sulfate (30.7%), secondary nitrate (23.1%), traffic (18.1%), industry (11.1%), biomass burning (9.7%), and soil dust (7.4%). In contrast, CMAQ-ISAM attributed the largest shares of PM_{2.5} to household emissions (H.H, 36.2%), long-range transport (LRT, 26.5%), and industrial sources (IND, 17.9%), with smaller contributions from open biomass burning (OBB, 5.7%), transport (ROA, 3.7%), and power generation (POW, 2.0%). Additionally, source attribution of these ions differed between methods: PMF captured them as distinct secondary aerosol sources, while CMAQ-ISAM linked them to precursor-based emission sectors. These results emphasize the importance of integrating receptor- and model-based source apportionment to provide complementary insights. PMF yields observation-driven source factors that encapsulate local emission signatures and secondary aerosol components, while CMAQ-ISAM attributes both primary emissions and secondary formation to specific sectors and regional transport processes. The combined application of these approaches enables a more comprehensive characterization of PM_{2.5} sources, thereby supporting the development of evidence-based air quality management strategies for Hanoi and comparable urban environments.

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Chapter 5 - General

Conclusions

5.1. General Conclusions

This research comprehensively assessed the sources and composition of fine particulate matter in Hanoi through a multi-faceted approach. The main findings from each part of the study are summarized as follows:

Chemical Characterization (Chapter 2): Extensive chemical analysis of PM_{2.5} revealed an exceptionally diverse mixture of constituents in Hanoi's air. In total, 288 distinct organic compounds spanning 19 chemical classes were identified in PM_{2.5} samples. This broad spectrum demonstrates the chemical complexity of the city's aerosols, reflecting its diverse emission sources including traffic, industry, domestic combustion, and agriculture. Among the identified groups, industrial intermediates and solvents accounted for the largest number of compounds (over 60 species), indicating strong influence from manufacturing activities. Antioxidants and plasticizers (e.g., bisphenol A and phthalates) were frequently detected, consistent with widespread use of plastics and rubber materials in the urban environment. Polycyclic aromatic hydrocarbons (PAHs) were also ubiquitous (23 PAH species, including 11 U.S. EPA priority pollutants), with high levels of carcinogenic compounds like benzo[a]pyrene pointing to vehicular and biomass combustion sources. A distinctive feature of Hanoi's organic aerosol profile was the significant presence of pesticide residues (over 100 pesticides, chiefly fungicides) – particularly at the Tay Ho site, reflecting intensive horticultural activity. Petroleum-related compounds were elevated at sites near waterways (e.g., Tay Ho, due to boat traffic on West Lake). Overall, the chemical profiles were highly site-specific, illustrating a hybrid pollution regime: the urban traffic site (Cau Giay) was dominated by traffic and domestic combustion markers, the industrial site (Pho Noi) showed an abundance of solvents and plasticizers from industrial processes, and the peri-urban site (Tay Ho) had a unique mix of agricultural pesticides and localized petroleum emissions. These results provided a first detailed insight into the complex chemical makeup of PM_{2.5} in Hanoi, underlining that multiple source types (and even some unexpected sources like pesticides) contribute to urban particulate pollution. Such complexity underscores the necessity of integrated air pollution control strategies that simultaneously address traffic, industrial, residential, and agricultural emissions. The chemical characterization presented in Chapter 2 shows that organic components contributed a relatively small fraction to PM_{2.5} mass during the study period, while water-soluble inorganic ions accounted for a substantially larger share. This compositional feature limits the representativeness of organic tracers for receptor-based source apportionment. Therefore, Chapter 3 focuses on the application of Positive Matrix Factorization (PMF) using major

inorganic ions and selected elemental species as primary input variables. By exploiting the higher concentrations and better analytical robustness of these species, the PMF analysis aims to achieve more stable factor resolution and more reliable identification of PM_{2.5} sources.

Receptor Modeling – PMF (Chapter 3): Source apportionment using Positive Matrix Factorization identified six major source factors contributing to Hanoi's ambient PM_{2.5}. These include secondary sulfate and secondary nitrate aerosols (formed from SO₂ and NO_x precursors), traffic emissions, industrial emissions, biomass burning, and soil/road dust. The PMF results indicated that secondary inorganic aerosols formed in the atmosphere constitute the single largest fraction of PM_{2.5} pollution in Hanoi. Specifically, a sulfate-rich factor – interpreted as aged, long-range transported pollution – accounted for roughly 30–40% of the fine particulate mass on average. Similarly, a nitrate-rich factor (ammonium nitrate associated with NO_x emissions) contributed around 20–25%. Together, these secondary aerosol factors made up over half of the PM_{2.5}, highlighting the dominant influence of atmospheric transformations (and their precursor emissions) on Hanoi's air quality. Among the primary source factors, traffic was a significant contributor (~15–20% of PM_{2.5}) characterized by markers such as elemental carbon and metals (e.g., Fe, Mn, Cu, Zn) from vehicle exhaust and non-exhaust (brake/tire wear, road dust) emissions. Biomass burning, encompassing both open burning (e.g. crop residues, waste) and residential fuel use, accounted for roughly 10% of PM_{2.5}; this factor was marked by elevated K⁺ (56% of K in PM_{2.5}) along with Cl⁻, Zn, and Pb, consistent with contributions from wood and agricultural burning. An industrial factor (~10–12%) was identified, enriched in trace metals (Pb, Zn, Cu, etc.) and also containing sulfate, suggesting emissions from manufacturing industries and coal combustion. Lastly, a crustal dust factor (soil/construction dust) contributed a smaller portion (~5–8%), characterized by high Al, Ca, and other crustal elements. The PMF analysis also revealed pronounced seasonal and spatial patterns in source contributions. During winter (dry season) episodes, Hanoi's PM_{2.5} had a much larger secondary sulfate component, indicating that transboundary pollution (e.g., coal combustion emissions transported from upwind regions in northern Vietnam and southern China) plays a major role in elevating fine particle levels. In summer (wet season), by contrast, regional background pollution was lower (due to cleansing monsoonal rains and shifts in wind patterns), and the relative contribution of local sources (traffic, construction dust, etc.) became higher. Spatially, a comparison between an urban background site (HQV) and a roadside site (NT) showed that the roadside location experienced a much greater share of traffic-derived PM_{2.5} (as expected), whereas the background site recorded higher contributions from secondary sulfate transported into the city. In summary, the receptor

modeling confirmed that Hanoi's fine particulate pollution is driven by a combination of local emissions and regionally transported secondary aerosols, with the latter often dominating the PM_{2.5} mass during severe pollution episodes. The receptor modeling results presented in Chapter 3 provide valuable insights into the source profiles and relative contributions of PM_{2.5} at the monitoring locations based on observed chemical composition. However, as a receptor-based approach, PMF is inherently limited in its ability to resolve spatially continuous source contributions, regional transport processes, and the formation pathways of secondary aerosols. To address these limitations and to extend source apportionment beyond the receptor scale, Chapter 4 applies a chemical transport modeling approach using the Community Multiscale Air Quality (CMAQ) model coupled with the Integrated Source Apportionment Method (ISAM). This model-based framework enables a process-resolved and spatially explicit assessment of emission-sector and regional contributions to PM_{2.5}, thereby complementing and strengthening the interpretation of the PMF results.

Chemical Transport Modeling – CMAQ-ISAM (Chapter 4): Using the WRF–CMAQ chemical transport model equipped with the Integrated Source Apportionment Method (ISAM), we quantified PM_{2.5} contributions from specific sectors and regions. The model was run for a full year (2023) over Hanoi, with emissions tagged into nine categories: Household (residential) combustion, Industry, Power generation, On-road transport (ROA), Other transport (e.g. aviation, rail), Open biomass burning (OBB), Other anthropogenic (OAN, mainly agricultural activities), Long-range transport (LRT, pollutants entering from outside the domain), and Natural sources. The CMAQ-ISAM results were broadly consistent with the PMF findings, but offered more detailed source attribution by sector. Household emissions (residential cooking and heating, small-scale commercial burning) emerged as the single largest contributor to Hanoi's PM_{2.5}, accounting for about 31% of annual average concentrations. The second-largest contributor was long-range transport, i.e. pollutants advected into Hanoi from outside, contributing roughly 23%. This substantial imported fraction underscores the importance of regional sources (e.g. industrial and agricultural emissions in neighboring provinces and countries) in Hanoi's air quality. Industrial activities within and around the city (manufacturing facilities, factories, craft villages, etc.) were the next major source, responsible for approximately 15–16% of PM_{2.5}. Notably, open biomass burning (agricultural field burning and occasional forest fires) contributed an estimated 5% on an annual basis. While modest on average, this source is highly episodic – for instance, model results (and observations) indicated that post-harvest rice straw burning can temporarily raise PM_{2.5} levels by substantial amounts in early summer and autumn. The agricultural ammonia

category (OAN) accounted for ~5–6%, primarily reflecting secondary ammonium nitrate and sulfate formed from farming-related NH₃ emissions. Meanwhile, on-road traffic was found to contribute a smaller fraction (~3–4%) of direct PM_{2.5}, and power plants within the domain contributed ~2%. (It should be noted that some fraction of traffic and power plant emissions also ends up as secondary particles captured in the above categories; for example, vehicle NO_x emissions contribute to the secondary nitrate fraction.) Natural sources (windblown dust, sea salt, biogenic aerosol) were negligible (<1%) in Hanoi's PM_{2.5} budget given the city's inland location and lack of nearby deserts or marine influence. These CTM results reinforce that virtually all of Hanoi's PM_{2.5} problem is anthropogenic in origin, and they illuminate the critical impact of regional pollutant transport: even if Hanoi were to eliminate all local emissions, a significant baseline concentration (on the order of 20–25 µg/m³ on average days) would remain due to transboundary inflows. The model-based source apportionment closely mirrored the PMF conclusions in terms of identifying major source categories, while providing clarity on their origins. For example, what PMF labeled “secondary sulfate” is in CMAQ-ISAM partially attributed to specific sectors like industrial coal burning and regional inflow (LRT), and the PMF “biomass burning” factor can be separated into contributions from open fires (OBB) vs. residential cooking (H.H) in the model. This sectoral perspective is invaluable for crafting targeted emission control policies.

Integration of Approaches: A key feature of this study is the combined use of receptor modeling and forward modeling, which provided a cross-check on source apportionment results. Overall, the two approaches converged on a consistent understanding of Hanoi's PM_{2.5} pollution: both identified that the bulk of fine particulate matter derives from combustion sources (vehicles, industry, biomass/residential burning) and secondary formation of sulfate/nitrate from precursor gases. Both approaches also underscored the influence of transboundary pollution in elevating Hanoi's particle levels, especially in the dry season. At the same time, the comparison revealed important nuances. The receptor model (PMF), based on measured chemical fingerprints, implicitly grouped certain emissions together (e.g. household cooking and field burning under a broad “biomass burning” factor, or all long-range secondary sulfate under one factor). In contrast, the CTM with ISAM explicitly separated those contributions (differentiating domestic vs. open burning, and isolating an LRT contribution). Likewise, PMF's “secondary nitrate” factor captures the aggregate nitrate aerosol, whereas CMAQ-ISAM could attribute portions of that nitrate to traffic, industry, or other NO_x sources. These differences highlight that while PMF provides an observation-based picture anchored in local data, CMAQ-ISAM provides a process-

based source tracing, and combining the two yields a more comprehensive view than either alone. By integrating findings, we improved confidence in source attribution and gained insight into phenomena that one method alone might misinterpret. For instance, the agreement between methods on the prominence of residential and industrial emissions strengthens the case for targeting those sectors, while the methods' different handling of secondary aerosol shows the value of having both perspectives to fully understand the local vs. regional contributions. In summary, the dual approach allowed us to validate and enrich the source apportionment, ensuring that conclusions are robust and well-grounded for decision-making purposes.

5.2. Scientific and Policy Implications

The findings of this dissertation have significant implications for both scientific understanding of air pollution and the development of effective air quality management policies:

- **Advancement of Scientific Knowledge:** This work is among the first to integrate detailed chemical speciation, receptor modeling, and advanced CTM source apportionment for PM_{2.5} in Vietnam. By addressing several research gaps (comprehensive organic compound screening, multi-site seasonal source apportionment, model–measurement comparison), it contributes a richer understanding of the sources and formation processes of PM_{2.5} in a Southeast Asian megacity. The extensive chemical dataset (including hundreds of organic pollutants) provides new insight into previously under-characterized emissions, such as the prevalence of agricultural pesticides and industrial chemicals in urban PM_{2.5}. These findings can inform toxicological studies and future source identification efforts by highlighting chemical markers of specific activities (e.g. fungicides for horticulture, phthalates for plastic use, etc.). Methodologically, the study demonstrates the value of combining receptor and chemical transport models for air pollution source assessment. It shows that despite differences, PMF and CMAQ-ISAM can be used together to validate results and reduce uncertainties in apportioning complex particulate mixtures. This integrated framework can be applied in other regions to improve source accountability. Moreover, the comparative analysis highlights areas for model improvement – for instance, we identified the need for updated CTM tools that can apportion secondary organic aerosol (a capability emerging in newer CMAQ versions). By documenting the agreements and discrepancies between PMF and CMAQ-ISAM, this work provides a reference for scientists attempting similar multi-method studies and underscores the importance of continuously refining both measurement and modeling techniques in air quality research.

- **Guidance for Air Quality Management:** From a policy perspective, the results

offer clear guidance on priority sources and mitigation strategies for Hanoi's PM_{2.5} pollution. Household (residential) emissions – primarily from cooking with charcoal, wood, or low-grade coal – were identified as the largest single contributor to fine particulate levels. This suggests that programs to transition households to cleaner cooking fuels and technologies (e.g., subsidizing LPG or electric stoves, biogas in peri-urban areas) could yield substantial reductions in PM_{2.5}. Industrial emissions were another major contributor (about one-sixth of PM_{2.5}), indicating the need for stricter control measures on factories and industrial zones. Enforcing emission standards (for example, requiring effective flue gas treatment on boilers and furnaces), relocating heavy industries out of densely populated areas, and accelerating the shift from coal to cleaner energy sources in industry would all help curb PM_{2.5}. The significant secondary aerosol fraction (sulfate and nitrate) points to controlling precursor gases: reducing SO₂ (from coal burning in power plants and industry) and NO_x (from vehicles and industry) is crucial for bringing down secondary PM_{2.5}. For example, speeding up the retirement or upgrade of coal-fired power plants, and adopting Euro VI vehicle standards or electric vehicles in transportation, would cut precursor emissions and thereby reduce sulfate/nitrate particulate formation. The identification of agricultural burning as an episodic source (~5% annual, but higher in certain seasons) underlines the importance of regulating open burning. Policies such as enforcing bans on post-harvest burning, providing farmers with alternatives (like mechanical straw management or biomass valorization programs), and rapid-fire detection and suppression can mitigate this source. Crucially, the transboundary contribution (~23%) means that Hanoi's air quality management must extend beyond city (and even national) boundaries. Regional cooperation is essential – Vietnam should continue to engage with neighboring countries through frameworks like ASEAN agreements or bilateral initiatives to address cross-border air pollution. Within Vietnam, coordination with upwind provinces is needed to reduce industrial and agricultural emissions that travel into Hanoi. This study's evidence for a persistent regional background pollution load highlights that Hanoi's PM_{2.5} problem is not solely a local issue, and thus solutions require integrated regional strategies. Lastly, while traffic emissions were a somewhat smaller fraction of PM_{2.5} in our results than expected, they remain important for public exposure, especially in roadside microenvironments, and they contribute to NO₂ and ozone problems. Continuing to expand public transit, encouraging cleaner vehicle technologies, and managing traffic congestion will have multi-pollutant benefits. In summary, the study provides policymakers with a prioritized list of sources to target: residential burning and industrial emissions (as the top local contributors), regional pollution inflows (calling for inter-provincial

and international action), and specific practices like open burning and traffic management. Implementing a combination of measures addressing these areas is likely to produce the most effective reduction in Hanoi's PM_{2.5} levels, leading to healthier air for its residents.

5.3. Limitations and Future Research

Despite its comprehensive scope, this study has several limitations, which point toward directions for future research:

- **Emission Inventory and Model Uncertainties:** The accuracy of the CMAQ-ISAM source contributions depends on the underlying emission inventory and model representation. Uncertainties in emission data (especially for the informal sectors like household cooking, small industrial workshops, and open burning) can affect the apportionment. For example, if residential biofuel use or cottage industry emissions were underestimated in the inventory, their true contribution could be higher than modeled. Additionally, the version of CMAQ-ISAM used did not explicitly track secondary organic aerosol by source, meaning contributions of VOC-rich sources (e.g. traffic, solvent use) to organic PM_{2.5} were not fully differentiated. Future studies should strive to improve emission inventories (through local measurements and updated activity data) and utilize the latest modeling tools that include full source tagging for secondary organics. Conducting sensitivity analyses (e.g. varying emission estimates for key sectors within plausible bounds) would also help quantify the robustness of the source contribution results.

Receptor Model Limitations: The PMF results carry the typical uncertainties of receptor modeling. While we applied diagnostics (bootstrapping, factor rotations) to ensure a stable solution, there is always some ambiguity in factor interpretation. Some source categories may overlap (for instance, emissions from traditional restaurants could produce a mix of markers that partially resemble both traffic and biomass burning profiles). Moreover, PMF cannot perfectly resolve sources that have similar chemical signatures or that vary rapidly in time. Our PMF factors explained the observed variations well, but resolving more granular sources (e.g., distinguishing gasoline vs. diesel vehicles, or different industrial sub-sectors) was beyond the scope of the measured dataset. Future receptor studies in Hanoi could benefit from measuring additional marker species – for example, specific organic tracers (like levoglucosan for biomass burning, or hopanes for vehicle exhaust) – to further resolve source signatures. Applying other receptor models (e.g., UNMIX, CMB, PCA methods) in parallel may also provide comparative insights and cross-validation of the source apportionment.

Spatial and Temporal Coverage: This study focused on a limited number of monitoring

sites within Hanoi and on one year of data. While the sites were chosen to represent different environments (urban, industrial, peri-urban), they may not capture all intra-city variability – for instance, neighborhoods with heavy construction or specific industrial facilities could experience different PM_{2.5} source mixes. Likewise, the year of study may not capture atypical events (e.g., extreme weather years, or the influence of COVID-19 lockdowns on emissions). Future research should expand spatial and temporal coverage, possibly deploying a network of sensors across the city and its surroundings to map spatial gradients of source impacts. Longer-term studies covering multiple years would help assess interannual variability and trends in source contributions, especially as government policies or economic conditions change emissions over time. Such extended monitoring and modeling would also allow evaluation of the effectiveness of any interventions implemented as a result of this research.

Health Impact Assessment: While this dissertation focused on source quantification, an important extension is to evaluate the health implications of the identified sources. Different sources emit particles with different toxicity – for example, vehicle exhaust and industrial emissions tend to produce more chemically reactive and toxic components (like PAHs, metals) compared to some natural sources. A logical next step would be to integrate the source apportionment results with epidemiological or toxicological studies to estimate which sources contribute most to health risk. This could involve calculating the population exposure attributable to each source and applying concentration-response functions for health outcomes. Additionally, the rich chemical composition data (especially the toxic organics and metals identified) could be used to inform health risk assessments (e.g., cancer risk from PAH exposure at different sites). Such health-oriented research can prioritize control measures not just by mass reduction but by potential health benefit, focusing on the most harmful emissions.

Continued Model Development and Scenario Analysis: On the modeling front, there are opportunities to refine and build on this work. Incorporating recent developments in CMAQ (as mentioned, source-specific SOA tracking, improved chemistry, higher-resolution modeling) will enhance source attribution fidelity. Running scenario simulations would directly support policy – for example, modeling a “clean stove” scenario where household emissions are reduced, or a “regional cooperation” scenario with lower inflow from upwind regions, to quantitatively predict how PM_{2.5} concentrations and episodes would change. This would allow policymakers to gauge the potential air quality improvements from different actions (e.g., how much would PM_{2.5} drop if residential emissions fell by 50%?). Another worthwhile direction is to use data assimilation or inverse modeling to adjust emissions based on observed concentrations, which could improve

source estimates. Furthermore, expanding the modeling domain to cover a larger region of Southeast Asia would capture more of the transboundary pollution processes; this could be paired with satellite data (e.g., for detecting fire counts or regional aerosol) to better constrain LRT contributions.

In conclusion, this dissertation provides an integrated, in-depth assessment of PM_{2.5} pollution sources in Hanoi. By synthesizing information from chemical measurements, receptor modeling, and CTM simulations, it offers a robust understanding of both local and regional contributions to Hanoi's air quality. The research outcomes not only fill critical gaps in the current knowledge of urban air pollution in Vietnam but also serve as a scientific foundation for air quality management. The evidence highlights that effective mitigation will require a multi-pronged approach – curbing emissions from households, traffic, and industries locally, while also engaging in regional emission reduction efforts – to achieve substantial and sustained improvements in air quality. These general conclusions reinforce the notion that air pollution in fast-growing cities is a shared challenge that must be addressed through integrated scientific insight and coordinated policy action.

Appendices

Appendix 1 - Supplementary materials to Chapter 3

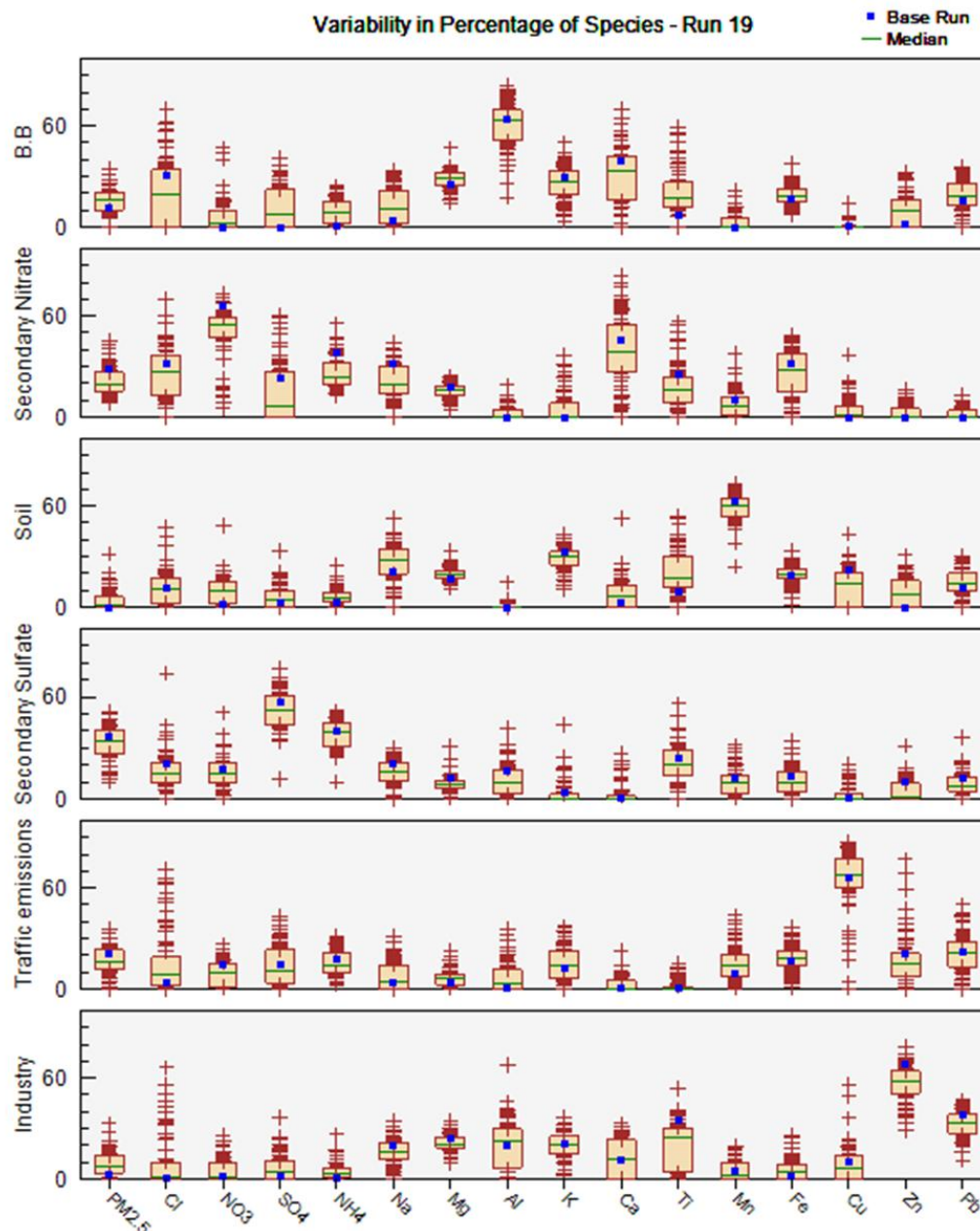


Figure A1.1. Percentage variability in species contributing to PM_{2.5} at both HQV and NT in 2022

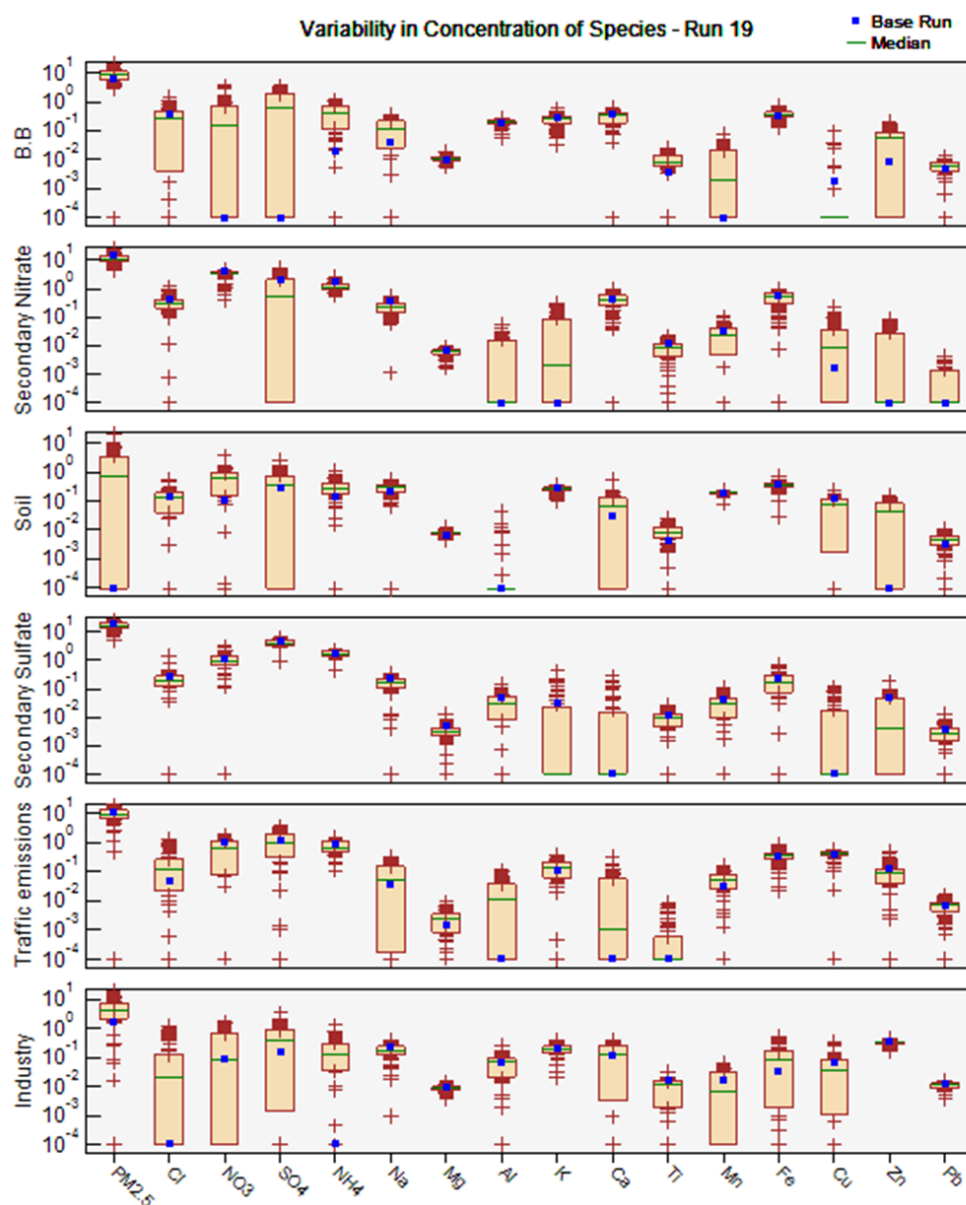


Figure A1.2. Concentration variability in species contributing to PM_{2.5} at both HQV and NT in 2022

Appendix II – Supplementary materials to Chapter 4

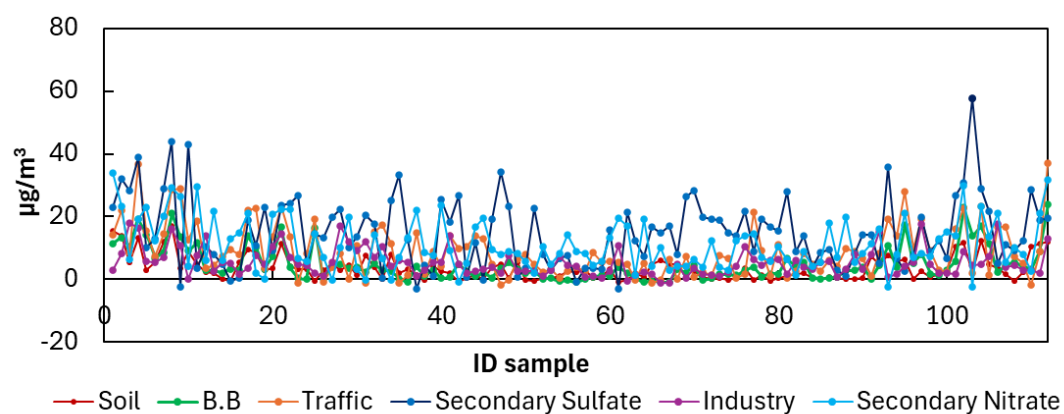


Figure A2.1. The graph of source apportionment concentrations in 112 ID samples

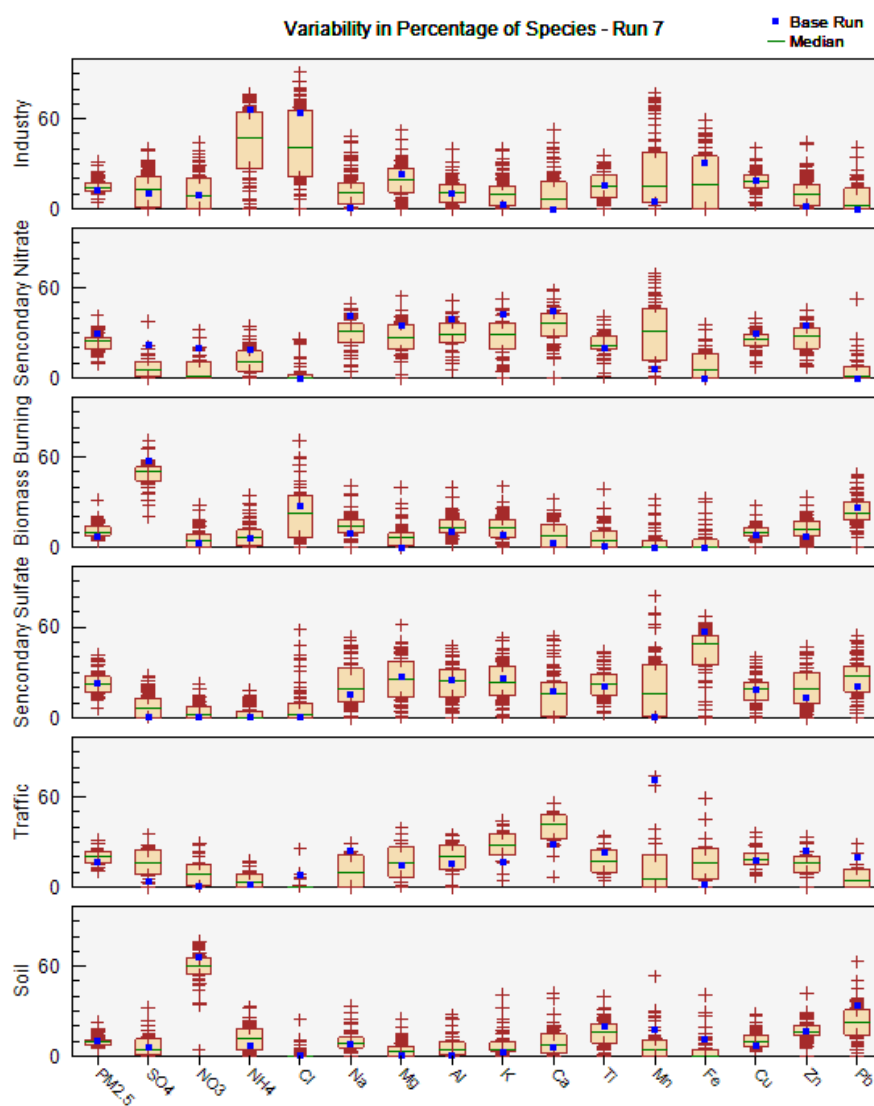


Figure A2.2. Percentage variability in species contributing to PM_{2.5} at HQV in 2023

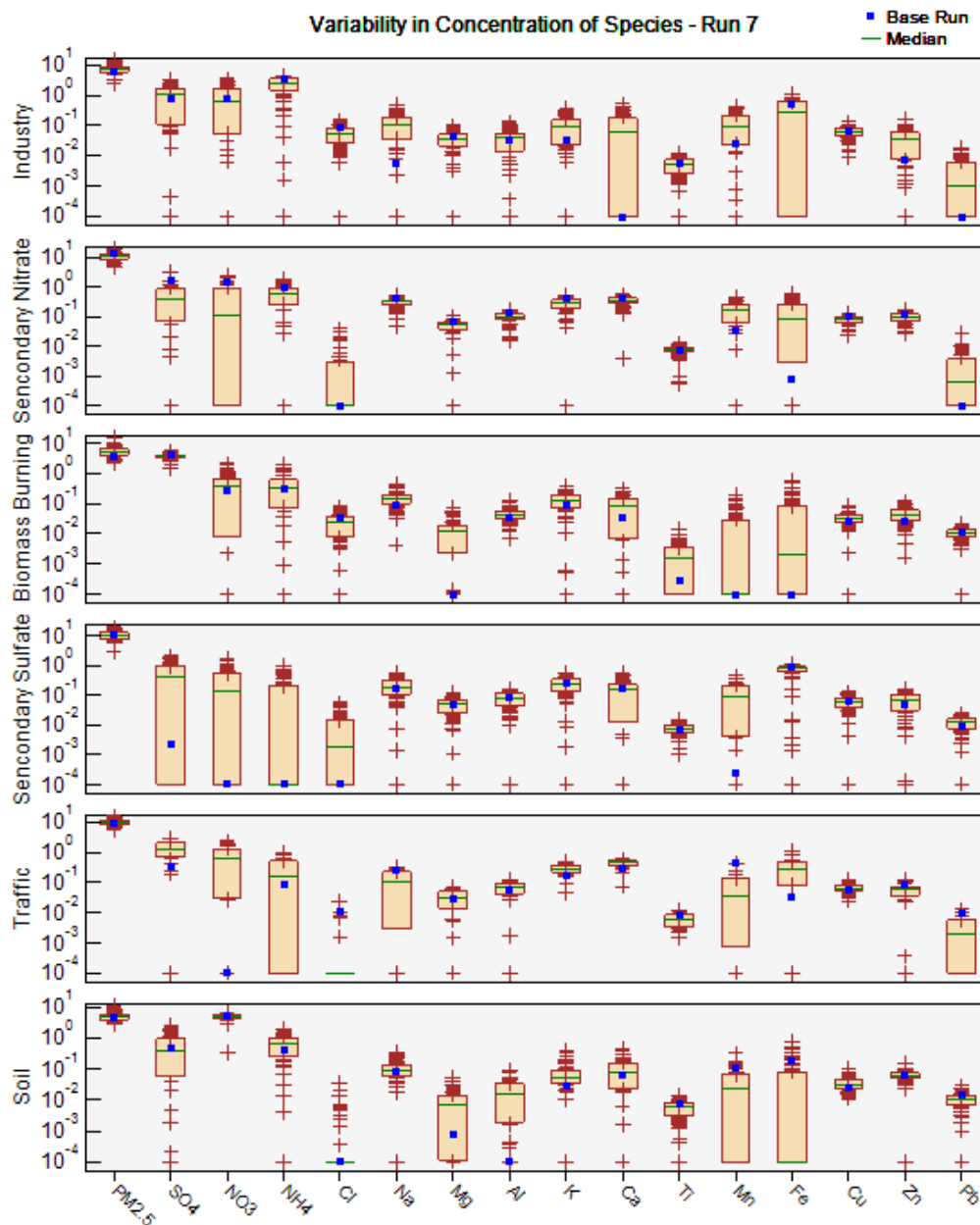


Figure A2.3. Concentration variability in species contributing to $PM_{2.5}$ at HQV in 2023

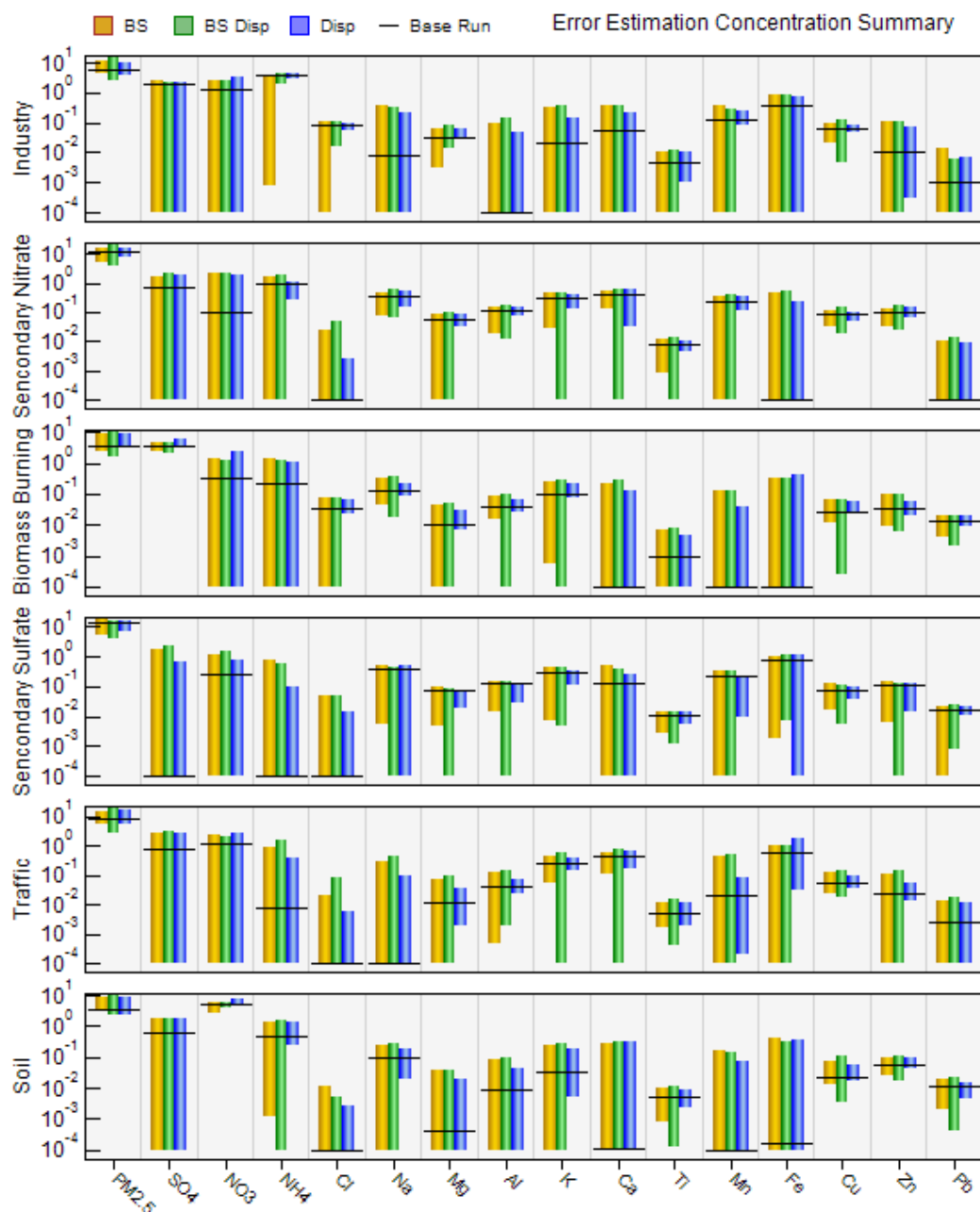


Figure A2.4. Error estimation of PM_{2.5} source contributions and species concentrations from the PMF model using bootstrap (BS), displacement (DISP), and combined BS-DISP approaches

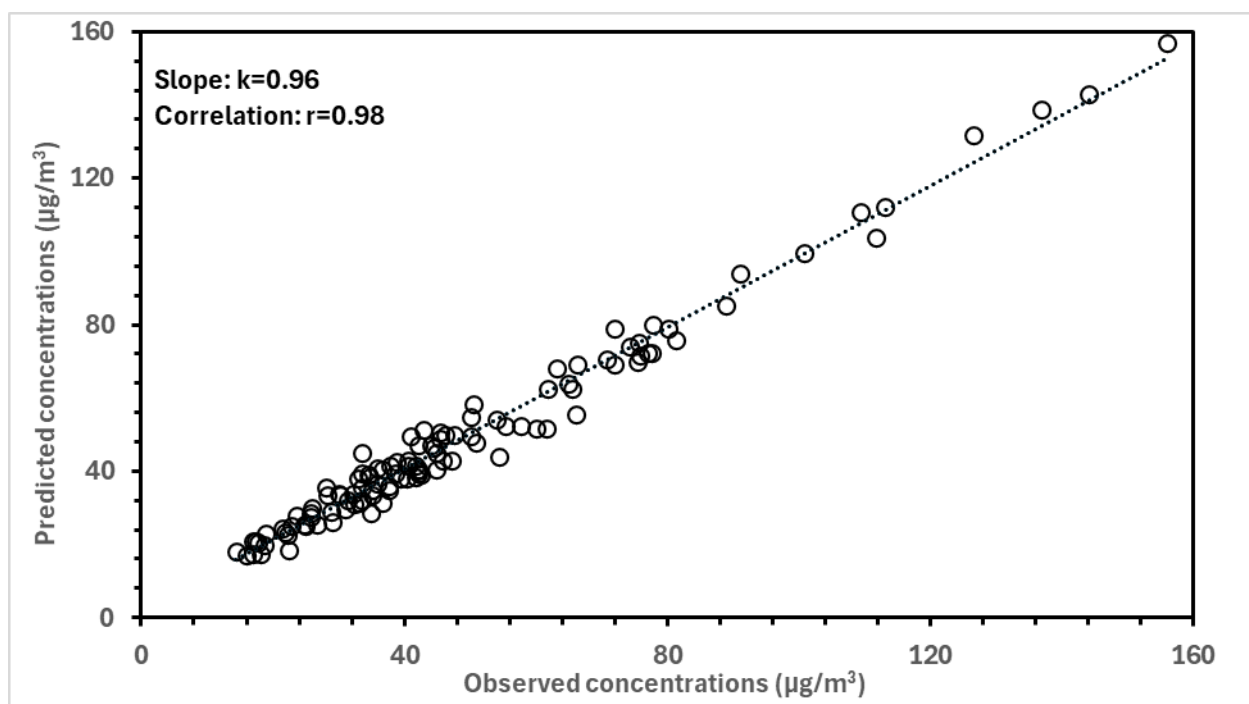


Figure A2.5. The scatter plot displays the performance of PMF modeling during the study period.

Table A2.1. Monthly and annual mean $\text{PM}_{2.5}$ and SOA concentrations with SOA contributions

2023	$\text{PM}_{2.5}$ ($\mu\text{g}/\text{m}^3$)	SOA ($\mu\text{g}/\text{m}^3$)	SOA (%)
Jan	76.0	6.7	8.8
Feb	48.9	4.7	9.6
Mar	52.5	7.1	13.5
Apr	58.1	11.7	20.1
May	33.8	8.7	25.7
Jun	22.9	4.0	17.5
Jul	16.3	2.4	14.7
Aug	18.8	2.6	13.8
Sep	24.6	3.5	14.2
Oct	43.9	6.0	13.7
Nov	54.8	6.7	12.2
Dec	62.6	5.9	9.4
Mean	42.8	5.8	13.6