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Air Pollution

Emerging Contaminants and Control Strategies

*Edited by Hugo Albeiro Saldarriaga Noreña
and Jose Gustavo Ronderos-Lara*



Air Pollution - Emerging Contaminants and Control Strategies

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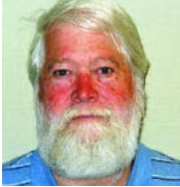
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Aims and Scope of the Series

Scientists have long researched to understand the environment and man's place in it. The search for this knowledge grows in importance as rapid increases in population and economic development intensify humans' stresses on ecosystems. Fortunately, rapid increases in multiple scientific areas are advancing our understanding of environmental sciences. Breakthroughs in computing, molecular biology, ecology, and sustainability science are enhancing our ability to utilize environmental sciences to address real-world problems.

The four topics of this book series - Pollution; Environmental Resilience and Management; Ecosystems and Biodiversity; and Water Science - will address important areas of advancement in the environmental sciences. They will represent an excellent initial grouping of published works on these critical topics.

Meet the Series Editor



J. Kevin Summers has been working as a Senior Research Ecologist at the Environmental Protection Agency's (EPA) Gulf Ecosystem Measurement and Modeling Division. He worked with colleagues in the Sustainable and Healthy Communities Program to develop an index of community resilience to natural hazards, an index of human well-being that can be linked to changes in the ecosystem, social and economic services, and a community sustainability tool for communities with populations under 40,000. He led research efforts for indicator and indices development. Dr. Summers is a systems ecologist and began his career at the EPA in 1989 and has worked in various programs and capacities. This includes leading the National Coastal Assessment in collaboration with the Office of Water, which culminated in the award-winning National Coastal Condition Report series (four volumes between 2001 and 2012), and which integrates water quality, sediment quality, habitat, and biological data to assess the ecosystem condition of the United States estuaries. He was acting National Program Director for Ecology for the EPA between 2004 and 2006. He has authored approximately 150 peer-reviewed journal articles, book chapters, and reports, and has received many awards for technical accomplishments from the EPA and from outside of the agency. Dr. Summers holds a BA in Zoology and Psychology, an MA in Ecology, and Ph.D. in Systems Ecology/Biology.

Meet the Volume Editors



Dr. Hugo Albeiro Saldarriaga Noreña is a Professor-Researcher at the Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos (México). His work focuses on emerging contaminants in environmental matrices, including analytical method development, adsorption/biosorption and nature-based remediation, and data-driven approaches for environmental monitoring. He collaborates on projects related to microplastics, pesticides, and air-quality-relevant pollutants, and has supervised and examined undergraduate and graduate theses. He serves as an academic editor and peer reviewer for international journals and edited volumes in environmental science.



Dr. José Gustavo Ronderos Lara is a Mexican academic researcher specializing in the study of emerging pollutants in various environmental matrices. His main scientific work focuses on developing analytical methods for detecting and quantifying endocrine-disrupting pollutants in air (PM_{2.5}), water, and sediments. Currently, his research is directed toward monitoring emerging pollutants and determining the estrogenic risks to human health and aquatic fauna posed by endocrine-disrupting pollutants in the environment. He has published articles in scientific journals and contributed chapters to various books.

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Preface

Air pollution remains a complex and evolving challenge for environmental science, public health, and policy. Over recent decades, significant advances in monitoring and regulation have been achieved for so-called “criteria pollutants”. However, growing evidence shows that the atmosphere also transports and transforms a broader array of chemical species and particles, often referred to as emerging contaminants, whose sources, fate, exposure pathways, and risks are not yet fully captured by traditional frameworks.

This book brings together international contributions that explore air pollutants through complementary lenses, chemical characterization, source apportionment, measurement science, exposure-relevant indicators, and mitigation strategies. A central theme across the chapters is that effective air-quality management depends on both robust data and mechanistic understanding: identifying dominant sources, tracing pollutant pathways, and translating findings into practical intervention options.

Several chapters focus on PM_{2.5} in real-world environments and the implications for urban air quality and health risk. Case studies include coastal/industrial conditions influenced by ship exhaust emissions, as well as campus-scale assessments that combine source attribution with toxicity potential and benchmarking against national and international guidelines. These contributions illustrate how local emission profiles and meteorology can shape exposure patterns and priority actions.

Beyond particulate matter, the volume highlights the importance of accurately measuring key gaseous species that influence atmospheric chemistry and control strategies. Atmospheric ammonia, for example, is an essential target because of its role in secondary inorganic aerosol formation and its relevance to emission control in agricultural and urban contexts. The chapter dedicated to ammonia measurement links emission sources, analytical methods, and mitigation approaches, providing an applied perspective that connects monitoring to decision making.

The book also offers a forward-looking perspective on ultrafine particles, emphasizing emerging approaches for identifying emission sources and improving predictive capabilities in complex urban areas. Finally, mitigation is addressed not only through conventional control thinking but also through nature-based and community-relevant options, including the assessment of tolerant plant species that could reduce pollution burdens.

We sincerely thank all contributing authors for their work and collaboration throughout the editorial process, and we acknowledge the support of the IntechOpen editorial team in guiding the preparation of this book.

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Introductory Chapter: Air Pollution – Emerging Contaminants and Control Strategies

Hugo Albeiro Saldarriaga Noreña and José Gustavo Ronderos-Lara

1. Introduction

Air pollution remains one of the most persistent environmental problems facing society today. Its impact is measured not only in economic losses and a reduced quality of life but also in direct effects on human health. According to the WHO, millions of deaths occur annually, attributable to exposure to air pollutants [1]. For decades, the scientific and regulatory focus has centered on criteria pollutants, such as particulate matter (PM_{2.5}), nitrogen oxides (NO_x), sulfur dioxide (SO₂), carbon monoxide (CO), and ozone (O₃). This approach has been essential and has led to significant progress in monitoring, exposure assessment, and mitigation. Recent studies have revealed the presence of emerging pollutants whose environmental fate, exposure pathways, and toxicology are not yet fully understood [2]. This group of pollutants primarily includes polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl and polyfluoroalkyl substances (PFAS), microplastics, endocrine disruptors, and ultrafine particles, which are most frequently detected in urban, industrial, and rural areas [3, 4].

2. Characteristics and relevance of emerging air pollutants

In this chapter, the term “emerging contaminant” is used for chemical or particulate species that are not routinely monitored but for which evidence is growing regarding adverse effects on ecosystems and/or human health, including through transformation products and complex exposure mixtures.

These contaminants are of particular concern because many are persistent, capable of long-distance transport, and accumulation in environmental compartments and food chains [2]. For example, PAHs produced by incomplete combustion processes can undergo atmospheric reactions that give rise to nitrated and oxygenated derivatives with greater mutagenicity [5]. Meanwhile, PFAS have been detected in atmospheric deposition and are linked to endocrine and

immunological effects [6]. Recent studies also confirm the atmospheric transport of microplastics, even to remote mountain and polar ecosystems [7].

3. Atmospheric sources and dynamics of air pollutants

The atmosphere is not merely a passive receptor of pollutants; it behaves as a chemically reactive medium, whose transformations are modulated by meteorology, radiation, and the availability of oxidants.

The main sources of emerging pollutants include industrial activities, vehicle emissions, biomass burning, domestic combustion, waste incineration, agricultural volatilization, and secondary formation through photochemical reactions [8]. Atmospheric oxidation by OH radicals, NO₃ radicals, or ozone leads to the formation of secondary organic aerosols (SOAs), which can incorporate toxic transformation products [9].

4. Health implications and environmental interactions

The health relevance of emerging air pollutants lies both in their direct toxicity and in how these pollutants interact with biological systems. Epidemiological and toxicological evidence links exposure to complex airborne mixtures with respiratory and cardiovascular impacts, carcinogenicity, endocrine disruption, and neurotoxic effects [10]. For example, ultrafine particles (<100 nm), due to their small size, can penetrate as far as the alveoli in the lungs, which could help explain the occurrence of systemic effects [11].

Some PAHs, such as benzo[a]pyrene, are classified as Group 1 carcinogens [4]. However, the risk to health and the environment does not depend on a single compound but rather on exposure to complex mixtures present in the air, including gaseous and particulate phases, parent compounds and transformation products, as well as co-exposures modulated by indoor and outdoor environments. Furthermore, atmospheric deposition transfers these pollutants to soils and water bodies, where their persistence and bioaccumulation can amplify impacts throughout food webs [2]. In this sense, air pollution control is also a key strategy for the protection of aquatic and terrestrial ecosystems.

5. Advances in detection and monitoring technologies

The increasingly frequent identification of emerging contaminants is closely linked to technological advances in their detection. In this regard, high-resolution mass spectrometry (HRMS), tandem techniques (gas chromatography tandem mass spectrometry [GC-MS/MS], liquid chromatography tandem mass spectrometry [LC-MS/MS]), and complementary elemental methods (inductively coupled plasma mass spectrometry [ICP-MS]) have improved the ability to identify and quantify compounds at trace levels, even within complex atmospheric matrices [6, 12]. Additionally, portable sensors and satellite observations further expand spatial coverage, while modeling, often enhanced through machine learning, facilitates source attribution and exposure prediction. However, the availability of advanced

analytical tools does not automatically translate into better management decisions. Challenges persist related to comparability between sites, standardization of sampling protocols, and the interpretation of results obtained through non-targeted screening. In this context, the most robust monitoring strategies tend to integrate multiple approaches, combining targeted quantification of priority compounds, exploratory screening for unknown contaminants, and modeling frameworks that connect sources with receptors.

6. Control strategies and public policy perspectives

Effective control of emerging pollutants requires a multidimensional approach that combines technology, policy, and behavioral change. End-of-process controls remain important; electrostatic precipitators, catalytic oxidation, and cleaner combustion technologies can reduce emissions of particulate matter and reactive precursors, particularly in industrial and energy settings. However, many emerging pollutants originate from diffuse sources (for example, consumer products, waste management, and agricultural volatilization), where conventional controls are insufficient.

Therefore, regulatory frameworks are evolving. In multiple jurisdictions, the focus is expanding to include PFAS and other persistent compounds, as well as broader categories of hazardous organic compounds and complex particulate mixtures [6, 13]. This evolution reflects a shift toward prevention throughout the product lifecycle, not just point-source emission limits.

At the same time, mitigation can be strengthened through nature-based actions and community-level measures. Urban green infrastructure can contribute to the interception and deposition of pollutants and can complement technological controls when properly designed [14]. Community-based measures, such as cleaner cookstoves and improved waste management, can also generate significant exposure reductions, especially where domestic combustion and open burning are major sources.

Rather than addressing these actions separately, an emerging best practice is to frame them as a whole: immediate exposure reduction where the health burden is greatest, reduction of structural emissions through cleaner energy and industrial processes, and long-term prevention through safer chemicals and circular economy approaches.

7. Conclusions

Emerging pollutants are redefining air pollution science by challenging traditional assumptions about what should be monitored, how to assess risk, and which interventions are most effective. Their study requires an interdisciplinary approach that integrates atmospheric chemistry, analytical techniques, toxicology, engineering, and public health [2, 10]. In this respect, this chapter lays the conceptual groundwork for subsequent contributions, highlighting that future progress will depend on the convergence of robust measurements, a mechanistic understanding of processes, and prevention-oriented control strategies.

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Accurate and Precise Atmospheric Ammonia Measurement: From Emission Sources, Analytical Methods to Mitigation Strategies

Hongming Yi

Abstract

Ammonia (NH_3) is a key reactive nitrogen species with critical roles in local, regional, and global nitrogen cycling, and it is increasingly recognized for its impact on environmental pollution and climate change. As a major precursor of secondary particulate matter, NH_3 contributes to fine aerosol formation, which adversely affects air quality and human health, particularly through respiratory and cardiovascular diseases. Accurate and precise measurement of atmospheric NH_3 is therefore essential to quantify its concentrations, elucidate sources and sinks, and understand deposition processes. This review systematically introduces and evaluates the current methodologies and instrumentation for NH_3 measurement, including chemical, electrochemical, optical, and remote-sensing approaches. The advantages, limitations, and comparative performance of these techniques are analyzed to provide guidance for selecting appropriate measurement strategies. Special emphasis is placed on open-path laser-based instruments, which enable high-sensitivity, high-temporal-resolution measurements in field campaigns, facilitating improved characterization of spatial and temporal NH_3 distributions, particularly in undermonitored regions. Finally, the review synthesizes current mitigation and control strategies for NH_3 emissions, highlighting approaches applicable to agricultural and industrial sectors. Policy implications and practical recommendations are discussed to support evidence-based decision-making for emission reduction. By integrating advances in measurement techniques with emission control strategies, this work aims to provide a comprehensive framework for understanding and managing atmospheric NH_3 , ultimately contributing to improved air quality, ecosystem protection, and human health.

Keywords: ammonia measurement, accuracy and precision, methodology, open-path instruments, emission and mitigation

1. Introduction

The atmospheric nitrogen cycle moves nitrogen among the air, land, and oceans through processes such as fixation, nitrification, assimilation, and denitrification. It is vital for all life because it helps produce proteins, DNA, and other essential molecules. This cycle supports plant growth, maintains soil fertility, and sustains healthy ecosystems across the biosphere. Ammonia (NH_3) is a key component of the atmospheric nitrogen cycle, playing a critical role in atmospheric chemistry and aerosol formation [1]. As a major precursor of secondary particulate matter, NH_3 strongly influences air quality [2, 3], climate, and human health. The pathways of atmospheric processing are illustrated in **Figure 1a** to facilitate

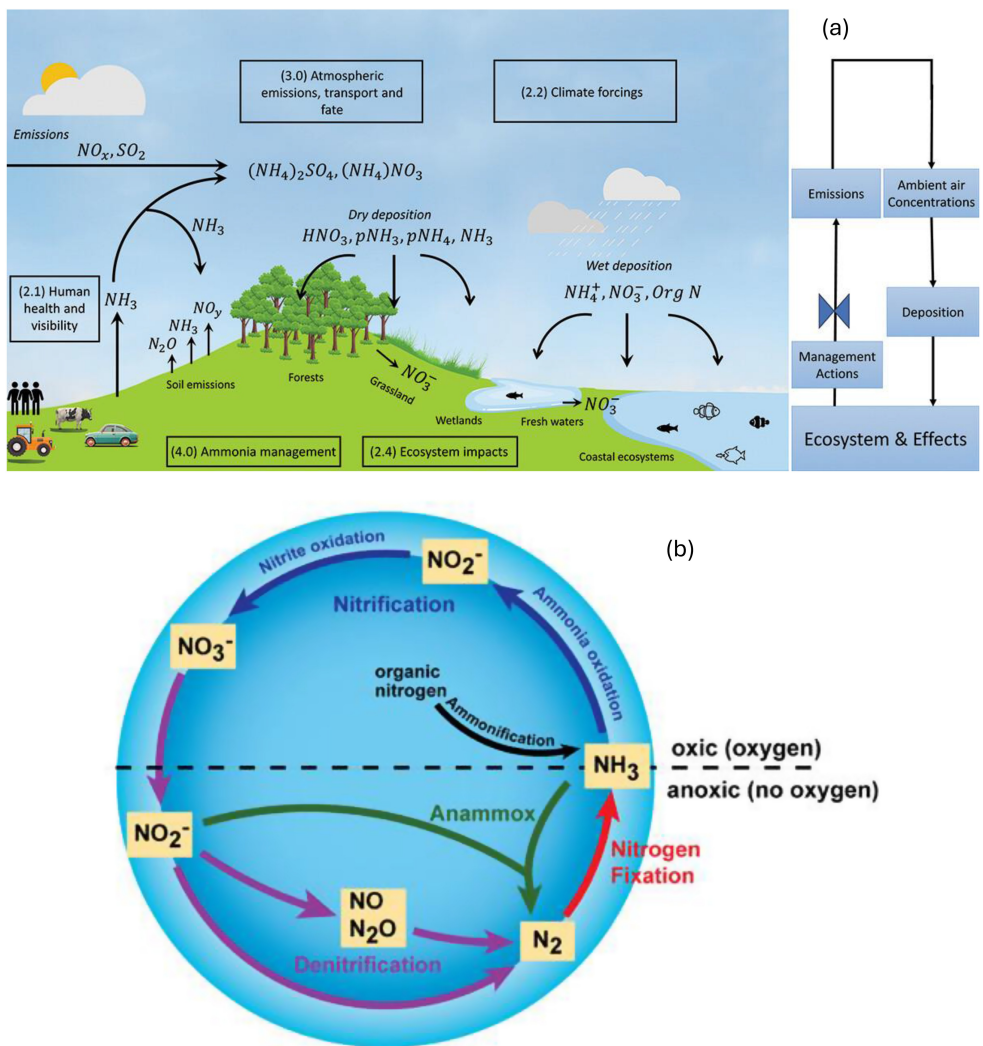


Figure 1. (a) Conceptual diagram of the nitrogen cycle highlighting the transformations, fate, and impacts of ammonia (NH_3) and ammonium (NH_4^+). The schematic aligns with key sections of this manuscript, including human health and visibility, climate forcing, ecosystem impacts, atmospheric emissions, transport and fate, and ammonia management [4]. (b) Major transformations within the nitrogen cycle and the associated chemical reactions [8].

understanding [4]. As the most abundant alkaline gas in the atmosphere, NH₃ readily neutralizes acidic components, modifying cloud pH and regulating overall atmospheric acidity. Beyond its neutralizing capacity, NH₃ contributes to new particle formation, increasing the number of airborne particles. For example, NH₃ reacts with acidic gases such as sulfuric acid (H₂SO₄) and nitric acid (HNO₃) to form ammonium salts (e.g., ammonium sulfate, ammonium nitrate), which are major constituents of fine particulate matter (PM_{2.5}) [5–8], as depicted in **Figure 1b** [8]. Furthermore, key chemical reactions underlying these processes are summarized in **Table 1** [5]. NH₃-driven PM_{2.5} formation degrades air quality, reduces visibility, and disrupts ecosystems [9]. Additionally, ammonia-mediated particulate matter can alter Earth’s radiative balance, influencing climate systems. Elevated PM_{2.5} concentrations are strongly associated with adverse health outcomes, particularly.

Respiratory and cardiovascular diseases [10–12]: In the United States and Europe [13–15], NH₃ contributes approximately 30% and 50% of PM_{2.5}, respectively. Ammonia runoff into water bodies promotes eutrophication, affecting aquatic life and drinking water quality, while deposition onto soils can increase acidity, reducing biodiversity and nutrient availability for plants. Consequently, it is essential to accurately and precisely measure NH₃ in the atmosphere to thoroughly understand NH₃ sources, deposition processes, and atmospheric behavior.

The ongoing rise in atmospheric NH₃ emissions poses substantial risks to environmental quality, public health, and climate. Over the past two decades, research at global, regional, and local scales has increasingly focused on these issues. Agricultural activities remain the dominant NH₃ source, primarily through fertilizer application and livestock emissions [3, 5, 14]. Additional contributions arise from

#	Reaction	Rate constant	Rate estimate at 298 K (with uncertainty factors)
R ₁	NH ₃ + OH → NH ₂ + H ₂ O	k ₁ = 1.7 * 10 ⁻¹² * e ^{-710/T}	1.6 (1.2) * 10 ⁻¹³ cm ³ molecule ⁻¹ s ⁻¹
R ₂	NH ₂ + O ₃ → NH ₂ O + O ₂	k ₂ = 4.3 * 10 ⁻¹² * e ^{-930/T}	1.9 (3.0) * 10 ⁻¹³ cm ³ molecule ⁻¹ s ⁻¹
R _{3a}	NH ₂ + NO ₂ → NH ₂ O + NO	k _{3a} = 2.0 * 10 ⁻¹¹ * (T/298) ^{-1.3} * (0.75)	1.5 (1.6) * 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
R _{3b}	NH ₂ + NO ₂ → N=N=O + H ₂ O	k _{3b} = 2.0 * 10 ⁻¹¹ * (T/298) ^{-1.3} * (0.25)	0.5 (1.6) * 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
R ₄	NH ₂ + NO → N≡N + H ₂ O	k ₄ = 4.0 * 10 ⁻¹² * e ^{450/T}	1.8 (1.3) * 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
R _{5a}	NH ₂ + HO ₂ → NH ₃ + O ₂	k _{5a} = 3.4 * 10 ⁻¹¹ * (0.85)	2.9 (2.0) * 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
R _{5b}	NH ₂ + HO ₂ → HNO + H ₂ O	k _{5b} = 3.4 * 10 ⁻¹¹ * (0.01)	3.4 (2.0) * 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
R _{5c}	NH ₂ + HO ₂ → NH ₂ O + OH	k _{5c} = 3.4 * 10 ⁻¹¹ * (0.14)	4.8 (2.0) * 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹
R ₆	NH ₂ O + O ₃ → NH ₂ + 2O ₂	k ₆ = 2.0 * 10 ⁻¹⁴	2.0 (± 1.5) * 10 ⁻¹⁴ cm ³ molecule ⁻¹ s ⁻¹
R ₇	NH ₂ O + OH → HNO + H ₂ O	k ₇ = 1.8 * 10 ⁻¹⁰	1.8 (10) * 10 ⁻¹⁰ cm ³ molecule ⁻¹ s ⁻¹
R ₈	HNO + O ₂ → NO + HO ₂	k ₈ = 3.65 * 10 ⁻¹⁴ * e ^{-4600/T}	7.2 (2) * 10 ⁻²¹ cm ³ molecule ⁻¹ s ⁻¹

Note [5]: Reaction R₈ is assumed to occur rapidly and is thus not explicitly simulated. Rate estimates are provided for each reaction at 298 K, with the uncertainty factor represented in red within parentheses in all cases, except for reaction R₆, where it represents an absolute error estimated by the study for the measurement at 296 K.

Table 1.
Rate constants (cm³ molecule⁻¹ s⁻¹) for representative chemical reactions involved in the ammonia oxidation process during atmospheric nitrogen cycling [5].

industrial processes, vehicular exhaust, and natural sources such as soils and oceans. Globally, agriculture accounts for approximately 80–95% of total NH_3 emissions, though fossil fuel combustion and vehicle emissions can be significant in certain regions [15].

The deposition of atmospheric ammonia (NH_3) has far-reaching ecological consequences [5, 14]. Excess nitrogen deposition can drive eutrophication and acidification in sensitive ecosystems – including forests, wetlands, and aquatic environments – resulting in biodiversity loss and ecosystem imbalance [15–17]. When NH_3 is deposited onto soils, it can cause direct foliar damage to vegetation and indirectly disrupt the nitrogen cycle by acidifying soils, thereby reducing soil quality, fertility, and long-term productivity. These effects underscore the dual role of NH_3 as both a pollutant and a driver of broader biogeochemical changes [18].

Despite its environmental significance, accurately measuring atmospheric NH_3 remains a major scientific challenge [16, 17]. As a highly reactive and “sticky” gas, NH_3 readily adsorbs to and desorbs from instrument surfaces, complicating its quantification due to the artificial loss mechanism. Meanwhile, its typically low and highly variable atmospheric concentrations – often in the parts-per-billion by volume (ppbv) range – further hinder detection. These challenges affect the accuracy, precision, comparability, and reliability of both ground-based and satellite observations [19–21]. Addressing these issues requires careful calibration, the development of robust measurement techniques, and the integration of complementary approaches, including in-situ monitoring, satellite remote sensing [22], and atmospheric modeling.

Advancing scientific understanding of NH_3 emissions and their impacts is critical for informing effective policy decisions. Identifying major emission sources, elucidating ammonia’s role in secondary particulate matter formation, and developing mitigation strategies are essential to reducing the environmental, climatic, and public health burdens associated with reactive nitrogen. This review, therefore, synthesizes current knowledge and outlines future research priorities through an integrated assessment of in-situ measurements, remote sensing datasets, modeling studies, and policy frameworks.

2. Ammonia emission sources and estimation

2.1 Ammonia (NH_3) emission sources

Ammonia emissions come from both human-related (anthropogenic) activities and natural processes-related sources. Agriculture is the dominant anthropogenic source of atmospheric NH_3 , primarily from livestock waste and synthetic fertilizer application, along with industrial processes such as fertilizer production and waste treatment. Other anthropogenic sources include biomass burning, mobile sources (e.g., vehicles), and power generation, as well as other unidentified or minor contributors. Natural sources, including soil and oceanic decomposition, also contribute to NH_3 emissions. **Table 2** summarizes these major emission sources. For illustration, **Figure 2** [4] presents the relative contributions of anthropogenic sources in the United States, providing insight into the characteristics and distribution of NH_3 emissions.

Ammonia sources	Detailed breakdown	Notes
Agriculture	Livestock waste	Urea in manure and urine converted to ammonia by enzymes in feces and soil. Ammonia volatilizes from manure, slurries, and storage.
	Fertilizer use	NH ₃ from the application of urea-based fertilizers and other nitrogen-rich fertilizers to fields, lawns, and crops.
	Industrial processes and fertilizer production	NH ₃ generated in the manufacturing of synthetic fertilizers, particularly in the fertilizer industry and through the Haber–Bosch process.
	Food and pharmaceutical production	NH ₃ from the processes involving the breakdown of organic matter or nitrogenous wastes.
	Waste treatment	NH ₃ emissions from the treatment of industrial and domestic sewage.
Natural and some anthropogenic sources	Decomposition	Natural degradation of proteins and urea by microorganisms in soil and other organic matter.
	Oceans	A significant natural source of ammonia.
Biomass burning	Wildfires	Release of ammonia during burning.
	Burning plant matter	
Mobile sources	Vehicles	A minor but present anthropogenic source.
Fossil fuel combustion	Burning: power plants and other applications	A smaller contribution.
Others	Unknown and unidentified	Contribution amount < 1%.

Table 2.
The main NH₃ emission sources summarized from recent publications [3, 4, 12, 14, 15].

Agriculture, as the largest global source of ammonia (NH₃), contributes approximately 80–95% of emissions in developed countries [3, 4]. The global average NH₃ emission from agriculture is about 81%, based on bottom-up and top-down estimation methods [3, 4, 18]. Global NH₃ emissions have nearly tripled between 1960 and 2022, with the vast majority of this increase originating from agricultural activities [18]. The 1960s marked the onset of the Green Revolution, particularly in Asia and Latin America, characterized by the widespread adoption of high-yield crop varieties and fertilizer-intensive production practices, often supported by government and international subsidies [15, 18]. During this period, the Haber–Bosch process for synthetic nitrogen fertilizer production matured and expanded globally. As a result, nitrogen fertilizer application to soils increased from 19 million metric tonnes in 1961 to 109 million metric tonnes in 2022, driving the substantial rise in agricultural NH₃ emissions [9, 15, 18].

Ammonia (NH₃) emissions are continuing to increase in many low- and middle-income countries (LMICs) [15, 18], including Nigeria, Indonesia, Pakistan, and India [18]. Several factors contribute to this trend. Rapid agricultural expansion driven by population growth has intensified cropping systems, particularly for nitrogen-demanding crops such as rice and wheat. Concurrently, livestock populations are growing to meet rising demand for meat, dairy, and eggs, leading to increased manure production [15, 16, 18, 23, 24]. In many LMICs, manure management

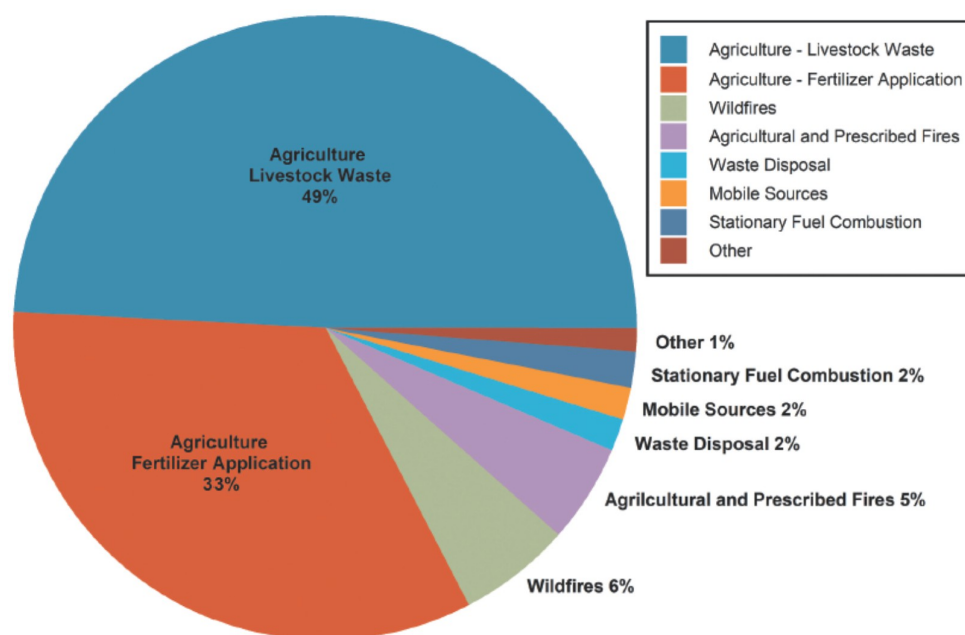


Figure 2.
The percentage contribution of NH_3 emission from anthropogenic sources in the United States in 2020, based on the analysis of U.S. EPA's 4.97 million tonnes of anthropogenic sources [4].

remains rudimentary, resulting in substantial NH_3 emissions. Regulatory frameworks for controlling ammonia emissions are generally weak or absent, and environmental enforcement is limited. Similar challenges are observed in wastewater treatment systems, further exacerbating NH_3 emissions.

2.2 Underestimations of the ammonia emission rate

Although the main sources of atmospheric ammonia (NH_3) have been identified and their contributions quantified, NH_3 emission rates are frequently underestimated due to limitations in emission inventories, measurement techniques, and modeling approaches [16–22].

Firstly, the underestimation of NH_3 emissions can largely be attributed to incomplete emission inventories and missing sources. Satellite observations indicate that global NH_3 emissions are substantially higher than those reported in bottom-up inventories. Some studies [16, 22] used remote sensing to quantify county-level annual NH_3 emissions and found that known anthropogenic sources are approximately 80% higher than inventory data suggest. When additional anthropogenic and natural sources are included, total emissions are up to four times greater than previously estimated. Newly recognized emissions, though small, are detectable over extensive regions, such as the Russian taiga, which had been assumed to have negligible NH_3 emissions. Observed emissions align more closely with reported values in countries with regulatory frameworks, such as those in the European Union. Despite differences in magnitude, satellite-based analyses reproduce familiar global hot spots, including central United States, northwestern

Europe, the Po Valley, the Nile Delta, the Indo-Gangetic Plain, and eastern China [13, 17, 18, 20]. Firstly, emission inventories often fail to account for all sources. Mobile emissions from on-road and off-road vehicles are frequently underestimated by factors of 2–5 in older inventories [21]. While many mitigation strategies focus on reducing nitrogen oxide (NO_x), some control systems, such as selective catalytic reduction, can lead to unintended increases in NH₃ emissions [17–21]. Industrial emission estimates often neglect indirect sources, including flue gas treatment by-products; in China, a 2025 study reported that industrial NH₃ emissions were 3–10 times higher than previous bottom-up estimates [22]. Agricultural NH₃ emissions are also highly uncertain, as limited data on practices such as fertilizer application timing and method can lead to skewed estimates, particularly at high spatial and temporal resolution. In addition, in many regions, contributions from sources such as vehicles and industrial processes have been overlooked or inaccurately quantified, resulting in underestimates [16, 17]. Improving these estimates is critical for understanding NH₃'s role in particulate matter formation and its broader ecological impacts.

Secondly, measurement challenges persist. The physical and chemical properties of NH₃ complicate accurate field measurement. Its high polarity causes molecules to adhere to sampling surfaces, leading to “stickiness” that underestimates true concentrations [25, 26]. Sampling design is critical [27, 28]; incomplete mixing in emissions from livestock facilities can produce estimates ranging from 50% to 200% of actual values. Instrument interference further complicates measurements [29]: Infrared-based sensors are sensitive to water vapor, while chemiluminescence methods can be affected by NO_x. Meteorological factors, such as low wind or temperature variations, can introduce significant errors in field methods such as energy balance measurements. Monitoring networks are limited; for instance, the U.S. Ambient Ammonia Monitoring Network (AMoN) [22] is sparse, heavily biased toward rural areas, and lacks the temporal resolution needed to capture urban emissions.

Thirdly, modeling and data limitations contribute to underestimation [16, 18, 22]. Atmospheric models contain inherent uncertainties due to simplified chemical mechanisms, deposition schemes, and coarse spatial resolution. Using uniform emission factors fails to capture local and seasonal variability – for example, NH₃ emissions from fertilizer applications differ according to crop schedules. Satellite observations, while valuable for spatial coverage, have limitations, including coarse resolution and uncertainties under low-temperature conditions, and their validation is constrained by sparse ground-based measurements. Inaccurate meteorological inputs, such as overestimated wind speeds, further bias model simulations, contributing to underestimates of NH₃ concentrations.

3. Ammonia measurement methods

Based on the analysis of the systematic underestimation of NH₃ emission rates, it is essential to develop improved methodologies for accurate and precise ammonia measurement. These methods should encompass a range of observational approaches, including satellite-based remote sensing, atmospheric modeling [16, 22], and advanced in-situ monitoring techniques. Given that atmospheric NH₃ typically exists at very low concentrations – often from sub-ppbv to a few ppbv

levels [27, 28, 30] – high-sensitivity in-situ measurement techniques are critically required to ensure reliable detection and quantification.

3.1 Satellites, remote sensing, and atmospheric model

Satellite-based infrared remote sensing provides a powerful approach for monitoring atmospheric ammonia (NH_3) by detecting its characteristic absorption features [31]. These observations enable global and regional assessments of NH_3 distribution, identification of emission hot spots, and analysis of long-term atmospheric trends. Satellite data are further integrated into atmospheric models to enhance simulations of NH_3 transport, chemical transformation, and interactions with aerosols and clouds, thereby improving the understanding of emission–concentration relationships.

Satellite remote sensing of NH_3 primarily relies on thermal infrared absorption spectroscopy. Because NH_3 absorbs radiation at specific infrared wavelengths, its presence and concentration can be retrieved from satellite measurements. Key instruments include the infrared atmospheric sounding interferometer (IASI) and the hyperspectral infrared atmospheric sounder (HIRAS). IASI has provided more than a decade of global NH_3 records, revealing significant spatial and temporal trends, while HIRAS produces global NH_3 distribution maps consistent with IASI observations [22, 31]. Both instruments retrieve total column NH_3 concentrations, representing the integrated abundance of ammonia from the surface to the top of the atmosphere. Satellite-based remote sensing thus offers consistent, large-scale monitoring, enabling global mapping of NH_3 emissions, long-term trend analyses, and hot spot identification – particularly in regions such as East Asia, India, and West Africa.

Atmospheric models [16, 31] play a complementary role by assimilating satellite-derived NH_3 data along with ground-based and meteorological observations to simulate transport processes, chemical transformations, and emission dynamics. These models provide an integrated framework to interpret satellite observations and assess the impacts of NH_3 on atmospheric chemistry and climate. Model validation is crucial for ensuring simulation accuracy, requiring high-quality observational datasets from both satellite and in-situ measurements [32].

Consequently, the continued development of precise and reliable in-situ NH_3 instrumentation remains essential for quantifying hot spots identified by satellite remote sensing and for advancing model performance and improving our understanding of the global nitrogen cycle.

3.2 In-situ measurement methods

In-situ monitoring of atmospheric NH_3 involves deploying sensors directly in the environment to obtain real-time, high-resolution concentration data. These techniques are essential for characterizing the complex spatiotemporal variability of NH_3 and for providing reliable datasets to support and validate atmospheric models discussed in Section 3.1. A variety of detection methods are available depending on sample type, required sensitivity, and specific application. Broadly, these methods can be categorized into chemical, electrochemical, semiconductor, and optical techniques [29, 33–35], as summarized in **Table 3**.

Method	Sample type	Advantages	Disadvantages	Typical application
Chemical and colorimetric	Gas and liquid	Low-cost, simple, visual indication, portable options.	Qualitative or semi-quantitative, affected by interferences.	Leak detection, water quality testing, laboratory screenings.
Electrochemical	Gas, liquid	High selectivity, accurate for low-range measurement, low power consumption, portable.	Limited lifetime, can be degraded by high concentrations, and sensitive to temperature/humidity.	Industrial and personal safety monitoring.
Semiconductor	Gas	Simple, low-cost, high sensitivity at high temperatures, durable.	Low selectivity, requires a high operating temperature, and is affected by humidity.	Industrial leak and process monitoring.
Optical method	Gas, liquid	Very high selectivity and sensitivity, wide dynamic range, long lifespan.	High cost, complex instruments, may require specialized calibration.	Trace analysis, environmental, and breath monitoring

Table 3.
The commonly used real-time NH₃ measurement methods.

Chemical and colorimetric methods rely on reactions that produce a measurable color change, such as those used in test papers, sulfur sticks, Nessler's reagent, the indophenol blue method, and colorimetric film sensors. These approaches are typically simple, low-cost, and suitable for rapid screening or qualitative detection of high NH₃ concentrations, such as the AMoN mentioned above in Section 2.2.

Electrochemical sensors determine NH₃ concentrations by converting electrochemical reactions into electrical signals. Ammonia diffuses into the sensor and undergoes oxidation or reduction, generating a current proportional to its concentration. These sensors are compact, energy-efficient, and relatively inexpensive, offering good linearity and specificity to NH₃, although they may exhibit cross-sensitivity to other gases. Electrochemical (EC) sensors are widely used in portable and stationary gas detectors for real-time air-quality and occupational safety monitoring.

Semiconductor, or metal-oxide-semiconductor (MOS), sensors measure changes in electrical resistance caused by the adsorption of gas molecules on a metal oxide surface. MOS sensors are simple, durable, and low-cost, making them widely used in industrial applications. However, they typically exhibit lower selectivity and sensitivity (parts per million by volume (ppmv) level or higher) compared with other methods and often require elevated operating temperatures.

Among all approaches, optical techniques [33–35] are the most sensitive and reliable for NH₃ detection. These advanced methods use light absorption or scattering to quantify ammonia with high sensitivity and selectivity. A detailed description and inter-comparison of optical instruments are presented in Section 3.3.

Among the four main categories of NH₃ monitoring technologies, chemical and optical instruments offer the highest sensitivity, capable of detecting atmospheric ammonia at sub-pptv (parts-per-trillion by volume) levels with response times ranging from milliseconds to minutes [33–35]. To date, numerous instruments have been developed for pptv–ppmv NH₃ detection across various temporal resolutions.

These include wet-chemical analyzers such as the annular rotating batch denuder (RBD), annular denuder sampling with online analysis (AMANDA), and AiRRmonia (an advancement of the AMANDA system); laser-based techniques such as quantum cascade laser absorption spectroscopy (QCLAS), including its dual-channel (DUAL-QCLAS) and compact (c-QCLAS) configurations; photoacoustic spectroscopy (PAS) [36–38], including microphone-based PAS [36, 37] and quartz-enhanced PAS (QEPAS) [38]; and other advanced optical and mass spectrometric methods, including cavity ring-down spectroscopy (CRDS) [33–35, 39], cavity-enhanced absorption spectroscopy (CEAS) [40], chemical ionization mass spectrometry (CIMS) [27, 28], ion mobility spectrometry (IMS) [33], mini differential optical absorption spectroscopy (MiniDOAS) [35, 41], gas chromatography (GC) [42], and open-path Fourier transform infrared spectroscopy (OP-FTIRS) [43].

Because NH_3 is highly adhesive and reactive, instead of closed-path QCLAS [44], open-path configurations are often employed in QCLAS, CRDS, DOAS, and FT-IR systems to minimize sampling losses and enhance measurement accuracy. The performance characteristics of these NH_3 measurement techniques are summarized in **Table 4**. Based on specific monitoring objectives, the most suitable instruments can be selected for individual applications. **Table 5** presents representative NH_3 concentrations observed worldwide using these instruments across various environmental conditions and national monitoring standards.

In summary, satellite data provide broad and repeatable coverage for observing large-scale patterns, identifying hot spots, and tracking long-term trends. When combined with atmospheric transport models, it can generate top-down estimates of NH_3 emissions, which can help validate or improve bottom-up emissions inventories. In contrast, in-situ measurements provide highly accurate, real-time data at specific locations, offering high precision, fine temporal resolution, direct surface-level measurement, and the ability to validate remote sensing data and model outputs. Among the various in-situ measurement methods – chemical, electrochemical, semiconductor, and optical techniques – chemical and optical methods offer the best sensitivity and selectivity. However, for closed-cell configuration instruments of both chemical and optical methods, their precision and accuracy can be affected by adsorption/desorption and artificial losses, instrument interference, calibration challenges, and signal attenuation in eddy covariance systems. Open-path laser spectroscopy sensors provide the most reliable option for real-time, precise, and robust NH_3 measurements, especially for eddy covariance flux measurement.

3.3 Open-path optical spectrometers for eddy covariance flux measurement

Among the various instruments summarized above, open-path quantum cascade laser absorption spectroscopy (OP-QCLAS) offers distinct advantages for atmospheric in-situ measurements by eliminating sampling biases and time delays inherent to closed-path systems [48, 49]. This technique measures gas concentrations directly in the open air along the optical path, making it well-suited for deployment on aircraft [47, 50], unmanned aerial vehicles, and mobile laboratory platforms for accurate NH_3 monitoring [50–53]. Compared with open-path MiniDOAS and FTIR systems, OP-QCLAS provides true “point-source”

Instrument	Manufacturer	Air flow rate [lmin-1]	Time resolution/time average [s]	Precision [ppbv]	Range [ppbv]	Accuracy [%] [References]
RBD	Energy Research	27	2400/3600	0.02	Not specified	Not specified [33]
AMANDA	Foundation of the Netherlands (ECN)	28	450/450	0.02	0.02–500	Not specified [33]
AiRRmonia	R&R Mechatronics	1	600/60	0.05	0.04–500	±31 [33]
DUAL- QCLAS	Aerodyne Research, Inc. (ARI)	15	0.2/60	0.018	Not specified	±52 [33]
c-QCLAS		8.9	1/60	0.05	Not specified	±101 [33]
PAS:WaSul- Flux	Hilase Ltd.	4	300–1800/ 300–1800	0.25	0.25– 1,000,000	Not specified [33]
PAS: Nitrolux- 100	Pranalytica Inc.	1.2–1.6	3/300	0.1	0.1–200	±43 [33]
CRDS, EnviroSense 1000 Analyzer	Picarro Inc., USA	1	3/300	0.07	0.07–25	±73 [33]
CRDS, Tiger-i 2000	Tiger optics, USA	0.48	1	0.83	0–20,000	±4 [35]
CIMS	Georgia Institute of Technology CIMS Team	19.5	1/60	0.94	Not specified	±44 [33]
IMS	Bruker Daltonik	0.4	4/60	Not specified	Variable	Not specified [33]
CEAS: AP2E	AP2E, France	1.0	60	10	0–10,000	n/a [35]
PAS: LSE	LSE monitors, NL	0.1	60	n/a	0–40,000	n/a [35]
PAS: TGA300 series	Omnisens S.A., Switzerland	≤5	3	0.1	0.1–3,000	0.25 or 1% [36]
QEPAS	Shanxi University	0.26	0.3/52	2.2/0.09	0–10,000	n/a [37]
CEAS: LGR	Los Gatos Research (LGR) Inc., USA	0.25	1	< 1.5 at 1 s	0.5– 10,000	n/a [35]
GC	TU Delft	0.0014	<300	150	100– 25,000	n/a [42]
OP-FTIRS	MIDAC Corp.	n/a	8/120	Not specified	Not specified	Not specified [33]

Instrument	Manufacturer	Air flow rate [lmin-1]	Time resolution/time average [s]	Precision [ppbv]	Range [ppbv]	Accuracy [%] [References]
OP- miniDOAS	RIVM, NL/ NTB, Buchs, CH	n/a	60	0.36	0.36–430	2 [35]
OP-CRDS	Colorado State University	n/a	3	0.6	0–500	n/a [45]
Open-path NH ₃ Analyzer	Healthy Photon Co., China	n/a	0.1	<0.3	0–2000	n/a [46]
OP-QCLAS	Princeton University	n/a	0.1	0.2	0–10,000	±20% [47]

Notes: RBD: annular rotating batch denuder, AMANDA: annular denuder sampling with online analysis, AiRRmonia: an advancement of the AMANDA system; QCLAS: laser-based techniques such as quantum cascade laser absorption spectroscopy, DUAL-QCLAS: dual-channel QCLAS, c-QCLAS: compact QCLAS, PAS: photoacoustic spectroscopy, QEPAS: quartz-enhanced PAS, CRDS: cavity ring-down spectroscopy, CIMS: chemical ionization mass spectrometry, IMS: ion mobility spectrometry, CEAS: cavity-enhanced absorption spectroscopy, MiniDOAS: mini differential optical absorption spectroscopy, GC: gas chromatography, OP: open-path, FTIRS: Fourier transform infrared spectroscopy.

Table 4.
Summary of the characteristics of the instruments.

detection capability, achieving sub-pptv precision and temporal resolution better than 0.1 s [54–56].

These characteristics of the open-path laser spectroscopy sensor make it an ideal instrument for high-resolution spatiotemporal NH₃ measurements, particularly in eddy covariance applications. Recent advancements in NH₃ flux measurements using the eddy covariance method – including instrumentation, time resolution, and detection limits – are summarized in **Table 6**.

4. Strategies and policies for ammonia mitigation

Because of the critical implications of atmospheric NH₃ for human health and environmental resilience, effective mitigation strategies and regulatory policies are essential [62–65]. Various efforts must primarily target the dominant emission sources – agriculture and industry. Agricultural mitigation focuses on best management practices, optimized fertilizer application, and dietary adjustments for livestock, whereas industrial mitigation emphasizes advanced emission capture technologies and the transition to cleaner energy systems [66, 67]. At both international and national levels, policies establish emission reduction targets and encourage the adoption of innovative technologies. Several effective strategies and initiatives have been implemented to reduce NH₃ emissions from agricultural and industrial sectors. A summary of these mitigation approaches, technologies, and policy frameworks is provided in **Tables 7, 8, and 9**.

As an example, for the strategy of manure handling and storage, the synthesized literature results [71] show that NBPT + NPPT reduced NH₃ loss by 75% (95% CI:

Locations	Type	Period	NH ₃ (ppb)	Methodology
Shanghai	Urban	2013.7–2014.9	6.2 ± 4.6	DOAS
China	Rural	2013.7–12, 2014.3–6	12.4 ± 9.1	MARGA
	Industrial	2014.1–6	17.6 ± 9	DOAS
Beijing	Urban	2007.1.23–2.14	7.21 ± 4.94	Aunular denuder
China		2007.8.2–31	33.46 ± 9.11	
Beijing	Urban	2008.2–2010.7	22.8 ± 16.3	Passive sampler
China	Rural	2007.1–2010.7	10.2 ± 10.8	
North Plain, China	Rural sites, suburban	2008.8–2009.9	20.6	Passive sampler
Kanpur	Urban	2007.4.8–6.30	23.7 ± 5.1	Online NOx–NH ₃
India		2007.12.1–2008.1.31	21.5 ± 6.6	Analyzer
Seoul	Urban/GJ	2010.9.1–2011.8.23	10.9 ± 4.25	WS-CRDS
Korea	Urban/GS		12.3 ± 4.23	
Lahore, Pakistan	Urban	2005.12–2006.2	30.3–116.9	Aunular denuder
Taiwan	Industrial	2003.9–2004.12	100.2 (Neipu) 72.8 (Pingtung) 84.9 (Pingtan)	Passive sampler
USA	Urban/Atlanta	2007.7–12	1.35 ± 1.19	Citric acid denuder
	Rural/Georgia		3.32 ± 2.37	Difference technique
Houston, TX	Urban	2010.2.12–3.1	2.42 ± 1.16	EC-QCL-based
USA		2010.8.5–9.25	3.07 ± 2.87	sensor
Wisconsin	Urban	2009.1.1–3.31	2.3	iCAMs
USA	Rural		2.4	
USA	Forest/Brent	2013.6.1–7.15	1–2	CIMS
	Urban/Kent	2013.8.31–9.20	Up to 6	
Ontario, Canada	Rural	2010.3.30–2011.3.29	4.71	Passive sampler
Vredaped, Netherlands	Rural	2009.12.16–2010.2.18	Up to 197.6	DOAS
Barcelona	Urban BC	2011.5.6–9.7	2.9 ± 1.3	Online instrument
Spain	Urban CC	2011.5.13–6.28	7.5 ± 2.8	

WS-CRDS: wavelength-scanned cavity ring-down spectroscopy; EC-QCL: external-cavity quantum cascade laser; iCAMs: inorganic continuous aerosol measurement system; CIMS: chemical ionization mass spectrometer.

Table 5.
Typical atmospheric NH₃ concentration observed by various instruments at different global locations in different countries [2].

58–82%, $n = 32$), 2-NPT by 70% (95% CI: 63–76%, $n = 19$), and NBPT by 61% (95% CI: 57–64%, $n = 165$), giving an average reduction of 69% across these three urease inhibitors. In contrast, MIP slightly increased NH₃ loss by 0.3% on average (95% CI: – 8–9%, $n = 40$). These findings broaden our understanding of urease inhibitor

Era [references]	Instrumental technique	Path	Key advancements	Time resolution	Detection limit
Early studies (Pre-2010s) [57]	Tunable diode laser absorption spectrometers (TDLAS)	Closed path	Use heated or inert-coated inlets to reduce adsorption effects.	~10 Hz, but often with an attenuated signal due to inlet losses.	~5 ng m ⁻² s ⁻¹ flux.
2010s [58, 59]	Quantum cascade laser (QCL) spectrometers	Closed path	Better sensitivity and precision incorporated hydrophobic coatings and heated cells to further minimize NH ₃ Adsorption.	~10 Hz, but still required corrections for high-frequency signal loss.	Low ppbv concentration limits, leading to improved flux detection limits.
2010s, 2020s [28, 59, 60]	Chemical ionization mass spectrometry (CIMS)	Closed path	Used electron transfer reaction ionization to measure NH ₃ Fluxes.	~1 second effective time resolution.	Sub-ppbv for concentration; ~5 ng m ⁻² s ⁻¹ for flux.
Mid-2010s [55, 61]	Open-path QCL spectrometers	Open path	Elimination of inlet-based adsorption issues by measuring NH ₃ directly in open air.	10 Hz.	Concentration: 0.30 ppbv; Flux: 1.3 ± 0.5 ng m ⁻² s ⁻¹ (for 30-minute intervals).
Recent advances (2020s) [49, 50, 52–56]	Portable, low-power open-path QCLs; open-path MiniDOAS	Open path	Further reduction in size, power consumption, and weight.	10 Hz.	Concentration: ~0.30 ppbv; Flux: 7.1 ± 1.1 g N m ⁻² h ⁻¹ (for 30-minute intervals).
Future development [62]	Next-generation open-path spectrometers	Open path	Real-time spectroscopic effect correction and more robust optical components. Potential for simultaneous measurement of multiple trace gases.	10 Hz.	Concentration: 0.2 ppbv for NH ₃ ; Flux: <1 ng m ⁻² s ⁻¹ .

Table 6.

Summary of instrumental progress for ammonia eddy covariance flux measurements.

efficacy under field conditions and highlight that not all products perform equally in reducing NH₃ emissions in practice.

Another study [72] showed that acidification is an effective and promising abatement technique to significantly reduce NH₃ emissions. By retaining more nitrogen in the manure, manure acidification increases the amount of plant-available nitrogen during land application. Ammonia emissions decreased by 77 ± 11% in housing, 63 ± 30% during storage, and 43 ± 18% after field application of acidified slurry. On average, NH₃ emissions were reduced by 60 ± 28% across all manure management stages.

Compared with traditional methods, these newer technologies [66, 73–75] offer several advantages, including lower energy consumption, reduced chemical use, and lower operating costs, along with the potential to recover valuable by-products such

Strategy type	Description	Specific actions
Feed management	Balancing animal diets to reduce excess nitrogen excretion, which is a key source of ammonia.	Reduce crude protein levels in livestock diets to better match an animal's needs.
Manure handling and storage	Managing manure to minimize the decomposition and volatilization of nitrogen into ammonia.	Use covers for solid manure and slurry storage to reduce air contact. Separate urine and feces using specific barn flooring designs. Acidify slurry to lower its pH and inhibit ammonia release. Add chemical amendments such as alum or biochar to manure to bind nitrogen.
Manure and fertilizer application	Optimizing the application of manure and fertilizers to increase nutrient uptake by crops and decrease emissions.	Incorporate manure into the soil quickly after spreading. Use low-emission slurry spreading equipment, such as trailing hoses or injection systems, instead of splash plates. Use nitrogen inhibitors with urea-based fertilizers to slow nitrogen loss. Use soil analysis and management plans to avoid over-fertilization.
Air treatment	Capturing and treating ammonia in the exhaust air from animal housing facilities.	Install air scrubbers or biofilters in buildings to remove ammonia from exhaust air.

Table 7.
Strategies focus on reducing ammonia emissions throughout the farming cycle, from livestock diets to manure application [67–70].

Technology	Description	Advantages and applications
Ammonia stripping	Forcing air or steam through wastewater at a high pH to convert ammonium to ammonia gas, which is then captured.	Cost-effective and relatively simple for treating high-ammonia wastewater streams.
Adsorption	Using porous materials such as zeolite or activated carbon to bind and remove ammonia molecules from wastewater.	Can be highly effective and reversible, though stability and efficiency are influenced by the operating conditions.
Membrane filtration	Employing semi-permeable membranes to filter and concentrate ammonia in wastewater, this process can be paired with other systems for recovery.	Can achieve high removal rates with low energy consumption and without chemicals, though membrane fouling can be an issue.
Biological systems	Using biological processes such as nitrification, denitrification, or anaerobic digestion to convert ammonia into less harmful nitrogen compounds.	An environmentally friendly, cost-effective option for wastewater treatment.

Table 8.
Innovative techniques are available for treating wastewater and industrial gas streams to remove or recover ammonia [66, 73–75].

as fertilizers or renewable fuels. However, there are also potential challenges and considerations, including economic viability, technical maturity and validation, market suitability of the products, operational complexity, and the need for adaptation and adoption.

Policy or regulation	Area	Key provisions
Gothenburg Protocol (UNECE)	International (Parties to the Convention on Long-Range Transboundary Air Pollution)	Sets NECs for various air pollutants, including ammonia, with reduction commitments for signatory countries. Requires countries to establish national codes of good agricultural practice to control ammonia emissions.
NECs Directive (EU)	European Union (EU)	Sets legally binding emission reduction commitments for EU member states for ammonia and other air pollutants, with targets for 2020 and 2030.
Common Agricultural Policy (EU)	European Union (EU)	Influences farm-level practices that can impact ammonia emissions by linking farm payments to environmental regulations.
Clean Air Act (CAA) (USA)	United States (federal level)	Provides federal authority to regulate emissions. While ammonia reporting exists, a comprehensive regulatory approach to agricultural emissions is still evolving.
Risk Management Plan (RMP) (EPA)	United States (EPA)	Requires facilities handling more than a threshold quantity of certain toxic substances to implement a chemical accident program and submit a plan to the EPA. However, agricultural nutrients are often excluded.

Table 9.

Governments and international bodies have implemented policies to reduce ammonia emissions, often focusing on the agriculture sector [67, 75, 77, 78].

Governments and international organizations have introduced a range of policies to mitigate ammonia emissions, primarily targeting the agricultural sector (see **Table 9**). A review of these efforts reveals both meaningful progress and ongoing challenges. Successful outcomes are generally linked to well-designed, science-based interventions that integrate technical innovation with practical implementation. However, persistent difficulties arise from competing environmental and economic priorities, the financial burden placed on farmers, and the structural and behavioral complexity of agricultural systems. These findings underscore the need for more coherent, incentive-driven policy frameworks that balance environmental goals with agricultural productivity and socio-economic sustainability.

The European Union (EU) [76–80] has established legally binding commitments to reduce ammonia (NH₃) emissions, requiring a 19% reduction by 2030 relative to 2005 levels. While these obligations are implemented through national legislation, the specific reduction targets vary among member states depending on country-specific conditions and policy frameworks. The principal regulatory instrument governing NH₃ emissions is the National Emission Ceilings (NEC) Directive (2016/2284/EU), which outlines two phases of binding reduction commitments based on 2005 baseline levels.

During the 2020–2029 period, the Directive [76–80] mandates an EU-wide average reduction of 6%. A 2024 progress report indicated that overall EU emissions had already declined by 17% between 2005 and 2023, thereby surpassing the collective target, although several member states did not achieve their individual ceilings. From 2030 onward, the Directive stipulates a more ambitious 19% average reduction requirement, reflecting the EU’s long-term strategy for mitigating agricultural air pollution and promoting sustainable nitrogen management.

5. Conclusions and outlooks

Atmospheric ammonia (NH_3) poses significant risks to air quality, ecosystems, and human health, primarily through its contribution to the formation of fine particulate matter ($\text{PM}_{2.5}$). The predominance of agricultural emissions underscores the complexity of managing NH_3 within both environmental and socio-economic systems. This review highlights recent advances in identifying emission sources, improving measurement precision, and developing mitigation strategies. Despite substantial progress in in-situ, remote-sensing, and sensor-based monitoring technologies, accurately quantifying NH_3 remains challenging due to its high reactivity, low ambient concentrations (pptv to ppbv), and pronounced spatiotemporal variability.

The outlook for NH_3 emission research, measurement, and policy reflects growing global concern over its environmental and health impacts. Key drivers include the expansion of agricultural production, increasing urban vehicle emissions, and the emergence of green ammonia as a potential clean fuel. These developments highlight the urgent need for precise measurement techniques and robust, internationally coordinated mitigation frameworks. Current research priorities focus on urban emission dynamics, declining acid gas concentrations, climate change feedbacks, and integrated modeling approaches.

Future research should prioritize the enhancement of in-situ and satellite-based observation systems to enable continuous, high-resolution monitoring, thereby refining emission inventories – particularly in regions with limited measurement capacity. Continued innovation in low-cost, durable sensors will be essential for long-term agricultural monitoring. Advances such as expanded ground-based networks, next-generation emission models, and high-resolution urban studies will further strengthen understanding and policy evaluation. Moreover, integrated atmospheric models that couple meteorological factors, climate drivers, and co-pollutant interactions are crucial for improving predictive capacity.

Effective NH_3 mitigation will rely on the coordinated application of advanced technologies, sustainable agricultural practices, and enforceable policy instruments. Key strategies include reducing agricultural emissions, leveraging trade and supply networks, transitioning toward clean ammonia production, and adopting holistic approaches that incorporate carbon accounting and life-cycle assessment. As emissions continue to rise globally – particularly in developing regions – international collaboration will be critical to implementing cost-effective and context-appropriate solutions. Strengthening the scientific understanding of the links between agricultural NH_3 , secondary aerosol formation, and human health impacts will further underscore the urgency of comprehensive global regulation and concerted action.

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Chapter 3

Evaluation of PM_{2.5} Air Quality at the University of Lagos, Nigeria: Source Attribution, Toxicity Potential, and Adherence to National and International Guidelines

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Abstract

The PM_{2.5} levels at the University of Lagos (UNILAG), Nigeria (Central Laboratory and the main campus gate) were assessed in order to share the results with those who will endeavor to reduce possible pollutants in the surrounding area. The Toxicity Potential (TP), Exceedance Factor (EF), and Air Quality Index (AQI) were calculated, and backward trajectories and possible PM_{2.5} source locations were tracked using the HYSPLIT model. Data on air quality for the 8-month periods was provided by AirQo at Makerere University in Uganda. A test of the Anderson-Darling Normality and other models were applied to the data. The Central Laboratory has the following: minimum (6.32 µg/m³), maximum (181.13 µg/m³), mean (24.26), Std. (20.86), and A-Squared (227.28), whereas the Main Gate has a minimum (7.23 µg/m³), maximum (180.50 µg/m³), mean (26.69), and Std. (19.07). Other results are: TP (0.42–12.04 (daily) and 1.26–36.23 (annual), EF (low, moderate, and critical pollution), and AQI (good, moderate, and very unhealthy). The results were compared with the National Environmental Standards and Regulations Enforcement Agency (NESREA) and World Health Organization (WHO) standards. The mean of the two locations was 1.34 times (Main gate) and 1.21 times (Central Lab) higher than the NESREA annual limit, and 5.34 times (Main gate) and 4.86 times (Central Lab) higher than the WHO annual limit. The air mass originated in the southwest from the ocean. Results illustrated the importance of local emission sources in influencing PM_{2.5} variations inside the university and the need for targeted mitigation strategies to address the severe environmental air pollution problems.

Keywords: PM_{2.5}, AirQo, UNILAG, NESREA, toxicity potential, exceedance factor, mitigation

1. Introduction

Particulate matter (PM) pollution is one of the most significant worldwide environmental and public health concerns of the twenty-first century. Both natural and man-made sources contribute to PM pollution, which is a complex mixture of small solid particles and liquid droplets with a diverse chemical composition. PM_{2.5} and PM₁₀ are particles with aerodynamic diameters less than 2.5 µm and 10 µm, respectively [1, 2]. PM_{2.5} particles are particularly dangerous because they can deeply enter the lungs' alveolar regions and cause and exacerbate serious health conditions like cancer, respiratory and cardiovascular diseases, asthma, and early death, whereas coarser PM₁₀ particles settle in the upper airways [3, 4]. Nearly 4 million premature deaths occurred globally in 2019 as a result of PM_{2.5} pollution alone, with the World Health Organization (WHO) estimating that 92% of the world's population is exposed to levels above its annual recommendation of 5 µg/m³ [5]. Singh et al. [2] claim that burning biomass, increasing industry, and car emissions exacerbate this environmental catastrophe in the rapidly urbanizing areas of emerging nations.

The use of inexpensive sensors, satellite models, citizen scientists, and non-scientists with a focus on a particular topic who collect or evaluate data to significantly advance scientific study or promote environmental or public health improvements is growing in popularity. By developing air quality toolkits for "citizen-science" and AQI modeled using satellite to obtain pollutant source data and using fresh, low-cost pollutants survey data to develop neighborhood air pollution surveys, a number of nonprofit organizations, such as the New York City Community Air Survey (NYCCAS), AirVisual, and Air Matters, to name a few, have made strides in this area of community involvement and community-based exploratory research. Another nonprofit air quality data provider is AirQo, based in Makerere University, Uganda. By offering precise, hyperlocal, and immediate air quality data, they hope to fill in knowledge gaps about air pollution and its impacts throughout Africa.

Determining the effects of environmental contaminants on human health requires an understanding of their potential toxicity. Research has consistently shown that exposure to hazardous chemicals has negative impacts. Chen et al. [6] discovered, for example, that long-term exposure to heavy metals like lead and mercury is linked to neurotoxicity, which results in cognitive deficits. These results highlight the necessity of a thorough comprehension of the toxicity potential of different environmental pollutants, offering important information for public health initiatives and regulatory actions [7]. These standards seek to guarantee that the AQI is easy to use, can function as an alert system, includes major air pollutants, can accommodate other pollutants, complies with National Ambient Air Quality standards, and is based on reliable air quality data from community-wide monitoring stations. In different capacities and locations, researchers from all over the world have occasionally examined differences in PM pollution concentrations, AQI based on PM concentrations, and exposure risk assessment [8].

This study is significant in that it addresses the pollution levels of an academic setting with a dense population of students, staff, and others. An assessment of PM_{2.5} was carried out based on the air quality data provided by AirQo at the University of Lagos, Nigeria, focusing on the institution's main gate and the central laboratory areas. Multifaceted approaches to this data focused on the exceedance factor (EF) analysis, toxicity potential assessments, and backward trajectory. The outcome of this study should have strong implications on the policy and public health. This study will be the first here and elsewhere to combine localized AirQo PM_{2.5} data with backward

trajectory, exceedance factor (EF) analysis, and toxicity potential assessments in an academic location. It will be a precedent for further air monitoring.

To evaluate the PM_{2.5} levels, sources, and health effects in the vicinity of the University of Lagos (UNILAG) and to compare them with national and international air quality guidelines.

1.1 Objectives

- i. To obtain the PM_{2.5} concentrations of the Central Laboratory and the Main Gate of the two study areas over an 8-month period (August 2023 to March 2024).
- ii. To track backward trajectories and determine the potential source locations contributing to PM_{2.5} pollution.
- iii. To compare the obtained PM_{2.5} levels with the guidelines set by the National Environmental Standards and Regulations Enforcement Agency (NESREA) and the World Health Organization (WHO).
- iv. To determine the Toxicity Potential (TP) and Exceedance Factor (EF) of PM_{2.5} at the study locations.
- v. To ascertain the Air Quality Index (AQI) and the potential health risks associated with PM_{2.5} exposure.
- vi. To recommend policy interventions for air quality management.

2. Materials and methods

2.1 Study area

The University of Lagos (UNILAG) is located in the Mainland of the city of Lagos in South Western Nigeria. The city of Lagos, the commercial and business capital of Nigeria, is located on 06°25'N 030 27'E on the West African Coast. The official population of Lagos State was 9,113,605 to the Nigeria 2006 population census. The environment is characteristic of coastal terrain with wetlands, low-lying sandy islands, and beaches. The university covers an area of about 860 hectares. The University of Lagos is a public research university located in Lagos, Nigeria, which was founded in 1962. UNILAG is one of the first-generation universities in Nigeria and is ranked among the top universities in Africa in major education publications. The university presently has three campuses in the Mainland of Lagos. Whereas two of its campuses are located at Yaba (the main campus in Akoka). **Figure 1** shows the relative location of the study in the Akoka campus.

The study is being conducted at two different locations: the main gate (latitude: 6°31'0"N, longitude: 3°23'10"E) which is the main entrance into the university campus and the central laboratory of the institution (latitude: 6°30'59.99"N and longitude: 3°23'5.99"E). The distance between the two locations is 2 km, and it takes 5 minutes to drive by bicycle and 9 minutes by car *via* University Road.

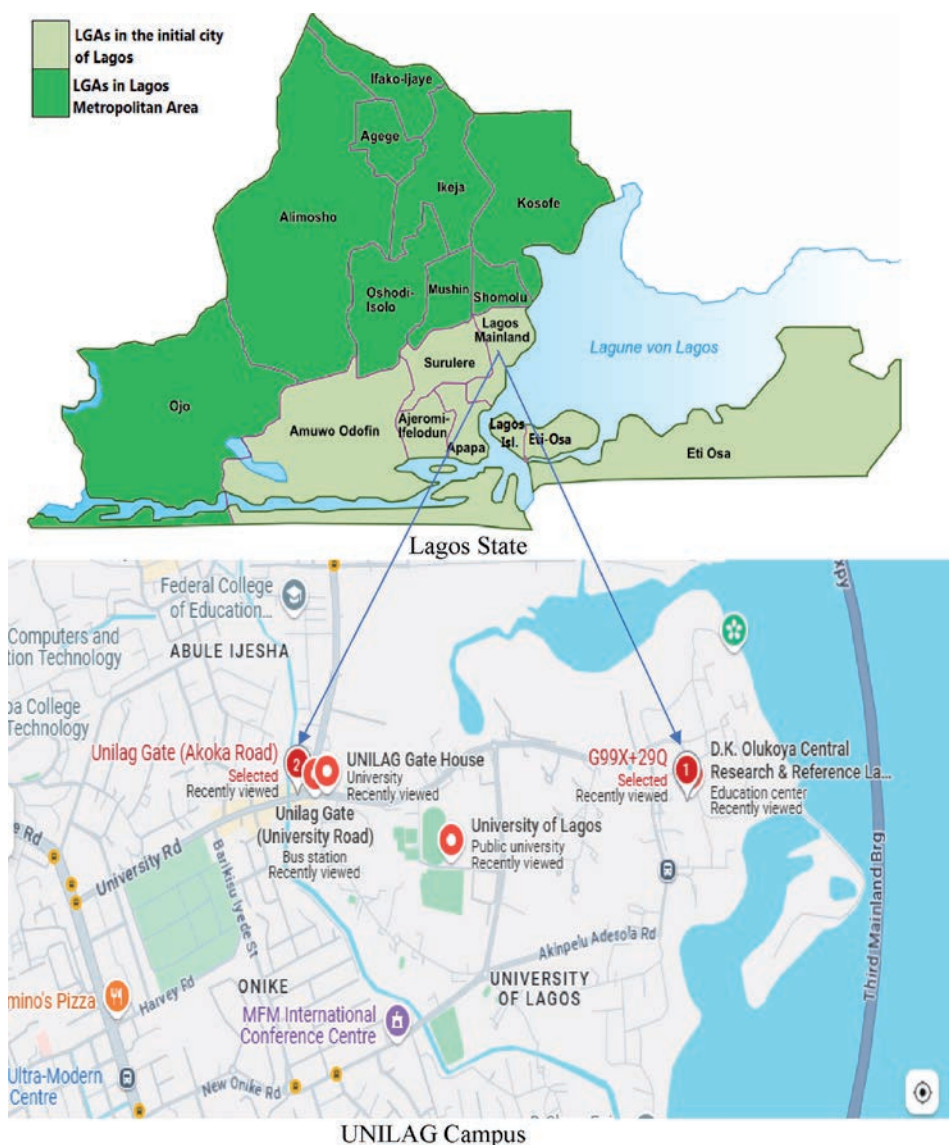


Figure 1.
The locations depicting Central Laboratory (1) and Main Gate (2), University of Lagos, Nigeria, where $PM_{2.5}$ was assessed.

For the evaluation of air quality of University of Lagos, all the information was collected and analyzed based on the data available from AirQo (<https://analytics.airqo.net/analytics>). In this study, 8 months (August 2023 to March 2024) data was obtained. AirQo was founded in 2015 at Makerere University to close the gaps in air quality monitoring across Africa. They provide accurate, hyperlocal, and timely data providing evidence of the magnitude and scale of air pollution across the continent in African Cities. The data was subjected to statistical analysis using Minitab 2023 and Excel 2013.

2.2 Methods

2.2.1 Air quality index

The degree of pollution-free and breathable ambient air is known as ambient air quality. The air quality index (AQI), a common numerical value, can be used to evaluate this [9]. The levels of air contaminants that are regarded as air quality standards are used to estimate the AQI. The air quality index was calculated using the atmosphere's pollutants' (PM) sub-air quality ratings. In the present investigation, the complete air quality index for each location was established using the worst sub-air quality indices. Eq. (1) was used to determine the sub-air quality indices for every air pollutant [10]:

$$I_p = (C_p - BP_{Lo}) \times \frac{I_{Hi} - I_{Lo}}{BP_{Hi} - BP_{Lo}} + I_{Lo} \quad (1)$$

where I_p : index value for the air pollutant.

C_p : concentration of air pollutant.

BP_{Lo} : lower breakpoint value of C_p .

BP_{Hi} : higher breakpoint value of C_p .

I_{Lo} : index breakpoint value of BP_{Hi} .

I_{Lo} : index breakpoint value of BP_{Lo} .

2.2.2 Toxicity potential (TP)

Toxic potential (TP) is a computed toxic equivalence which is helpful in determining the possible harm that air pollution particulates from various locations may bring to human health, according to Ayodele et al. [11]. Eq. (2) was used to determine the daily and yearly TP related to PM_{2.5} in the two sites. P_s stands for the air pollution standard, TP for the pollutant's toxicity potential, and P_c for the measured pollutant concentration. The well-being of the local population is at risk whenever TP is greater than one, which indicates that there exists an elevated level of PM_{2.5} in the area. The WHO [12] standard is used in this study to calculate the TP:

$$TP = \frac{P_c}{P_s} \quad (2)$$

2.2.3 Exceedance factor (EF) methodology

The exceedance factor methodology was used to assess the air quality situation (air pollution status) in the study area [1, 13]. When a pollutant's level surpasses the limits set by law or standards for air quality, this is known as an exceedance. In this study, exceedance days for the two sites were determined using WHO Air Quality Standards (Table 1).

In accordance with Roy and Singha [1] and Chowdhury et al. [14], the exceedance factor (EF) was computed using Eq. (3):

Pollutant	Averaging period	WHO guideline value ($\mu\text{g}/\text{m}^3$)
PM _{2.5}	24 h	15
PM _{2.5}	Annual	5

Table 1.
WHO recommended values for the level of PM_{2.5} [5].

Air quality categories	EF range
Low (L)	$\text{EF} < 0.5$
Moderate (M)	$0.5 \leq \text{EF} < 1.0$
High (H)	$1.0 \leq \text{EF} < 1.5$
Critical (C)	$\text{EF} \geq 1.5$

Table 2.
Categories of grouping the exceedance factor.

$$\text{EF} = \frac{C_o}{C_i} \quad (3)$$

where C_i is the relevant pollutant's WHO air quality recommendation, and C_o is the average concentration of each pollutant during the study. **Table 2** lists the four air quality categories according to the exceedance factor [1, 15].

2.2.4 Backward trajectory of air mass

The Air Resources Laboratory (ARL) of the National Oceanic and Atmospheric Administration (NOAA) produced the helpful and flexible HYSPLIT model [16, 17]. The path and total dispersion of pollutants originating from a line, area, or point source can be computed using the model. The hybrid model HYSPLIT employs both Eulerian and Lagrangian computation methods. The Real-time Environmental Applications and Display System (READY) website (<https://ready.arl.noaa.gov/index.php>) runs the dispersion models used in the present study interactively. By locating the origin location using the Global Positioning System (GPS), the release type of microparticle scenarios was determined. At elevations ranging from 0 to 100 meters, the hourly average emission of pollutants was taken into consideration.

To evaluate the disparities between the sample sites, the mean and standard deviation of PM_{2.5} (Anderson-Normality Test) were computed for the two locations during the season. Variance, skewness, kurtosis, and confidence interval were used to analyze the variations in the concentrations. Statistically significant seasonal differences were evaluated at a 95% confidence level (p value = 0.05) using a paired t-test. Additionally, statistical analyses were performed on the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT), TP, and Exceedance Factor (EF). Minitab software was used for all statistical analysis.

3. Results and discussion

The findings of the Anderson-Darling Normality Test are displayed in **Table 3** and **Figure 2** (pictorial). This dataset provides a statistical summary of the PM_{2.5}

Statistical parameter	Central laboratory	Main gate
P-value	<0.005	<0.005
N	2667	1542
Mean	24.26	26.70
Standard Deviation	20.86	19.07
Variance	434.96	363.67
Minimum	6.32	7.23
Maximum	181.13	180.58
Q1	12.20	14.44
Q3	28.82	32.50
A-squared	227.28	104.28
Skewness	2.65	1.84
Kurtosis	9.28	4.73
AQI (Mean)	79 (Moderate)	84
AQI (Minimum)	35 (Good)	40
AQI (Maximum)	256 (Very Unhealthy)	256

Table 3.
Anderson-darling normality test (showing the basic description of the results).

concentrations in the two research locations. Consistent patterns of contamination are demonstrated by the statistically significant P-values (<0.005). Poor air quality is indicated by results of 24.26 µg/m³ (central lab) and 26.70 µg/m³ (main gate), which are higher than the WHO (5 µg/m³) [5] and NESREA (20 µg/m³) [18] yearly limits. Both locations' PM_{2.5} measurements show a high degree of variability, indicating periodic increases in pollution. Greater dispersion as a result of different emission sources was suggested by variances of 434.96 µg/m³ (Central lab) and 363.67 µg/m³ (Main gate). The maximum levels are significantly higher than the NESREA 24-hour limit (150 µg/m³) and WHO 24-hour (15 µg/m³), indicating acute pollution episodes, but even at minimum levels, PM_{2.5} exceeds the WHO 24-hour limit (5 µg/m³), posing health hazards. Since Q1 and Q3 results are significantly higher than WHO limits, they suggest poor air quality. Positively skewed skewness (central lab, 2.65, and main gate, 1.84), with heavy tails pointing to the right, indicates that extreme pollution events predominate. There are several extreme outliers in the kurtosis; this implies the presence of variable pollution patterns. Because of the results' deviation from a normal distribution (A-squared), non-parametric models are justified. The two places' relative AQIs (mean, minimum, and maximum) are moderate (posing health hazards to those who are vulnerable), good (clean for many people), and very unhealthy (triggering health alerts). The main gate is poorer than the central laboratory in terms of AQI. Due to traffic congestion, the main gate appears to be a hotspot for pollution (Table 4).

The results of this study have a wide range of variability, indicating a combination of both high and low pollution sources; similarly, South Africa, Senegal, Ethiopia, Ghana, and Malawi were reported to have significant variation [1, 22, 23, 25, 27] respectively, while Francophone nations reported lower variability than the data set of this study. The disparities can result from fewer vehicles, a

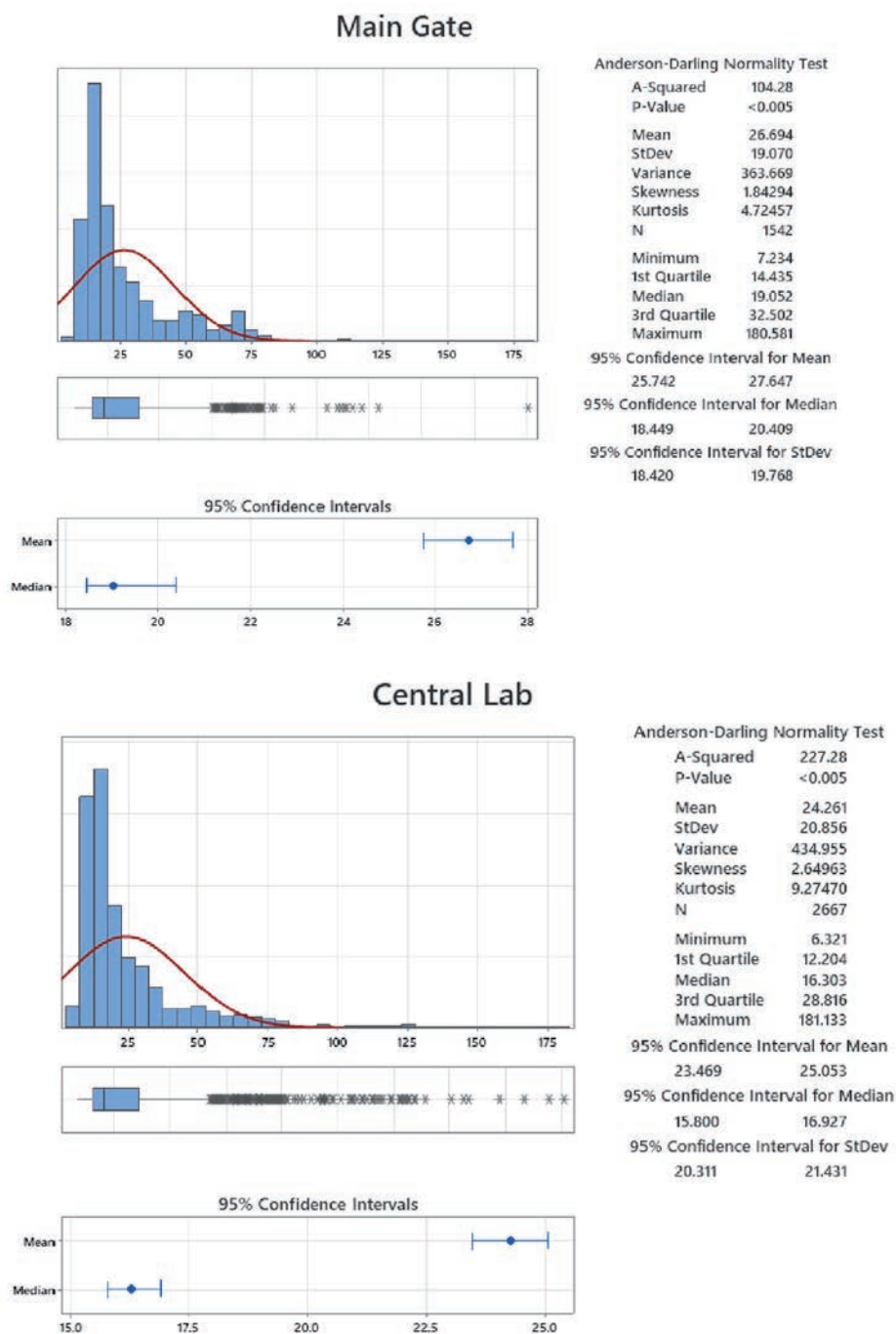


Figure 2.

PM_{2.5} concentration analysis results at main gate and central laboratory—University of Lagos, Nigeria.

smaller population, and less industry. Even if the findings from Ghana, Niger, and Kinshasa were different from ours [28], this might be because of widespread regional air pollution linked to urbanization and uncontrolled emissions. It is

City, Country	Study focus	Measurement method	Mean ranges (µg/m ³)	Reference
Unilag, Lagos		Satellite data	Central Lab: 6.32–181.13 Main gate: 7.23–180.58	This study
Agege, Lagos	The level of PM _{2.5} and the elemental compositions of some potential receptor locations in Lagos, Nigeria	Gravimetrically	6 to 14	Alani et al. [19]
57 cities in Ghana	Comprehensive health risk assessment of urban ambient air pollution (PM _{2.5} , NO ₂ , and O ₃) in Ghana	Satellite measurements	50.79–6797	Ababio et al. [20]
Lebanon	Assessment of the exposure to PM _{2.5} in different Lebanese microenvironments at different temporal scales	low-cost particle counter	24.2 µg/m ³ (Mean)	Faour et al. [21]
Blantyre City, Malawi	Assessment of PM _{2.5} in Blantyre City, Malawi	Laser Particle Counter	1.31–42.57	Thulu et al. [22]
Hawassa City, Ethiopia	Concentration of traffic air pollutants and influencing metrological factors in Hawassa City roadways, Ethiopia	Aero-Qual Series 300/500	95–178.7	Yirdaw et al. [23]
Thohoyandou, South Africa	Health Risk Assessment of PM _{2.5} and PM _{2.5} -Bound Trace Elements in Thohoyandou, South Africa	Gravimetric	Annual average 11	Edlund et al. [24]
Dakar, Senegal	Source Apportionment and Assessment of Air Quality Index of PM _{2.5-10} and PM _{2.5} in at Two Different Sites in Urban Background Area in Senegal	Gravimetric	280.58–302.73	Kebe et al. [25]
Niger	Assessment of variability in PM _{2.5} and its impact on human health in a West African country	Remotely sensed satellite	68.85–70.47	Tariq et al. [26]
Gauteng Province, South Africa	Investigating PM _{2.5} pollution patterns in South Africa using space-time analysis	Satellite-based measurement	6.59–53	Kabanda [27]
Kinshasa, the Democratic Republic of Congo	Assessment of Respiratory Health Impacts of PM _{2.5} by AirQ+ Software in a Sub-Saharan African Urban Setting	Low-cost sensor	Average annual concentration was 43.5	Ngutuka Kinzunga et al. [28]
12 French-speaking African countries	Impact of air pollution on mortality: Geo-epidemiological study in French-speaking Africa	Obtained from explore the data website	1.76–6.99	Capitanio et al. [29]

Table 4.
The comparison of the results of this study with other regional research works.

noted that exposure to high levels of PM_{2.5}, particularly in Dakar, Lagos, and other nations, is linked to increased all-cause mortality, stroke, heart difficulties, and cognitive impairment in both adults and children. PM_{2.5} toxicity is mostly attributed to its size and composition [12]. Extended exposure has been associated with lung issues, asthma, and potentially early mortality [30]. This table suggests that PM_{2.5} is a regional issue in all regions, with Lagos and Dakar having very high levels and other countries reporting consistently dangerous levels. It also suggests that regional policy harmonization is required (**Table 5**).

In the 24-hour standard, the PM_{2.5} TP value ranged from 0.47 to 12.00 (main gate) and 0.41 to 12.02 (central laboratory). In the annual range, it ranged from 1.44 to 36.11 (main gate) and 1.25 to 36.22 (central lab), which is comparable to the range of 1.40 to 10.3 reported by Zaman et al. [31] in a hospital setting in Dhaka, Bangladesh; Abulude et al. [32] in a commercial setting in Akure, Nigeria; Akteruzzaman et al. [33] for an assessment in Bangladesh; and Fakinle et al. [34] in the airshed of a university farm. Both the 24-hour and annual PM_{2.5} mean and maximum values were higher than the permissible ratio of 1. Except, at the very least, for the full 24 hours in the central laboratory and the front gate. The highest PM_{2.5} TP values (12.0–12.02) per 24 hours and 36.11–36.22 per annum represent serious health hazards for the local population. The substantial percentage of TP in areas suggests a considerable potential health risk, especially for children and other vulnerable individuals, due to prolonged exposure to various pollutants [35]. In many poor and undeveloped nations, children suffer from severe respiratory issues as a result of the growing dangers associated with using solid biomass fuel for food preparation [36]. Consequently, appropriate action ought to be taken to guarantee the environment's inhabitants' health and safety.

Throughout the study, the indicators from the two places have had a very high and severe toxicity potential for the people who occupy the gate's offices, the laboratory, and the surrounding area. Therefore, in order to control the sources of air pollution, authorities should act right now by creating a standard framework for managing air quality [31]. The strategy that permits a general improvement in air quality and reduces management expenses should be taken into account when creating the framework for air quality management [37]. In order to safeguard hospital residents, policymakers should also urge people to abide by the rules.

Location	24 h*	Annual*
Main gate		
Mean	1.77	5.34
Minimum	0.47	1.44
Maximum	12.00	36.11
Central laboratory		
Mean	1.82	5.51
Minimum	0.41	1.25
Maximum	12.02	36.22

*TP calculations using WHO [5] standards for 24 h and Annual limits.

Table 5.
Toxicity potential values of PM_{2.5} of the two locations—main gate and the central laboratory both 24 h and annual exposures.

3.1 Exceedance factor (EF) analysis

For both sampling locations, **Table 6** displays the PM_{2.5} daily and annual exceedance factor values along with the respective air quality categories. The exceedance results do not differ all that much. The mean, lowest, and maximum daily results for the main gate are 1.78, 0.48, and 12.04, which correspond to C, L, and C, respectively. The main gate's mean and minimum values are somewhat greater than those of the central laboratory. Days that fall into the high (H) or critical (C) air quality categories and are above the threshold are referred to as exceedance days.

According to **Table 6**, the main gate site had higher yearly PM_{2.5} exceedance levels, which translated into critical and medium pollution levels. According to this, the main gate is especially vulnerable to elevated pollution levels, most likely as a result of greater human activity and perhaps laxer enforcement of pollution control regulations during certain periods. Additionally, it was noted that there are no regular patterns in the months; instead, the exceedance factors vary significantly, with the Central laboratory site often having greater exceedance factors than the main gate for maximum values throughout the sampling period. The WHO's air quality standards from 2021 suggest levels and short-term goals for PM, O₃, NO₂, and SO₂, which are common air pollutants [5]. When compared to the 2005 air quality norms, the approved 2021 levels are in the 99th percentile, meaning that there are three to four exceedance days annually. According to the study's stated exceedance levels, the annual PM_{2.5} values at the two locations exceeded the WHO guideline limit for at least 90% of the days throughout the entire sample period, while the daily measurements had an exceedance percentage of over 50%. This suggests that a significant portion of the PM concentrations in the regions are made up of PM_{2.5}. Additionally, it could be inferred that the two locations exhibit different patterns of PM exceedance. There are serious pollution problems at both sites, especially in the important PM_{2.5} category. Low and critical pollution levels are commonly experienced at the two locations, suggesting a mixture of pollution levels with sporadic periods of acceptable air quality.

According to the health consequences of these exceedances, children and the elderly are the most vulnerable populations in the critical classification if they are exposed over an extended period of time. Asthma, cardiovascular problems, and respiratory distress can be brought on by short-term exposure, usually during periods

Location	EF (24 h)	EF (Annual)
Main Gate		
Mean (Category)	1.78 C	5.34 C
Min (Category)	0.48 L	1.45 M
Max (Category)	12.04 C	36.12 C
Central Laboratory		
Mean (Category)	1.62 C	4.85 C
Min (Category)	0.42 L	1.26 M
Max (Category)	12.08 C	36.23 C

(L = Low, M = Moderate, H = High, C = Critical Pollution)

Table 6.
Exceedance factor values of PM_{2.5} of the two locations—main gate and the central laboratory, both 24 h and annual exposures.

of high traffic or during the dry season. While the central laboratory PM_{2.5} spikes point to regional or atmospheric causes, the levels of PM_{2.5} outside the campus' main gate may be caused by vehicle emissions during the entry and leave of various vehicle kinds and others outside the gate premises. In order to help the public adjust in the event of air pollution (risk), it is crucial to routinely monitor and identify the periods of peak pollution.

The main gate and central lab's daily and annual mean PM_{2.5} levels are shown in bar charts in **Figure 3** in comparison to the WHO [5] and NESREA [18] standard limits. While the limits of 150 µg/m³ and 45 µg/m³ (daily) NESREA and WHO, respectively, are higher than the mean levels (main gate, 26.7 µg/m³ and central lab, 24.26 µg/m³) of the current study, the locations' levels exceeded the national and international standards of 20 µg/m³ and 5 µg/m³ annual limits, respectively. Because

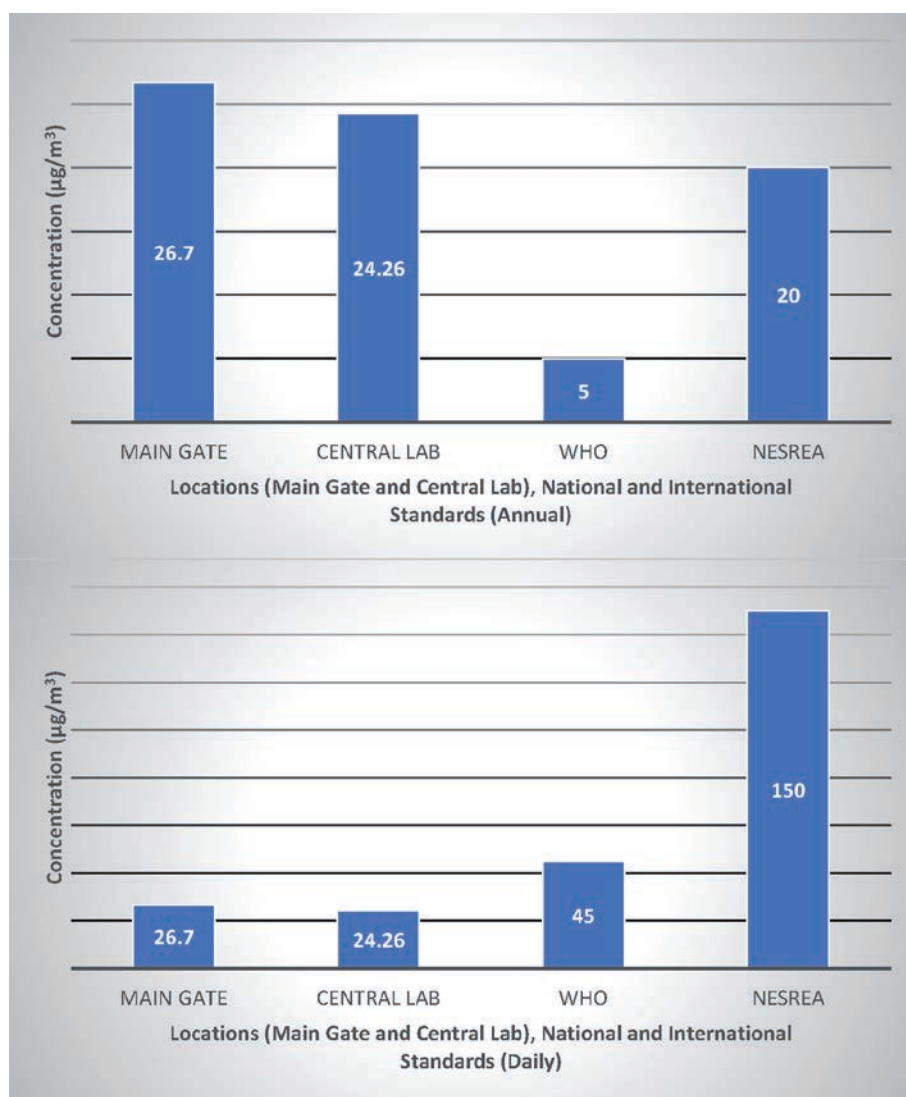


Figure 3. Comparison of the results with the national [18] and international [5] standards. Source: This study.

Main Gate is close to the vehicle and other activities, it recorded higher levels than the central lab in this study [38]. Both the main gate and the central laboratory levels in this study are five times higher than the national and international standards, and ongoing exceedance indicates polluted air, putting people's lives in danger. Other issues include visibility issues, the possibility of solar panel damage, increased heating, ventilation and air-conditioning (HVAC) system maintenance, and laboratory instrument maintenance, to name a few.

The daily average PM_{2.5} values in comparison to the standards are also shown in **Figure 3**. The two places meet the requirements. They could be considered relatively high for educational institutions even based on this assumption. The implication is that the health of staff and students may be impacted by respiratory and asthmatic issues that affect the vulnerable. Long-term exposure to activities in these places still carries a significant amount of TP, even when the daily mean levels appear to be good (**Figure 4**).

Although two locations were employed for the study (UNILAG's main gate and Central Laboratory), this figure shows the HYSPLIT map "72 h backward trajectory

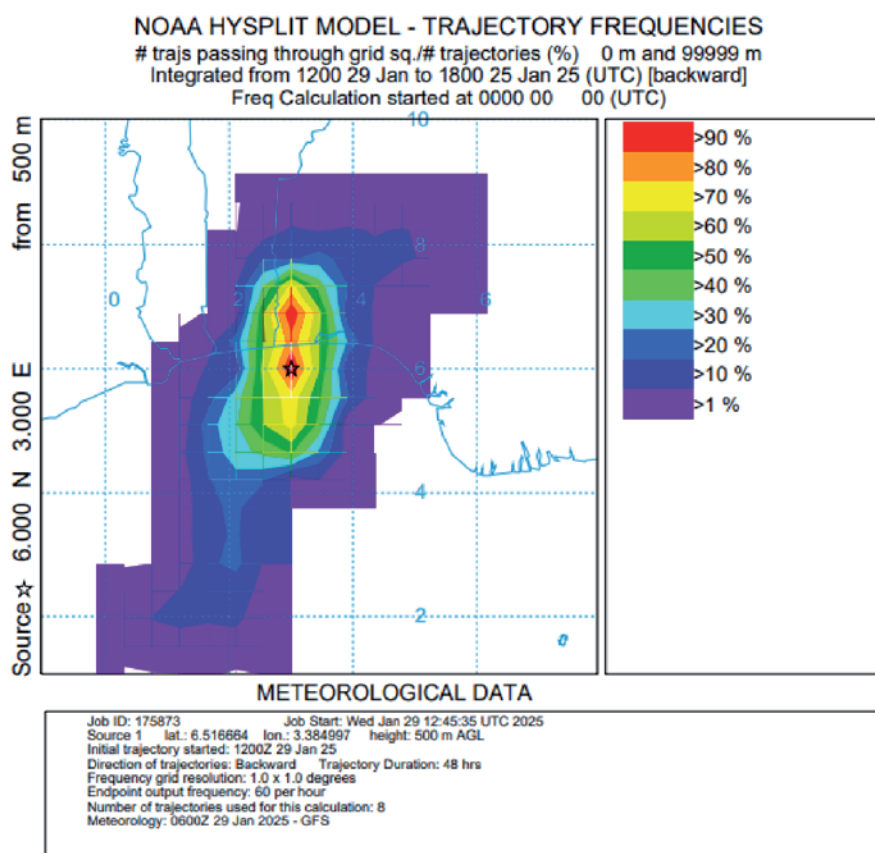


Figure 4. Backward trajectory showing the origin of air masses arriving at Lagos, Nigeria (University of Lagos) over a 72-hour period. The simulation, performed using the HYSPLIT model, indicates that the prevailing air originated from the southwest over the Atlantic Ocean, suggesting minimal influence from inland industrial emissions during this period.

from 10:00 UTC, June 2024”) of the area in Lagos that is the subject of the investigation. The route that starts offshore in the Atlantic Ocean and winds its way toward Lagos is seen in the figure. This makes a small inland circle. Accra, Lome, Cotonou, and Lagos are among the nearby nations (towns) that are included in the figure. The origin of offshore marine vessel movements (ship cargo, oil exploration, port activities) may be the cause of the air movement pattern. Given that it is one of Africa’s busiest cities, the area can be considered a crucial zone for air pollution from industry, cities, and ships. Maritime activities (SO_x , NO_x , and $\text{PM}_{2.5}$), vehicular activities (CO , NO_2 , and black carbon), open waste burning (dioxins, PM , and volatile organic compounds (VOCs)), industrial activities (PM , SO_2 , and VOCs), dust, and harmattan winds (PM) are the main sources of air pollution in Lagos, with a focus on the study areas. There are several obstacles to clean air in this study area, such as inadequate air quality monitoring equipment, no national AQI platform, little or no regional cooperation on cross-border maritime activities, a lack of public air data, and inadequate implementation of policy regarding fuel and vehicle emission standards. These factors have led to $\text{PM}_{2.5}$ levels exceeding WHO guidelines (both annually and daily) and the premature deaths of more than 28,000 Nigerians each year [12]. More ground-based sensor deployment, cross-border cooperation, satellite monitoring to supplement local monitoring, raising public awareness, using clean fuels, and enforcing transportation laws will all be necessary to address these issues.

4. Conclusion

This study analyzed the variations in $\text{PM}_{2.5}$ levels at two monitoring sites, Main Gate and Central Laboratory, within a Nigerian university. The findings reveal that both locations consistently exceeded the air quality limits established by the World Health Organization (WHO) and Nigeria’s National Environmental Standards and Regulations Enforcement Agency (NESREA). The data distributions were notably skewed, and the presence of extreme values indicates recurrent pollution spikes, particularly at the Main Gate, which can be classified as a pollution “hotspot.” The Air Quality Index (AQI) values ranged from “Good” (minimum) to “Very Unhealthy” (maximum), with average values falling within the “Moderate” category. While the majority of Toxicity Potential (TP) values were below 1, the high kurtosis and skewness suggest that extreme pollution events are not isolated occurrences. These findings highlight a substantial public health concern, especially for vulnerable populations in the vicinity. Finally, a comparison with studies from other African and global urban regions underscores that $\text{PM}_{2.5}$ pollution is not an isolated issue but rather a widespread regional environmental challenge, necessitating urgent and targeted mitigation strategies.

5. Recommendations

Mitigation strategies should involve:

- i. Awareness of about air pollution and its attendant problems should be intensified.
- ii. Emissions at the campus gate (entry points) should be controlled.

- iii. Installation of more calibrated real-time sensors and satellite data should be encouraged.
- iv. The use of green buffer zones are used around high-traffic areas to absorb particulates.
- v. Air quality audits should be used throughout the different seasons to track sessional variations.
- vi. Installation of early warning systems and pollution alert apps around hotspots.
- vii. Encourage the use of solar to replace generators for the purpose of clean air.
- viii. Enforce vehicle emission standards in the campus.
- ix. The data should be utilized for immediate government and institution policy formulations to improve/safeguard public health.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this chapter.

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Chemical Characteristics, Source Apportionment, and Potential Impacts of PM_{2.5} Emitted from Ship Exhausts at an Asian Industrial Seaport on Urban Air Quality

*Yu-Lun Tseng, Chung-Shin Yuan, Kuo-Cheng Lo,
Kwok-Wai Wong and I-Chieh Tu*

Abstract

The chemical characteristics, spatiotemporal variation, and source apportionment of PM_{2.5} emitted from ship exhausts in Kaohsiung Harbor and its impact on Metro Kaohsiung are investigated. The highest PM_{2.5} concentrations were observed in winter, and followed by fall, spring, and summer, primarily driven by poor dispersion conditions during the Northeastern Monsoon. Chemical analysis revealed that PM_{2.5} is dominated by water-soluble ions (WSIs), particularly secondary inorganic aerosols (SIAs). Crustal elements such as Mg, Al, and Ca dominate the metallic content of PM_{2.5}, while elevated V/Ni ratios highlighted the contribution of ship emissions, particularly in summer. Ship emissions including main and auxiliary engines played a crucial role in PM_{2.5} levels. Main engines contributed 2.9–5.3% of PM_{2.5} in Metro Kaohsiung, primarily during shorter navigation periods, whereas auxiliary engines contributed 3.8–8.3% during longer berthing periods. The disparity between main and auxiliary engine contributions reflects their operational differences, with auxiliary engines producing sustained emissions that exacerbate urban air quality impacts. PM_{2.5} in Metro Kaohsiung was closely correlated with harbor emissions, indicating strong port-urban interactions. Higher SO₄²⁻ concentrations in the harbor areas are linked to industrial and ship emissions, while mobile sources primarily influenced urban PM_{2.5}. Secondary organic aerosols (SOAs) from long-range transport and local photochemical reactions further contribute to PM_{2.5}, worsened by high atmospheric stability and low mixing layer heights. Sea breezes transport harbor-originated emissions toward inland, with summer amplifying the maritime impact through strong solar radiation and thermal convection, leading to intensified urban air quality degradation.

Keywords: PM_{2.5}, spatiotemporal variation, chemical fingerprints, source apportionment, harbor-metro interactions

1. Introduction

1.1 Introduction to part I

Seaports play a crucial role in the economic development of coastal areas, facilitating commerce and tourism. However, they might also pose environmental challenges, with ship emissions potentially impacting ambient air quality and human health [1, 2]. Ocean-going cargo ship is a primary source of global particulate matter emissions that significantly affect coastal and marine air quality. Fine particles (PM_{2.5}) are critical air pollutants that pose adverse effects on human health [3] and also cause atmospheric visibility reduction, climate change, and ecosystem damage. PM_{2.5} is composed of organic matter, inorganic contents, and trace metals [4]. Atmospheric particles are originated from direct emissions and might be also formed through secondary photochemical reactions.

Long-term exposure to PM_{2.5} leads to respiratory and cardiovascular diseases [5]. Sensitive groups are especially vulnerable to the harmful impacts of PM_{2.5}. Previous studies have estimated that ship emissions result in approximately 60,000 deaths per year due to cardiovascular diseases and lung cancer [6]. These impacts are particularly severe in the coastal regions of Asia and Europe.

In Asian coastal regions, ship emissions account for 7–26% in PM_{2.5} [7]. Particularly, in Xiamen Port, ship emissions contribute 26.1% in PM_{2.5} [8]. Kaohsiung Harbor is located on the southwestern coast of Taiwan Island, which is at the intersection of the Taiwan Strait and the Bashi Channel at the latitude and longitude of 22°36'47" and 120°16'40". The main fairways inbound and outbound of the Kaohsiung Harbor are Port Entrances I and II, with a total length of 18 km [9]. Kaohsiung Harbor is divided into eight commercial port areas, including five large-scale container centers with 124 terminals [8]. There are six types of terminals in the Kaohsiung Harbor, including bulk cargo terminals, container terminals, passenger terminals, cement wharf, industrial terminals, and yacht terminals [10]. Kaohsiung Harbor is the largest international port in Taiwan, and it ranks as the 15th largest container throughput globally. It handles 62% of Taiwan's cargo throughput and emits 6.9 million tons of NO_x, 6.5 million tons of SO₂, and 1.6 million tons of particulate matter (PM) annually. North-eastern monsoons commonly occur in fall and winter seasons in East Asia and worsen air quality by transporting air pollutants from the upwind sources to the downwind harbor areas. This study examines PM_{2.5} at Kaohsiung Harbor by investigating its chemical fingerprints, spatiotemporal variations, and source apportionment during four seasons.

1.2 Sampling sites in the harbor area

This study collected PM_{2.5} samples at three port sites in Kaohsiung Harbor including Qichou (Site QH) at Port Entrance I, Zhangdao (Site ZD) at commercial port area, and Zhanghe (Site ZH) at Port Entrance II (see **Figure 1**). Port Entrance I is located at the harbor's northwestern tip near Qijin and Gushan Districts and is a main shipping fairway with a 98 m wide, 12.5 m deep channel. Port Entrance II is located at the southwestern tip and accommodates larger ships with modern terminals and proximity to major industrial facilities. While, Site Zhangdao is located at the central part of Kaohsiung Harbor near an Export Processing Zone and primarily serves medium-tonnage bulk carriers due to its older infrastructure. Three PM_{2.5} samplers (BGI, PQ-200) were used

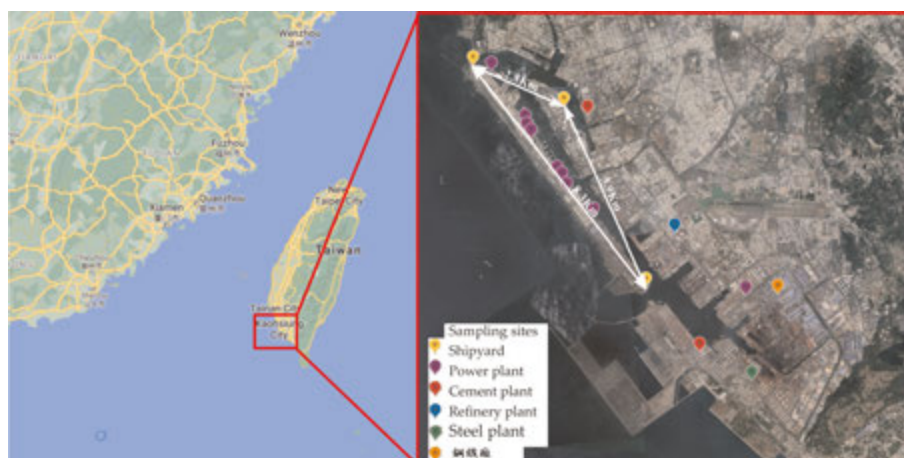


Figure 1. Location of PM_{2.5} sampling sites at (a) the Port Entrance I, (b) the Zhongdao commercial port area, and (c) the Port Entrance II.

to simultaneously collect PM_{2.5} at the port sites from February 2020 to February 2021. The dates of PM_{2.5} sampling at the three port sites were February 18–24, 2020 (Winter), May 6–12, 2020 (Spring), July 21–27, 2020 (Summer), November 4–5 and 8–12, 2020 (Fall). Quartz fibrous filters (Advantec, QR-100, 47 mm) were used for PM_{2.5} sampling. Overall, PM_{2.5} samples were collected by employing 24-hr PM_{2.5} sampling for 7 consecutive days in each season. 24-hr PM_{2.5} was sampled simultaneously, starting from 8:00 am to 8:00 am of the next day. After sampling, the PM_{2.5} filters were conditioned in a desiccator with a relative humidity of $40 \pm 5\%$ and a temperature of $20 \pm 5^\circ\text{C}$ for at least 48 hr. to avoid the interference of moisture. PM_{2.5} filters were then precisely weighed by an analytical microbalance (Sartorius, MSA6.6S) with a precision of $1 \mu\text{g}$. We further repeated the above steps two times to determine PM_{2.5} concentration by averaging the two weighing results (the deviation between these two weighing values should be less than $15 \mu\text{g}$). After weighing, further used an ion chromatography (Thermo Fisher, Dionex, ICS-1100) to analyze 10 water-soluble ionic in PM_{2.5}. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Perkin Elmer, Optima 2000DV) to analyze 17 metallic elements in PM_{2.5}. The carbonaceous contents were determined using an elemental analyzer (EA) (Elementar, Vario MICRO cube). Additionally, high-performance ion chromatography (HPIC) (Thermo Fisher, Dionex, ICS 5000+) was used to analyze organic acids and anhydrosugars. Furthermore, the quality assurance and quality control (QA/QC) of chemical species analyzed for PM_{2.5} analysis including method detection limits (MDL), determination coefficient (R²), and recovery rate (RR).

1.3 Spatiotemporal variation of PM_{2.5} concentration in Kaohsiung Harbor

Figure 2 illustrates the spatiotemporal variation of PM_{2.5} concentrations at three port sites in Kaohsiung Harbor from February to November 2020. There is an obvious spatial and seasonal variation of PM_{2.5} concentrations at three port sites. However, the spatial distribution of PM_{2.5} at the Kaohsiung Harbor during the winter season is in the order of ZD > ZH > QH. The Pearson's correlation coefficients (r) of PM_{2.5} concentration between two out of three sampling sites were 0.993, 0.997, and 0.990,

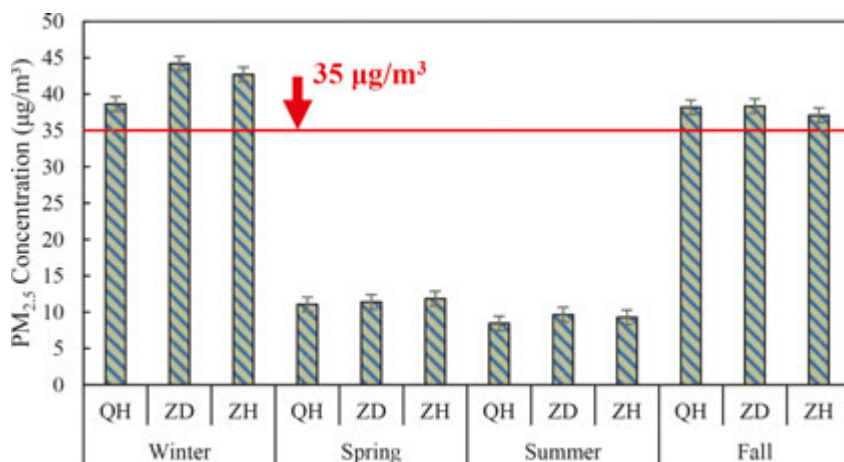


Figure 2.
Spatiotemporal variation of PM_{2.5} concentrations at the Kaohsiung Harbor during the sampling periods.

respectively, indicating similar sources of PM_{2.5} at the three port sites in the Kaohsiung Harbor. During the fall season, the Asian continent's cold high-pressure anti-cyclone system creates Northeastern Monsoons, which could bring air pollutants to Kaohsiung Harbor and thus elevate PM_{2.5} concentrations. During the summer season, Southwestern Monsoons created by the West Pacific's warm low-pressure cyclone system could bring relatively clean marine air. Additionally, high air temperatures occurring during summer and fall seasons could promote vertical convection of air pollutants. As a result, these two meteorologic factors enhance atmospheric dispersion, resulting in low PM_{2.5} concentrations.

1.4 Chemical fingerprints of PM_{2.5} in Kaohsiung Harbor

As shown in **Figure 3**, WSIs constituted 46.3–59.8% of PM_{2.5} at QH, ZD, and ZH in Kaohsiung Harbor. Dominant WSIs included SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , and Na^+ , representing SIAs and sea salts. During the fall and winter seasons, cooler air temperatures promote the atmospheric reaction of ammonia (NH_3) and nitric acid (HNO_3) to form ammonium nitrate (NH_4NO_3) [11], resulting in higher concentrations of NO_3^- and NH_4^+ than those during the spring and summer. Seasonal WSI

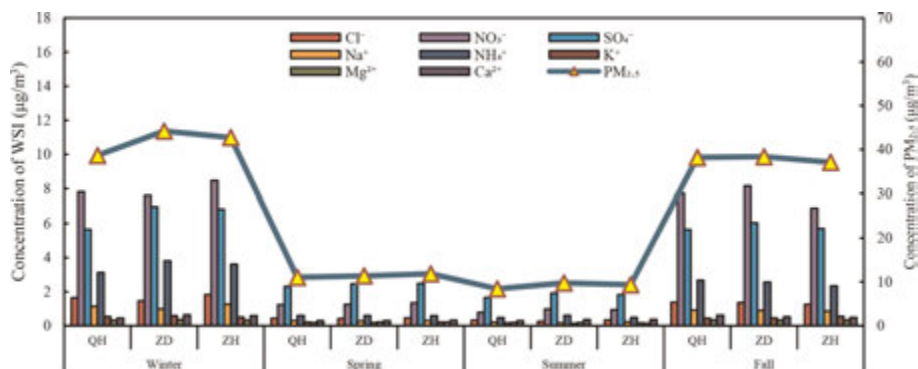


Figure 3.
Spatiotemporal variation of water-soluble ions in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

concentrations basically follow PM_{2.5} variation trends with higher WSI levels during the fall and winter seasons (**Figure 4**).

The seasonal ratios of SIAs and WSIs (SIAs/WSIs) in PM_{2.5} ranged from 66.8–84.3%, with the seasonal variation as fall (80.4%) > winter (79.0%) > spring (73.6%) > summer (71.8%). The results show the influence of anthropogenic aerosols transported by Northeastern Monsoons from northern Taiwan and Northeast Asia, including Mainland China, Korea, and Japan.

The neutralization ratio (NR) of PM_{2.5} calculated using the equivalent concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺ revealed a seasonal variation of NR in the order of winter (0.84) > fall (0.70) > summer (0.69) > spring (0.67). The NR values below unity indicated excess acidity in PM_{2.5} due to insufficient NH₄⁺ to completely neutralize nss-SO₄²⁻ and NO₃. The acidic nature of PM_{2.5}, consistent with other industrial port studies, highlights the significant contribution of secondary aerosols and ocean-derived sulfate [12, 13].

During the sampling periods, metallic elements in PM_{2.5} at the three port sites show a seasonal trend of winter > fall > spring > summer (see **Figure 5**). Among the metallic elements, crustal elements (Mg, Al, Ca, Fe, and K) dominated, comprising 84.6–89.9% of total metallic content. However, the enrichment factor (EF) of trace elements (Ni, V, Cr, Cu, Zn, and Pb) is above 10 (**Figure 6**), indicating significant anthropogenic contributions from industrial emissions, vehicular exhausts, and ship/vessel emissions. Notably, the EF values of V and Ni increase during the spring and summer seasons, mainly influenced by Southwestern Monsoons carrying PM_{2.5} from ships docked or navigated in Kaohsiung Harbor:

$$EF = \frac{\left(\frac{Tr}{Ref}\right)_{PM}}{\left(\frac{Tr}{Ref}\right)_{crust}} \quad (1)$$

where Tr: trace elements.

Ref: reference elements (e.g., Al, Fe, and Si).

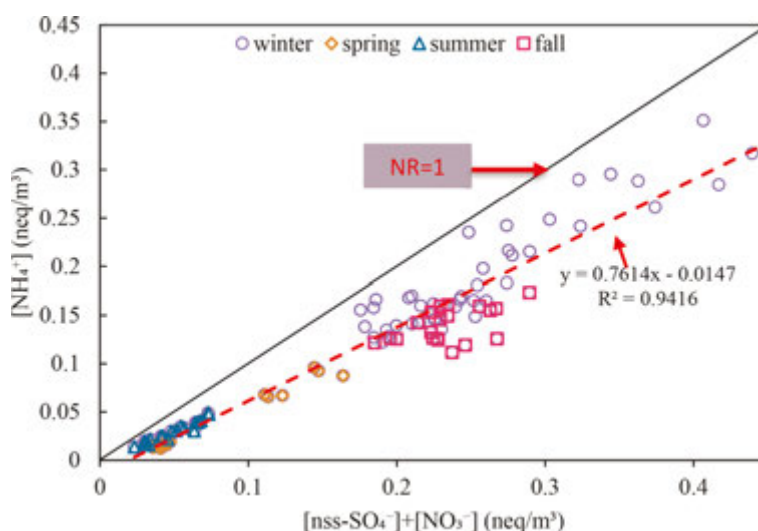


Figure 4.
 Plot of [NH₄⁺] vs. [nss-SO₄²⁻] and [NO₃⁻] in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

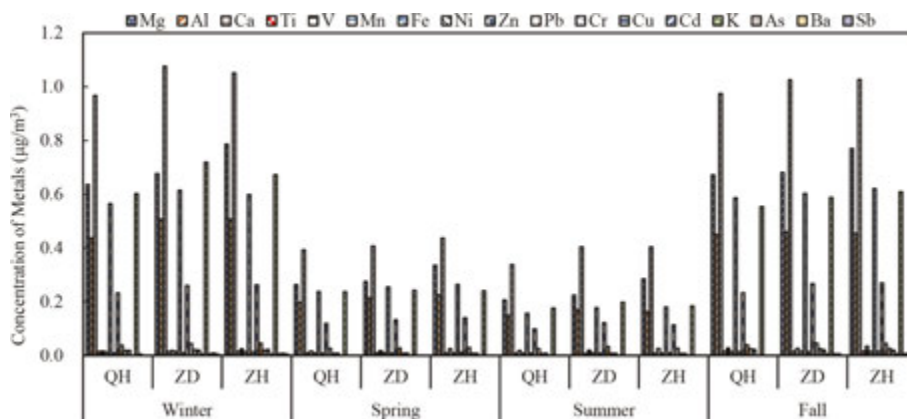


Figure 5.
Spatiotemporal variation of metallic elements in $PM_{2.5}$ at the Kaohsiung Harbor during the sampling periods.

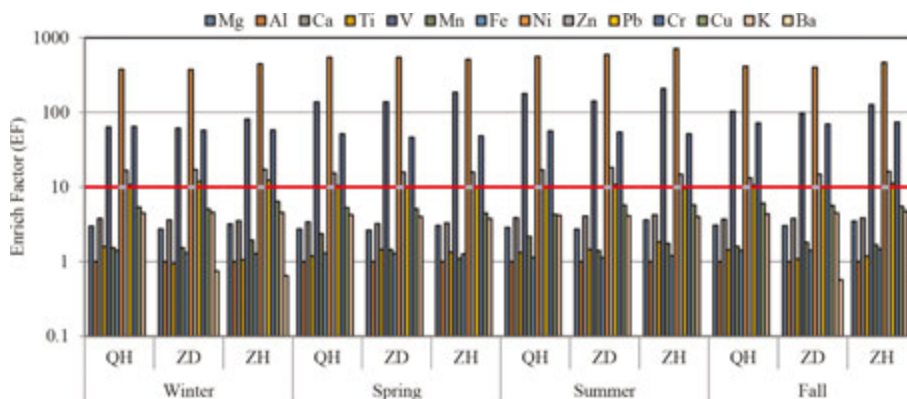


Figure 6.
Spatiotemporal variation of enrichment factors (EF) of metallic elements in $PM_{2.5}$ at the Kaohsiung Harbor during the sampling periods.

$(Tr/Ref)_{PM}$: concentration ratio of trace elements to reference element in the suspended particles.

$(Tr/Ref)_{crust}$: concentration ratio of trace elements to reference element in the crustal materials.

Moreover, the ratio of vanadium and nickel (V/Ni) has been identified as an indicator of $PM_{2.5}$ emitted from ship exhausts, typically ranging from 2.5 to 4.0 [14, 15]. As shown in **Figure 7(a)**, the seasonal variation of V/Ni ratio show the seasonal variation of summer (2.44) > spring (2.08) > fall (2.07) > winter (1.83). A new low-sulfur fuel policy ($S < 0.5\%$) significantly alters the V/Ni ratio since vanadium content consistently decreases with sulfur levels in bunker fuels [16]. The highest V/Ni ratio commonly occurred during summer is mainly attributed to south-western monsoons transporting ship emissions from the ocean to Kaohsiung Harbor.

The spatial distribution of V/Ni ratios is in descending order as: Site ZH (2.13) > Site QH (2.01) = Site ZD (2.01) (**Figure 7(b)**). A higher V/Ni ratio at Site ZH suggests influence from ship emissions related to large bulk carriers at Port Entrance 2. Additionally, the nearby petroleum refinery in the Linhai industrial

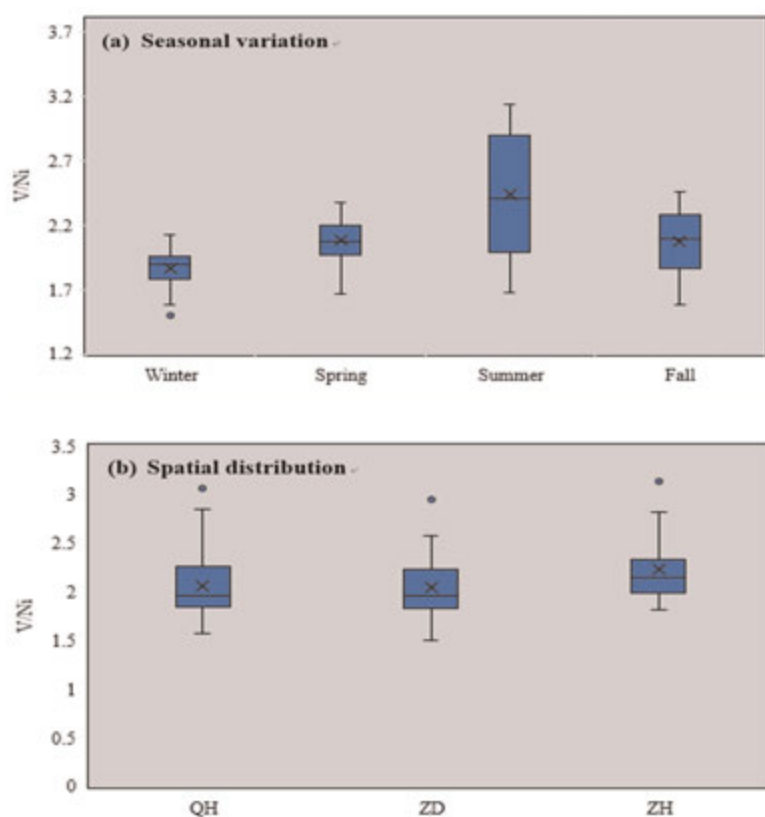


Figure 7.
 (a) Seasonal variation and (b) spatial distribution of V/Ni ratios in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

complex contributes to V/Ni ratios due to refinery processes and oil-fired boilers, especially for nighttime land breezes during the summer season. This aligns with previous studies showing V/Ni ratios of 1–3 for PM_{2.5} emitted from the refinery processes [17].

As shown above, vanadium (V) came mainly from ship emissions, while nickel (Ni) might have other sources except ship emissions [18, 19]. Previous research reported that the contribution of ship emissions to primary PM_{2.5} could be evaluated by considering V as a marker for the fuel combustion in ship engines [20–22]. The primary contribution of ship emissions to PM_{2.5} in Kaohsiung Harbor could be estimated by Eq. (1) [23]:

$$PM_a = \langle r \rangle \times V_a / F_{V,HFO} \quad (2)$$

where PM_a is the estimated primary PM_{2.5} concentration ($\mu\text{g}/\text{m}^3$); $\langle r \rangle$ is the average ratio of PM_{2.5} to the normalized V emitted (per ppm) based on the heavy fuel oil (HFO) burning experiments for ship engines; V_a is the *in-situ* ambient V concentration in PM_{2.5} ($\mu\text{g}/\text{m}^3$); and $\langle F_{V,HFO} \rangle$ is the average V content (ppm) of HFO used by vessels in the harbors. In this study, $\langle r \rangle$ was set as 8205.8 ppm obtained from [24], since it was suggested to be universally applied to other locations with HFO-burning ship emissions. Moreover, $\langle F_{V,HFO} \rangle$ was set as 93 ppm for the average V content of HFO.

At Kaohsiung Harbor, primary $PM_{2.5}$ emitted from ship traffic ranges from 1.45 to $11.86 \mu\text{g}/\text{m}^3$ with an average concentration of $6.24 \mu\text{g}/\text{m}^3$ (**Figure 8**). Ship emissions contribute 20.8% of $PM_{2.5}$ during the spring and summer seasons, which are higher than those during the winter and fall seasons. However, during the spring and summer seasons, ambient air quality becomes better, and air pollutants are not complicated, which caused the ship emissions to be higher than those during the winter and fall seasons.

Figure 9 illustrates that the carbonaceous content of $PM_{2.5}$ in Kaohsiung Harbor is dominated by organic carbon (OC). Seasonal ratios of organic carbon and elemental carbon (OC/EC) are in descending order: winter (2.18) > fall (2.06) > spring (1.87) > summer (1.73). OC/EC ratios above 2.0 in $PM_{2.5}$ during the fall and winter seasons indicate SOA formation from local emissions and cross-boundary transport.

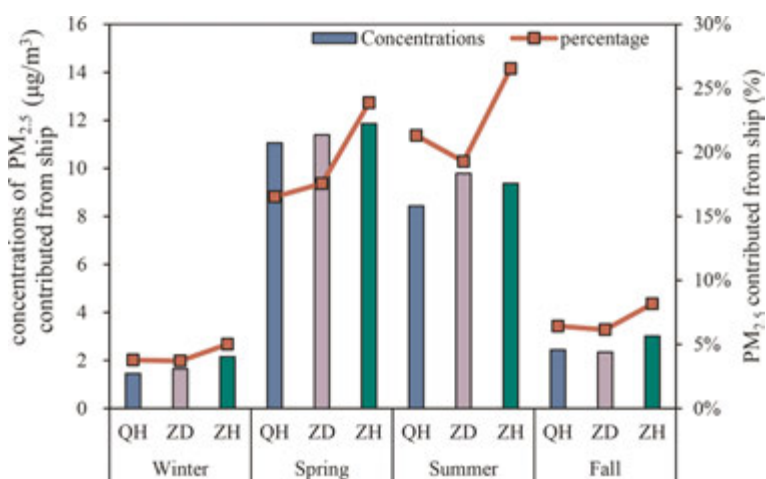


Figure 8.
Contribution estimate to $PM_{2.5}$ from ship traffic emissions in Kaohsiung Harbor.

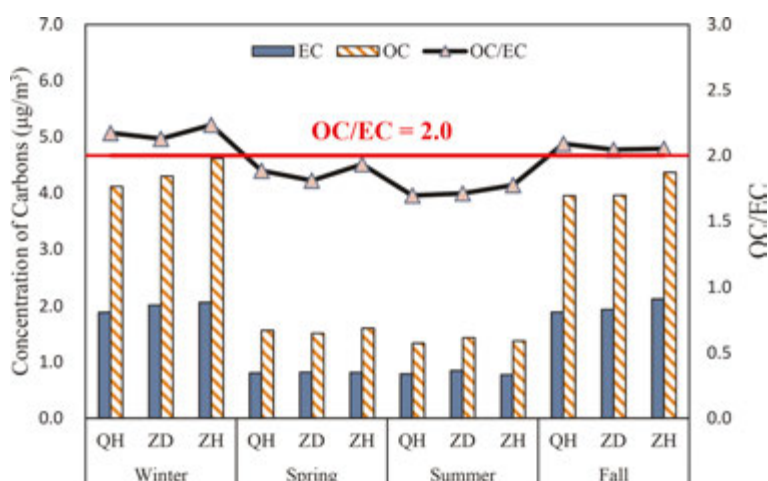


Figure 9.
Spatiotemporal variation of (a) carbonaceous content in $PM_{2.5}$ at the Kaohsiung Harbor during the sampling periods.

OC/EC ratios below 2.0 during the spring and summer seasons suggest minimal SOA formation [25–27].

This study further used a minimum OC/EC ((OC/EC)_{min}) ratio to estimate secondary organic carbon (SOC), which can be expressed by Eqs. (3) and (4) [28, 29]:

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC/EC})_{\text{pri}} \quad (3)$$

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC/EC})_{\text{min}} \quad (4)$$

where (OC/EC)_{pri} is the OC/EC ratio of primary organic aerosols; (OC/EC)_{min} is the minimum OC/EC ratio of PM_{2.5} measured annually at the sampling site. Since (OC/EC)_{pri} is not available in reality, this study thus uses (OC/EC)_{min} as (OC/EC)_{pri} to estimate the concentration of SOC in PM_{2.5} at each sampling site in the Kaohsiung Harbor by Eq. (3). However, the replacement of (OC/EC)_{pri} with (OC/EC)_{min} might slightly underestimate the concentration of SOC.

The SOC levels and SOC/OC ratios during the fall and winter seasons are commonly higher than those during the spring and summer seasons (**Table 1**). North-eastern Monsoons transported air pollutants from East China's eastern coastal regions and West Taiwan's local sources near industrial complexes, increasing SOC formation through either gas–solid or photochemical reactions. During summer, strong solar radiation could enhance photochemical reactions, but better atmospheric dispersion would reduce the concentration of VOCs, thus limiting the accumulation of SOC in the low atmosphere.

Except for levoglucosan, mannosan, and galactosan were not detected in the anhydrosugars of PM_{2.5} at port sites in the Kaohsiung Harbor. Due to its better thermal stability, levoglucosan is abundant in PM_{2.5} released from biomass burning and can be easily detected. Thus, it is commonly considered as an important tracer of biomass burning except for K⁺ and OC [30–32]. Seasonal variation of levoglucosan in

Seasons	Sampling Sites	EC	OC	TC	OC/EC	TC/PM _{2.5}	SOC	SOC/OC
Winter	QH	1.89	4.11	6.00	2.17	15.7%	1.34	32.0%
	ZD	2.02	4.30	6.32	2.13	14.5%	1.34	31.6%
	ZH	2.06	4.62	6.68	2.23	15.7%	1.58	34.0%
Spring	QH	0.81	1.57	2.38	1.88	24.3%	0.38	20.7%
	ZD	0.82	1.52	2.34	1.81	23.1%	0.31	17.3%
	ZH	0.82	1.60	2.42	1.93	22.8%	0.41	23.2%
Summer	QH	0.79	1.34	2.13	1.69	26.3%	0.18	12.7%
	ZD	0.85	1.44	2.29	1.71	24.0%	0.19	13.5%
	ZH	0.78	1.38	2.15	1.77	23.7%	0.24	16.8%
Fall	QH	1.89	3.95	5.84	2.09	15.3%	1.17	29.2%
	ZD	1.94	3.96	5.90	2.04	15.5%	1.11	27.8%
	ZH	2.12	4.37	6.49	2.05	17.6%	1.24	28.0%

units: µg/m³; QH: Qichou at the Port Entrance I; ZD: Zhungdao commercial port area; ZH: Zhanghe at the Port Entrance II.

Table 1.
Seasonal variation and spatial distribution of carbonaceous content in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

PM_{2.5} is in descending order as: winter (72.5 ng/m³) > fall (59.7 ng/m³) > spring (29.2 ng/m³) > summer (19.3 ng/m³) (**Figure 10**). Furthermore, correlation analysis of levoglucosan with K⁺ reveals a positive relationship ($r = 0.576$, $P = 0.025$), with the strongest correlation in winter ($r = 0.484$, $P = 0.036$) (**Figure 11**). This indicates that PM_{2.5} in winter is significantly influenced by biomass burning compared to other seasons.

Organic acids are key components of SOAs and are dominated by dicarboxylic acids, including oxalic, malonic, and succinic acids (**Figure 12**). Oxalic acid is the most abundant organic acid, and followed by malonic and succinic acids. Malonic acid formed through the photochemical degradation of succinic acid indicates SOA formation solely when the mass ratio of malonic acid and succinic acid (M/S) ratio exceeds unity. M/S ratios at all three port sites are consistently above unity, confirming significant SOA formation in the Kaohsiung Harbor. High air temperatures and strong

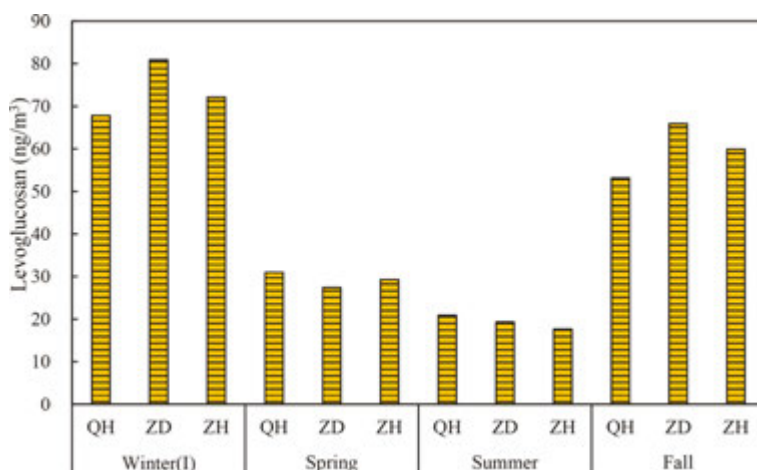


Figure 10. Spatiotemporal variation of levoglucosan in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

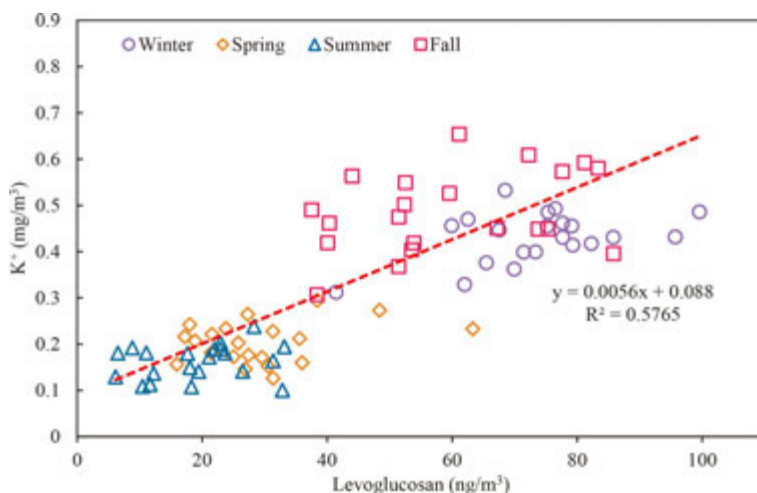


Figure 11. Plot of levoglucosan vs. K⁺ in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

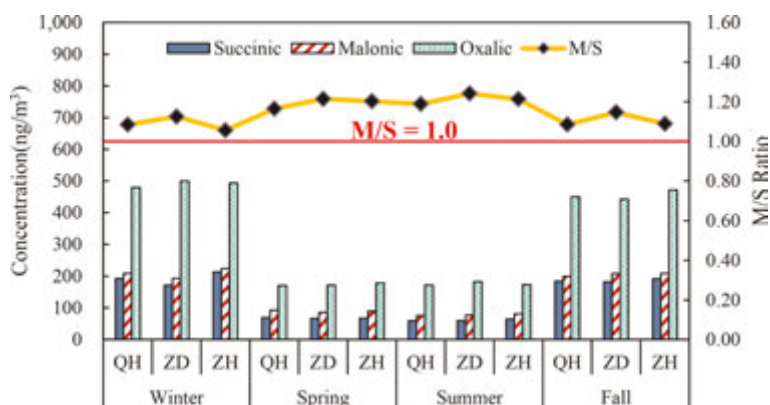


Figure 12.
 Spatiotemporal variation of organic acids in PM_{2.5} at the Kaohsiung Harbor during the sampling periods.

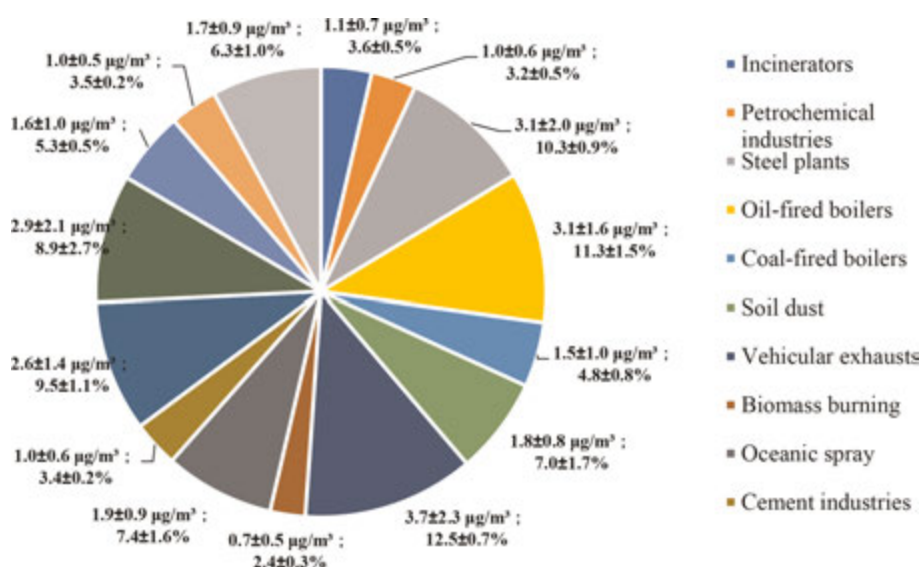


Figure 13.
 Source apportionment of PM_{2.5} at the Kaohsiung Harbor during the sampling periods resolved by CMB receptor model.

solar radiation in late spring and summer enhanced atmospheric photochemical reactions, thus increasing dicarboxylic acid levels [33, 34].

1.5 Source apportionment of PM_{2.5}

As depicted in **Figure 13**, the Chemical Mass Balance (CMB) receptor model identified 14 emission sources in 7 categories, with industrial emissions as the largest contribution in PM_{2.5} (33.8–36.5%), followed by secondary aerosols (20.9–26.1%), vehicular exhausts (11.5–13.2%), and oil-fired boilers (9.2–12.9%). Seasonal variation reveals higher contributions of industrial emissions, secondary aerosols, vehicular exhausts, and biomass burning during the fall and winter seasons due to lower air

temperatures, reduced mixing heights, and prevailing Northeastern Monsoons transporting air pollutants from the northern sources. In late spring and summer, higher air temperatures and improved atmospheric dispersion increase the contributions of road dust from truck driving and cargo handling. Moreover, ship emissions were gradually higher in summer due to being transported by Southwestern Monsoons, while oceanic spray and oil-fired boiler contributions are greater during fall and winter seasons.

2. Impacts of ship emissions and sea-land breeze on urban air quality

2.1 Introduction to part II

Continuous growth of the global population and manufacturing scale results in exponential increases in energy extraction, processing, and consumption. It has created conflicts between natural resources, the environment, and economic development, making it challenging to govern ecosystems. One of the significant environmental concerns impacting human health, environmental production, and the quality of life on a global, regional, and local scale is air pollution [35, 36]. This risk is particularly pronounced in densely populated metropolitan regions nearby a seaport [36, 37].

For the past decades and in the future, marine transportation has played a crucial role in the development of world economy. While seaports offer economic advantages, they could frequently pose environmental and health challenges due to their potential contribution to air and water pollution [1]. In particular, seaport is thought as a significant origin of particulates due to marine transportation, bulk materials handling, and road dust re-entrained by traffic and/or winds, which are the primary sources of particulate matter (PM) in the port areas [38]. Notably, a large portion of ship emissions, approximately 70% of nitrogen and sulfur emissions, would influence the inland areas within 400 km of the coastline [39, 40]. Air pollutants emitted from ship exhausts might be transported over long distances for hundreds of kilometers inland, leading to elevated PM_{2.5} levels in the affected areas [41, 42]. In addition to the deterioration of marine air quality during the navigation of ships over the open sea routes, ships and vessels could also substantially emit PM_{2.5} while navigating or docking in the inner and outer harbors [43]. It is especially concerned that harbors are mostly situated near densely populated metropolitan areas in East Asia, leading to the potential increasing exposure of local population to harmful contaminants [44].

Overall, approximately 14% of gross nitrogen oxide (NO_x) emissions and up to 4% of gross sulfur dioxide (SO₂) emissions from fossil fuel combustion are attributed to ship exhausts [45]. The discharge of air pollutants from ships frequently occurs near other sources, such as industrial complexes and cargo hubs for importing and exporting goods. In the vast regions of the North Hemisphere and certain parts of the South Hemisphere, sulfur emissions from ships/vessels are similar in quantity to the naturally occurring biogenic emissions from the ocean [8, 46]. In the heavily trafficked ocean areas, the emission of air pollutants from ships/vessels can raise the concentrations of nitrogen oxides (NO_x) by over 100 times of their normal levels [47]. Seaports are often located near urban areas in the Asian harbor cities, which would cause serious environmental problems related to air and water pollution and even waste management in the adjacent metropolitan areas. Accordingly, previous investigations have evaluated the impacts of ship emissions on ambient air quality and

microclimate in the coastal regions. Many efforts have been made to characterize PM_{2.5} emitted from ships/vessels and estimate their influences on the ambient air quality of nearby metropolitan areas [48].

This study investigates the impact of PM_{2.5} emissions from Kaohsiung Harbor on ambient air quality in the adjacent metropolitan area. It involves seasonal PM_{2.5} sampling, chemical characterization, and air dispersion modeling to identify spatio-temporal variations, chemical fingerprints, and source contributions in both port and urban areas.

2.2 Sampling sites in the Kaohsiung Harbor and metro Kaohsiung

As shown in **Figure 14**, PM_{2.5} samples were collected at four sites in Kaohsiung Harbor and Metro Kaohsiung from August 2020 to May 2021. Sampling occurred over a continuous seven-day period in each season, with 12-hour samples taken during the daytime (08:00–20:00) and nighttime (20:00–08:00). Two harbor sites are Qiho security checkpoint (Site QH) near Port Entrance I and Zhunghe Security Checkpoint (Site ZH) near Port Entrance II. Two urban sites were Mincyuan Elementary School (Site MC) in Qianzhen District and Fengshan High School (Site Fengshan Senior High School (FS)) in Fengshan District, the latter being Metro Kaohsiung's largest commercial and residential area. This setup enables the comparison of PM_{2.5} concentrations and chemical compositions between the harbor and urban regions. Following the PM_{2.5} samplings, each PM_{2.5} filter was divided into four identical portions for further analysis of the chemical composition of PM_{2.5} after conditioning and weighing. The chemical components analyzed for PM_{2.5} included water-soluble ions, metallic elements, carbons, anhydrosugars, and organic acids. The analytical instruments used for these measurements are detailed in Section 1.2.



Figure 14. Location of four PM_{2.5} sampling sites in the Kaohsiung Harbor and Metro Kaohsiung (a) Qiho security checkpoint (QH Site), (b) Zhunghe security checkpoint (ZH Site), (c) Mincyuan Elementary School (MC Site), and (d) Fengshan Senior High School (FS Site).

2.3 Spatiotemporal variation of PM_{2.5} in the Kaohsiung Harbor and metro Kaohsiung

The seasonal and diurnal variations of PM_{2.5} concentrations in Kaohsiung Harbor and Metro Kaohsiung are summarized in **Figures 15** and **16**. Seasonal PM_{2.5} concentrations follow the descending order as: winter > spring > fall > summer, with higher PM_{2.5} levels in the harbor area than those in the urban area. The four-season averages follow the descending order as: Site ZH (26.28 $\mu\text{g}/\text{m}^3$) > Site QH (21.40 $\mu\text{g}/\text{m}^3$) > Site FS (19.97 $\mu\text{g}/\text{m}^3$) > Site MC (17.38 $\mu\text{g}/\text{m}^3$). Overall, winter and spring seasons exhibit higher PM_{2.5} concentrations due to cold air masses and atmospheric stability, while sea-land breezes regularly transport air pollutants back and forth across the coastline but allow better atmospheric dispersion in summer.

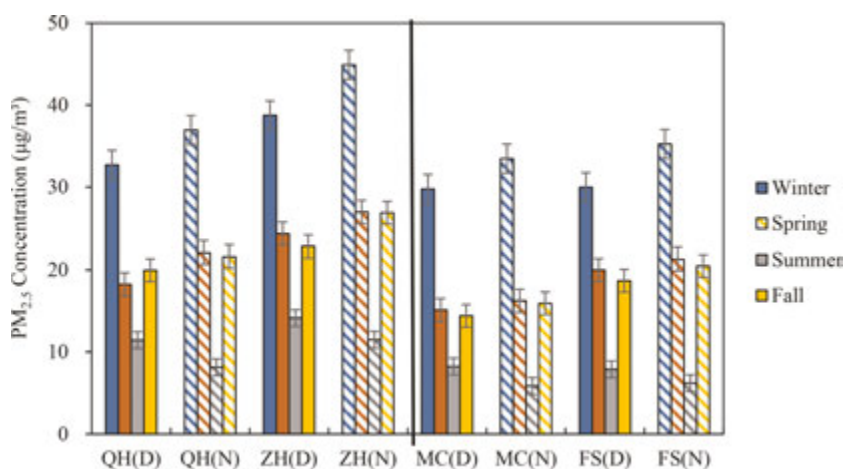


Figure 15. Spatiotemporal variation of PM_{2.5} concentration at (a) the Kaohsiung Harbor and (b) the Metro Kaohsiung during the sampling periods.

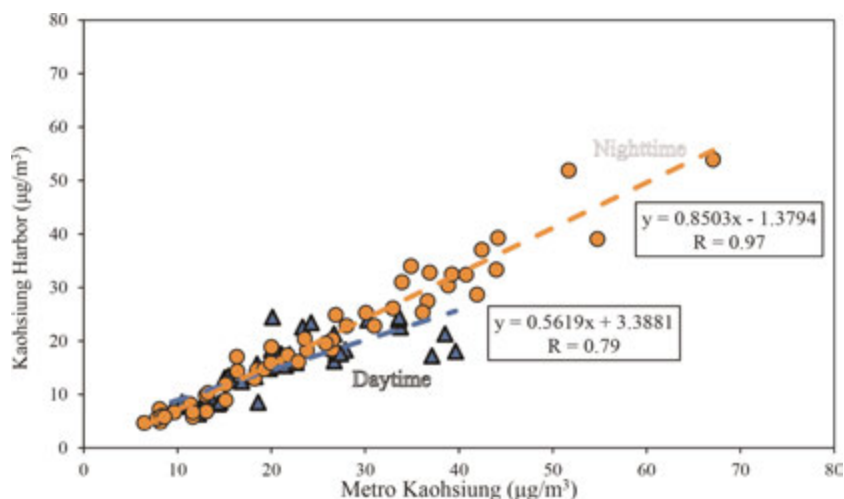


Figure 16. Correlation between PM_{2.5} in the daytime and nighttime at the Kaohsiung Harbor and Metro Kaohsiung.

Diurnal variation shows higher PM_{2.5} concentrations at nighttime, especially during the winter, spring, and fall seasons. The mass ratios of daytime and nighttime PM_{2.5} concentrations (D/N) range from 0.85–0.89 in winter to 1.23–1.41 in summer. Additionally, nighttime PM_{2.5} concentrations are primarily influenced by poor atmospheric dispersion conditions, while daytime PM_{2.5} levels in summer rise up due to sea breezes bringing air pollutants from offshore. PM_{2.5} in Metro Kaohsiung is affected by harbor ship emissions and urban vehicular exhausts, deteriorating ambient air quality in both areas.

2.4 Chemical fingerprints of PM_{2.5} in Kaohsiung Harbor and metro Kaohsiung

Seasonal and diurnal variations of PM_{2.5} concentrations and its water-soluble ions (WSIs) are evident (**Figure 17**). It shows that the highest concentrations of WSIs are frequently observed during winter (18.86 $\mu\text{g}/\text{m}^3$), followed by spring, fall, and summer, accounting for 31.3–55.1% of PM_{2.5}. WSIs at nighttime are generally higher than those in the daytime during winter, spring, and fall seasons due to lower air temperatures, higher humidity, and worse atmospheric dispersion, while the summer season shows an opposite trend due to better atmospheric dispersion in the daytime.

Spatially, WSIs in the port areas (Sites QH and ZH) are higher than those in the urban areas (Sites MC and FS). SIAs including NH_4^+ , NO_3^- , and SO_4^{2-} decrease significantly from winter to summer. Similarly, the concentration of sea salt spray also reduces by 2.3 times. SO_4^{2-} , predominantly emitted from ship and industrial emissions, is 1.44 times higher than NO_3^- in the port areas, while NO_3^- , primarily from vehicular exhausts, is 1.20 times higher in the urban areas. Such a pattern highlights the influences of port activities and urban vehicular exhausts on the spatial distribution of PM_{2.5} concentrations.

The seasonal and diurnal variations of metallic elements in PM_{2.5} show the highest concentrations during winter, followed by spring, fall, and summer (**Figure 18**). Spatially, metallic concentrations in the port area (3.30 $\mu\text{g}/\text{m}^3$) were higher than those in the urban area (3.01 $\mu\text{g}/\text{m}^3$), with a strong correlation between the two areas

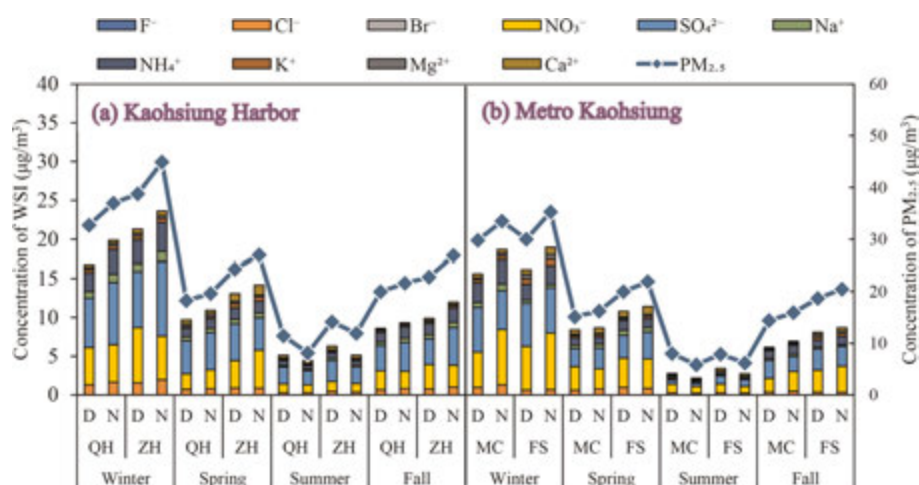


Figure 17. Spatiotemporal variation of water-soluble ions in PM_{2.5} at (a) the Kaohsiung Harbor and (b) the Metro Kaohsiung during the sampling periods.

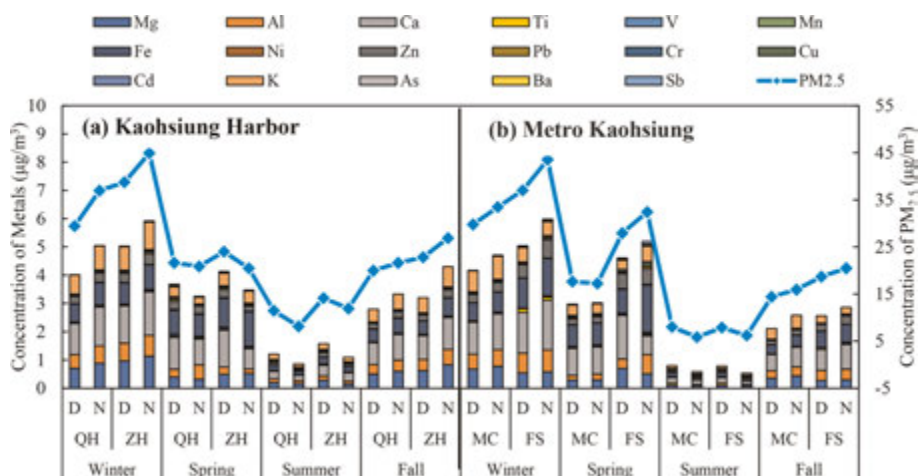


Figure 18.

Spatiotemporal variation of metallic elements in $PM_{2.5}$ at (a) the Kaohsiung Harbor and (b) the Metro Kaohsiung during the sampling periods.

($r = 0.93$). $PM_{2.5}$ concentrations in the nighttime exceeded in the daytime in winter, spring, and fall, consistent with overall $PM_{2.5}$ trends.

Crustal elements such as Mg, K, Ca, and Fe dominate metallic elements in both areas, accounting for 86.3% and 82.0% of total metallic elements in the port and urban areas, respectively. These elements primarily originated from crustal and road dust. The port areas show higher concentrations of V and Ni, key markers of ship emissions. Moreover, V/Ni ratios (1.54–2.85) in port areas are significantly higher than those in urban areas (0.97–2.34). In Metro Kaohsiung, metallic elements such as Zn, Cu, and Al are associated with vehicular emissions including tail exhausts, brake wear, and road dust. Industrial sources contribute minimally, with certain metals near or below detection limits. These findings highlight the distinct influences of ship emissions in the port areas and vehicular emissions in the urban areas.

The carbonaceous content of $PM_{2.5}$ reveals significantly higher OC/EC ratios in Kaohsiung Harbor than in Metro Kaohsiung (**Figure 19**). OC/EC ratios exceeding 2.0 during fall and winter indicate the potential formation of SOA, influenced by Asian Northeastern Monsoons transporting air pollutants to the Kaohsiung region. During summer, OC/EC ratios above 1.0 suggest a stronger impact of traffic-related emissions in both areas. OC/EC ratios at nighttime consistently exceed those in the daytime, highlighting higher nighttime contributions of OC.

Organic carbon (OC) in $PM_{2.5}$ is derived from primary organic carbon (POC) sources such as cooking, vehicular exhausts, and industrial combustion, and secondary organic carbon (SOC) is formed through atmospheric reactions. SOC concentrations at nighttime are consistently higher than those in the daytime, with Kaohsiung Harbor showing greater levels than Metro Kaohsiung. Field measurement results indicate predominant SOA generation in the harbor at nighttime, as evidenced by elevated levels of SOC in $PM_{2.5}$. This highlights the harbor's significant role in producing SOAs.

The analytical results of anhydrosugars show that neither mannosan nor galactosan is detected (i.e., non-detectable; ND) in this study (**Figure 20**). Thus, this section solely discusses the spatiotemporal variation of levoglucosan concentration. Seasonal average concentrations of levoglucosan in Kaohsiung Harbor are the highest in winter

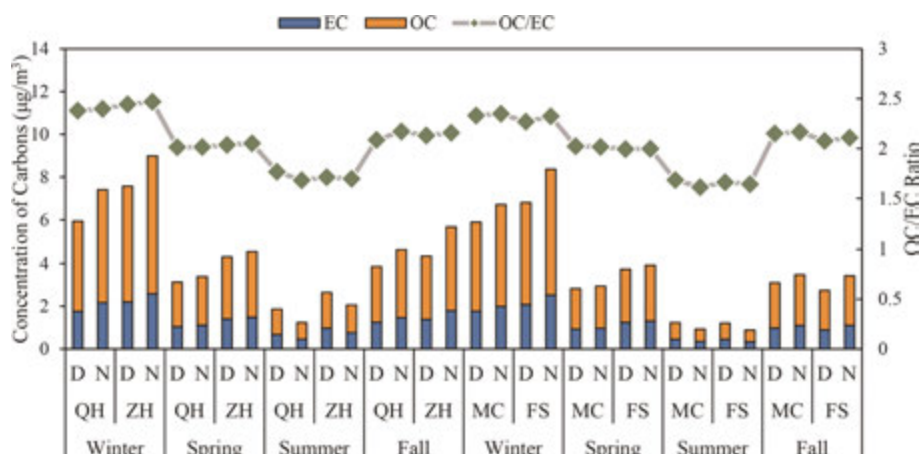


Figure 19.
 Spatiotemporal variation of carbonaceous content in PM_{2.5} at (a) the Kaohsiung Harbor and (b) the Metro Kaohsiung during the sampling periods.

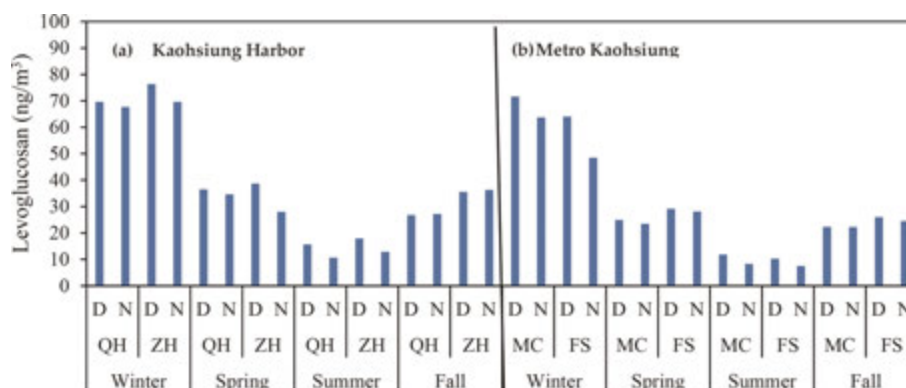


Figure 20.
 Spatiotemporal variation of levoglucosan in PM_{2.5} at (a) the Kaohsiung Harbor and (b) the Metro Kaohsiung during the sampling.

(70.85 ng/m³) and the lowest in summer (14.28 ng/m³), with similar trends in Metro Kaohsiung. Diurnally, daytime levoglucosan concentrations exceeded nighttime (D/N ratio = 0.58–3.49), implying that the burning of agricultural debris is the major source of levoglucosan mostly occurred in the daytime.

As illustrated in **Figure 21**, the concentrations of organic acid (OA) in PM_{2.5} follow the seasonal trends similar to PM_{2.5} levels, with higher PM_{2.5} concentrations in Kaohsiung Harbor than those in Metro Kaohsiung. Seasonal M/S ratios, an indicator of SOA formation, are the highest in summer (1.17 ± 0.02 ng/m³) and the lowest in fall (1.05 ± 0.05 ng/m³), with M/S ratios in port areas slightly higher than those in urban areas. Annual averaged M/S ratios exceeding unity confirm the formation of SOA, driven by strong solar radiation and high air temperatures in summer. Diurnal variations show higher daytime M/S ratios, highlighting atmospheric photochemical reactions, which are major contributors to the potential formation of SOA.

Chemical Mass Balance (CMB) receptor model identifies 14 PM_{2.5} sources and their contributions in Kaohsiung Harbor and Metro Kaohsiung, varying seasonally and

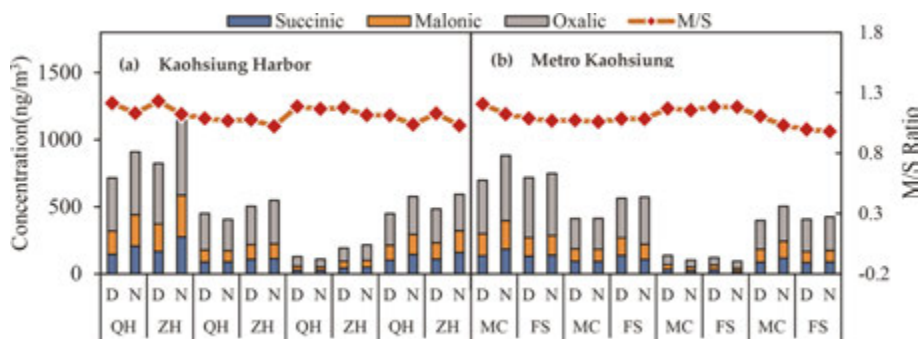


Figure 21. Spatiotemporal variation of organic acids in $PM_{2.5}$ at (a) the Kaohsiung Harbor and (b) the Metro Kaohsiung during the sampling periods.

diurnally (Tables 2 and 3). During the winter and spring seasons, secondary aerosols, mobile sources, and industrial emissions are dominant sources due to better atmospheric stability and worse vertical dispersion, while summer shows increased contributions from fugitive dust and ship emissions due to higher air temperatures and southwesterly monsoons. Ship emissions, sea salt spray, and heavy fuel oil burning are more prominent in the harbor areas, while Metro Kaohsiung is influenced by mobile sources, fugitive dust, and waste incinerators.

Daytime source contributions in Kaohsiung Harbor rank mobile sources and steel plants the highest, while steel plants dominate at nighttime, with similar patterns observed in Metro Kaohsiung. Seasonal trends reveal higher $PM_{2.5}$ contributions from ship emissions and secondary aerosols during winter and spring, while summer shows increased fugitive dust and sea salt spray. Urban areas are more affected by vehicular exhausts and industrial activities, whereas the harbor is influenced by maritime activities, highlighting distinct pollution dynamics between port and urban areas.

2.5 Model simulation for the interaction effects of $PM_{2.5}$ dispersion

In this section, a CALPUFF model is applied to simulate $PM_{2.5}$ dispersion in the region of Kaohsiung Harbor and Metro Kaohsiung under different meteorological conditions. Four cases covering winter, spring, summer, and fall highlight seasonal and diurnal variations in $PM_{2.5}$ contributions from the harbor to the urban area. During the winter and spring seasons, Asian Northeastern Monsoon (ANM) dominates the entire East Asia where is characterized by high humidity, low mixing layers, and weak wind speeds, which limited the dispersion of air pollutants. $PM_{2.5}$ emitted from main and auxiliary ship engines to Metro Kaohsiung account for 2.9–5.3% and 3.8–8.3%, respectively, with commonly higher $PM_{2.5}$ levels at Site MC located close to the port areas. During the summer and early fall seasons, both Southwestern Monsoons and sea-land breeze (SLB) enhance the transportation of air pollutants from offshore to inland, with the highest contributions in summer. Main engines contribute up to 6.60% at Site MC, while auxiliary engines reach 11.48%, driven by prolonged operation during berthing.

The meteorological analysis reveals that $PM_{2.5}$ dispersion is primarily influenced by monsoon patterns, with air pollutants transporting eastward to inland areas by weakening ANMs and/or intensified sea breezes. Daytime $PM_{2.5}$ concentrations during summer are lower due to strong solar radiation and thermal convection, while

Seasons			Incinerator	Petro chemical industry	Steel Plant	Oil- fired boilers	Coal- fired boilers	Fugitive Dusts	Diesel Vehicles	Gasoline Vehicles	Biomass Burning	Sea Salt Spray	Cement Industry	Shipping	Secondary Sulfate	Secondary Nitrate	Organic Carbon	Elemental Carbon	Others
Winter	QH	D	4.95	3.05	8.02	7.21	6.41	5.62	7.74	1.82	3.75	7.94	3.45	8.67	8.90	9.16	5.04	2.84	5.43
		N	7.30	4.85	8.97	5.34	6.88	6.84	5.15	6.77	3.46	7.17	3.42	7.25	8.26	7.28	4.16	3.24	3.67
	ZH	D	3.33	4.24	10.25	6.70	5.99	5.41	8.23	2.16	3.70	6.40	4.04	7.50	9.39	8.43	5.73	3.17	5.34
		N	5.14	5.27	13.81	6.15	6.23	6.24	7.65	1.76	1.95	6.17	3.26	6.12	9.80	8.50	5.78	2.72	3.45
Spring	QH	D	4.80	2.96	7.79	7.00	6.22	5.45	3.46	5.64	3.64	7.71	3.35	8.41	8.64	8.89	4.89	2.75	8.40
		N	7.16	4.75	8.80	5.24	6.75	6.71	8.87	2.58	3.39	7.03	3.35	7.11	8.10	7.13	4.07	3.17	5.79
	ZH	D	3.23	4.12	9.95	6.50	5.82	5.25	4.05	6.03	3.59	6.21	3.92	7.27	9.12	8.18	5.56	3.08	8.12
		N	5.04	5.17	13.54	6.03	6.11	6.12	7.54	1.69	1.91	6.05	3.20	6.00	9.61	8.33	5.67	2.66	5.35
Summer	QH	D	6.90	4.67	8.65	5.25	6.51	6.47	8.76	2.51	3.33	7.05	3.29	8.7	7.96	7.01	4.00	3.12	5.85
		N	4.86	2.99	7.87	7.21	6.29	5.51	3.63	5.75	3.68	7.95	3.39	7.1	8.73	8.99	4.94	2.78	8.29
	ZH	D	4.95	5.08	13.06	6.04	6.00	6.02	3.44	5.63	1.88	6.06	3.14	7.5	9.44	8.19	5.57	2.62	5.37
		N	3.26	4.16	10.05	6.70	5.88	5.31	8.12	2.08	3.63	6.41	3.97	6.0	9.22	8.27	5.62	3.11	8.20
Fall	QH	D	4.73	2.95	7.75	6.89	6.13	5.37	7.43	1.62	3.62	7.67	3.30	8.37	8.60	8.85	4.96	2.71	9.04
		N	7.12	4.68	8.76	5.21	6.71	6.67	4.84	6.56	3.49	7.00	3.34	7.22	8.34	7.10	4.05	3.16	5.75
	ZH	D	3.59	4.06	9.75	6.47	5.79	5.22	7.96	1.97	3.23	6.18	3.86	7.24	9.07	8.06	5.48	3.06	9.00
		N	5.01	5.14	13.43	6.00	6.02	6.03	7.51	1.67	1.88	5.96	3.18	5.91	9.47	8.29	5.64	2.65	6.20
Unit: %																			

Table 2.
Source apportionment of PM_{2.5} resolved by CMB receptor modeling in the Kaohsiung Harbor in four seasons.

Seasons			Incinerator	Petro chemical industry	Steel Plant	Oil-fired boilers	Coal-fired boilers	Fugitive Dusts	Diesel Vehicles	Gasoline Vehicles	Biomass Burning	Sea Salt Spray	Cement Industry	Ship Emissions	Secondary Sulfate	Secondary Nitrate	Organic Carbon	Elemental Carbon	Others
Winter	MC	D	4.61	3.85	7.47	4.92	5.96	4.53	11.39	4.26	4.27	5.05	4.90	5.30	8.89	9.91	4.47	3.42	6.77
		N	5.49	5.37	8.65	4.72	5.56	5.01	7.07	8.05	3.36	4.70	4.16	3.40	8.40	9.93	5.52	3.49	7.14
	FS	D	5.75	5.70	7.98	4.19	5.96	4.00	5.79	7.19	5.09	3.59	4.88	5.51	7.85	11.62	4.25	3.09	7.56
		N	5.80	5.58	8.72	4.46	6.04	3.69	11.72	4.48	4.58	5.69	4.11	3.52	7.08	11.69	3.84	2.47	6.54
Spring	MC	D	4.52	3.78	7.33	4.83	5.85	4.49	11.30	4.20	4.19	4.95	4.80	5.20	8.71	9.71	4.39	3.35	8.40
		N	5.49	5.37	8.65	4.72	5.56	5.06	7.16	8.11	3.36	4.70	4.16	3.40	8.40	9.93	5.52	3.49	6.94
	FS	D	5.75	5.70	7.98	4.19	5.96	4.04	9.86	3.24	5.09	3.59	4.88	5.51	7.85	11.62	4.25	3.09	7.39
		N	5.69	5.47	8.55	4.37	5.92	3.65	7.62	8.41	4.49	5.58	4.03	3.45	6.94	11.46	3.77	2.42	8.18
Summer	MC	D	5.08	4.98	8.01	4.93	5.85	4.45	7.22	8.14	4.19	5.05	4.81	5.3	8.72	9.72	4.39	3.36	5.79
		N	4.70	3.93	7.62	4.63	5.35	4.82	10.73	3.82	3.24	4.61	4.00	3.3	8.08	9.56	5.31	3.36	12.89
	FS	D	5.75	5.70	8.40	4.37	5.96	4.00	10.18	3.45	5.09	5.59	4.88	4.6	6.87	11.62	4.25	3.09	6.18
		N	5.69	5.48	8.13	4.36	5.93	3.62	5.94	7.29	4.50	3.74	4.04	3.5	6.95	11.47	3.77	2.42	13.18
Fall	MC	D	4.46	3.76	7.22	4.80	5.82	4.42	11.26	4.17	4.17	4.88	4.73	5.17	8.58	9.57	4.37	3.34	9.28
		N	5.46	5.29	8.61	4.65	5.53	5.03	7.03	8.02	3.35	4.63	4.14	3.35	8.36	9.88	5.43	3.44	7.81
	FS	D	5.67	5.67	7.86	4.17	5.87	4.02	9.83	3.22	5.02	3.58	4.81	5.49	7.74	11.45	4.18	3.07	8.36
		N	4.61	3.85	7.47	4.92	5.96	4.53	7.57	8.38	4.27	5.05	4.90	5.30	8.89	9.91	4.47	3.42	6.77
Unit: %																			

Table 3.
Source apportionment of $PM_{2.5}$ resolved by CMB receptor modeling in the Metro Kaohsiung in four seasons.

nighttime $PM_{2.5}$ levels increased as land breezes pushing air pollutants westward to offshore areas. Spatially, Site MC experiences higher impacts from harbor emissions compared to Site FS, highlighting the proximity effect of port activities. Harbor-originated emissions are relatively higher during summer, reaching a maximum contribution of 13.6%, with auxiliary engines contribution of 8.3%.

Comparison with other global seaports shows that the contribution of ship emissions in Kaohsiung Harbor (7.3–13.6%) is consistent with other seaports such as Hong Kong (17–25%) [49] and Barcelona (6–8%) [50]. Auxiliary engines are identified as a significant $PM_{2.5}$ source due to extended operation during berthing. To mitigate these impacts, implementing shore power systems (SPS) for all docks is highly recommended to replace auxiliary engine operations during berthing. This measure would significantly reduce $PM_{2.5}$ emissions, improving air quality in the port areas and adjacent urban areas (**Figures 22–25**).

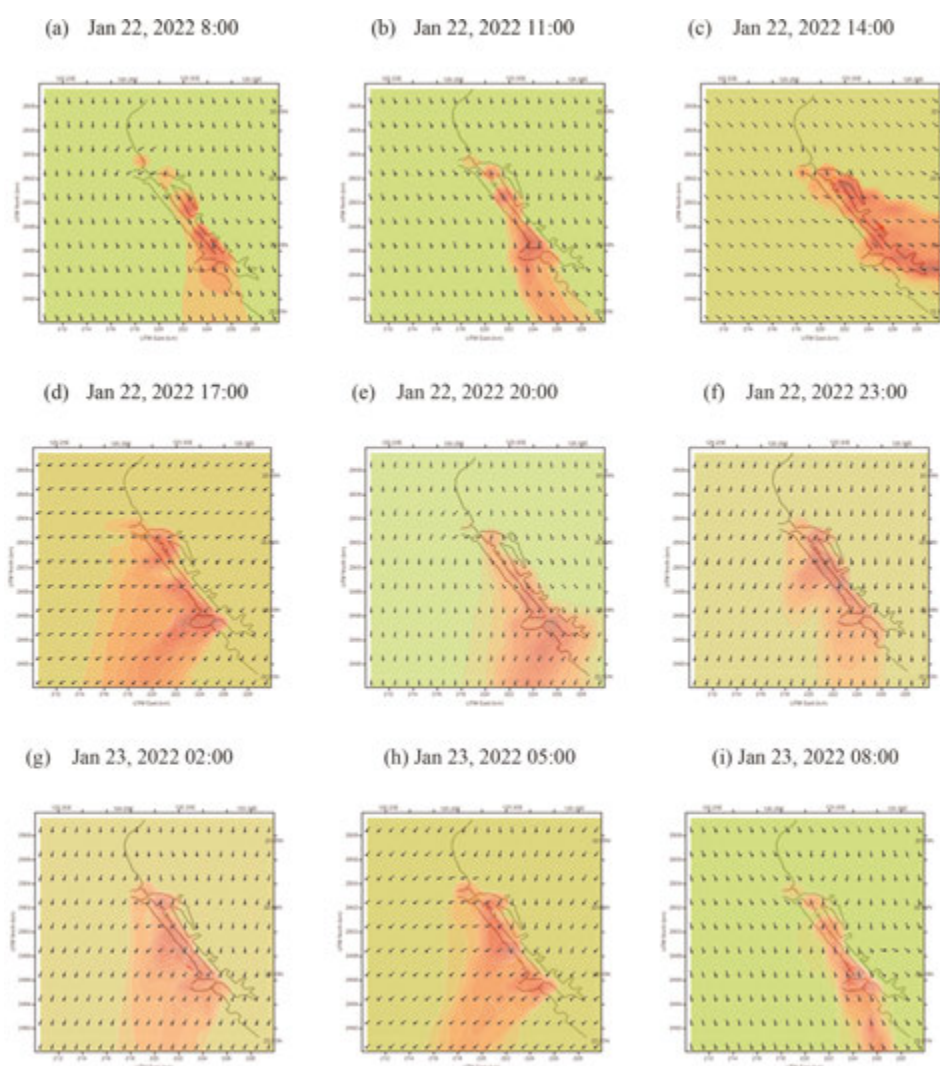


Figure 22.
 Pollution dispersion of $PM_{2.5}$ in the Kaohsiung Area on January 22–23, 2022.

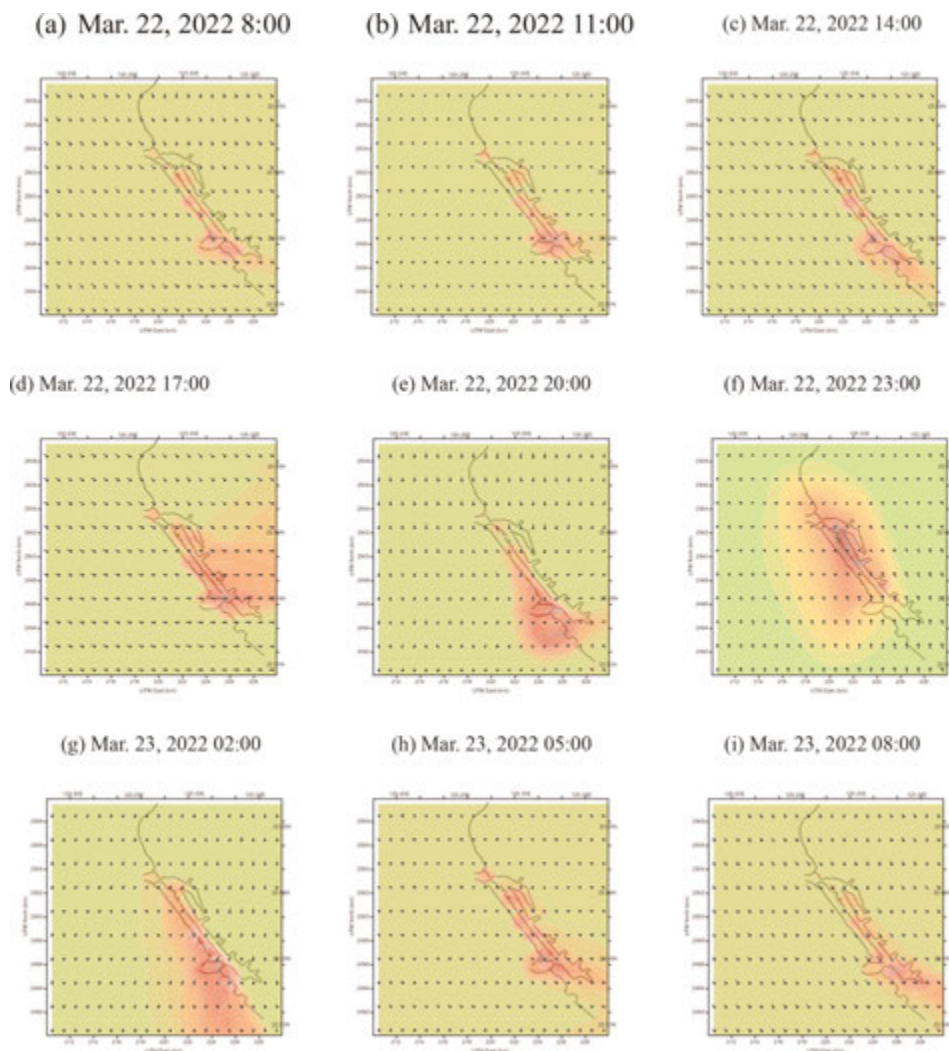


Figure 23.
Pollution dispersion of $PM_{2.5}$ in the Kaohsiung Area on March 22–23, 2022.

3. Conclusions

This study comprehensively explores the chemical fingerprints, spatiotemporal variation, and source apportionment of $PM_{2.5}$ in Kaohsiung Harbor and its potential impacts on the adjacent Metro Kaohsiung. The seasonal variation of $PM_{2.5}$ in the port areas is significantly influenced by topography and meteorology, with the highest $PM_{2.5}$ concentrations during winter, and followed by fall, spring, and summer. Poor atmospheric dispersion conditions during the periods of ANMs exacerbate the contributions of industrial emissions, secondary aerosols, and ship emissions, whereas oil-fired boilers and sea salt spray dominate $PM_{2.5}$ during late spring and summer seasons under Southwestern Monsoons. Moreover, diurnal variations show consistently higher $PM_{2.5}$ concentrations at nighttime during the winter, spring, and fall seasons, whereas a daytime peak was commonly observed during summer, resulting from sea-land breeze and enhanced thermal convection.

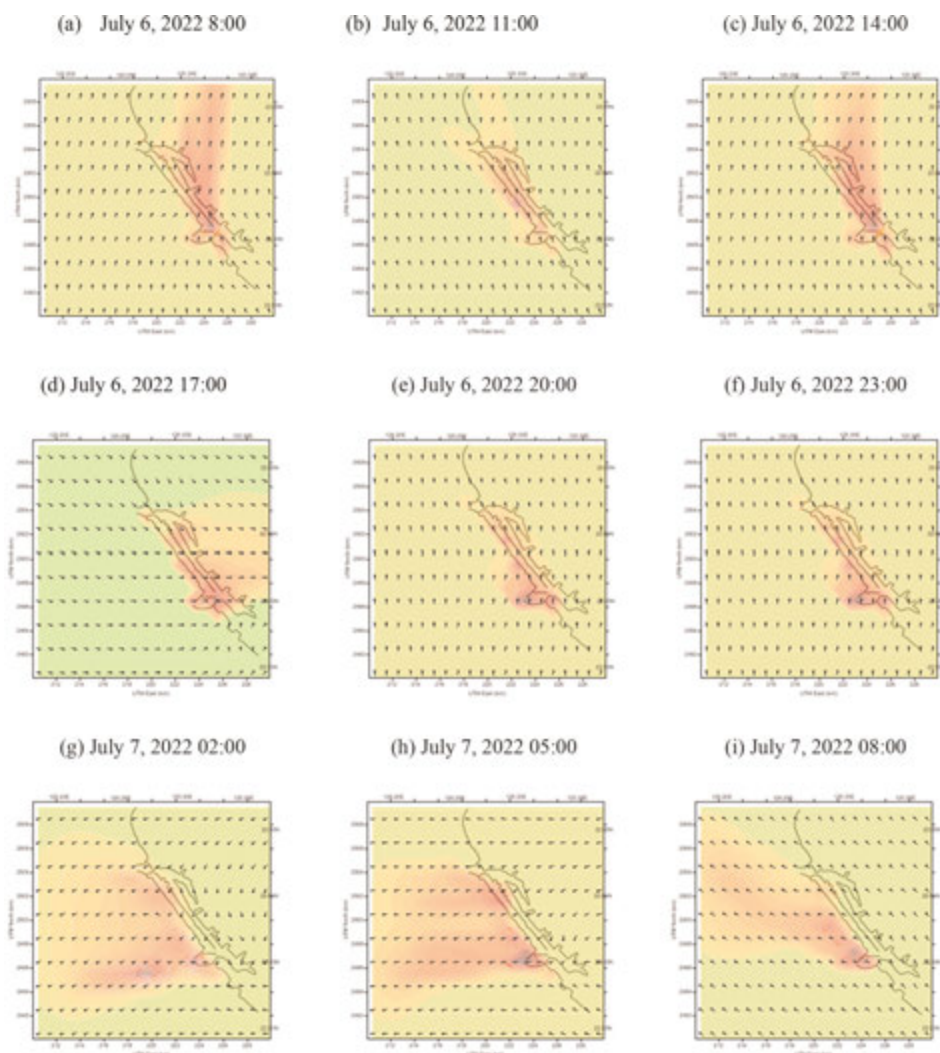


Figure 24.
 Pollution dispersion of PM_{2.5} in the Kaohsiung Area on July 6–7, 2022.

By chemical composition analysis with dispersion modeling, this study provided a more effective approach to clarifying the characteristics and contributions of ship emissions in the port area. Chemical characteristics of PM_{2.5} in Kaohsiung Harbor are dominated by WSIs, especially SIAs, and exhibit an acidic nature due to insufficient NH_4^+ to neutralize NO_3^- and non-sea salt SO_4^{2-} . Additionally, the port areas also show elevated crustal elements such as Mg, Al, Ca, Fe, and K, comprising 84.6–89.9% of the metallic elements, while enrichment factors (EFs) are observed for trace metals such as Ni, V, Cr, Zn, and Pb. Moreover, seasonal V/Ni ratios indicate ship emissions as the primary contributor, particularly during the summer season when auxiliary engines operate extensively. In contrast, primary PM_{2.5} from ship emissions accounts for 20.8% of PM_{2.5} during the spring and summer seasons, much higher than those during the winter and fall seasons. Furthermore, high OC/EC and SOC/OC ratios of PM_{2.5} during the fall and winter seasons indicate significant formation of SOA, driven

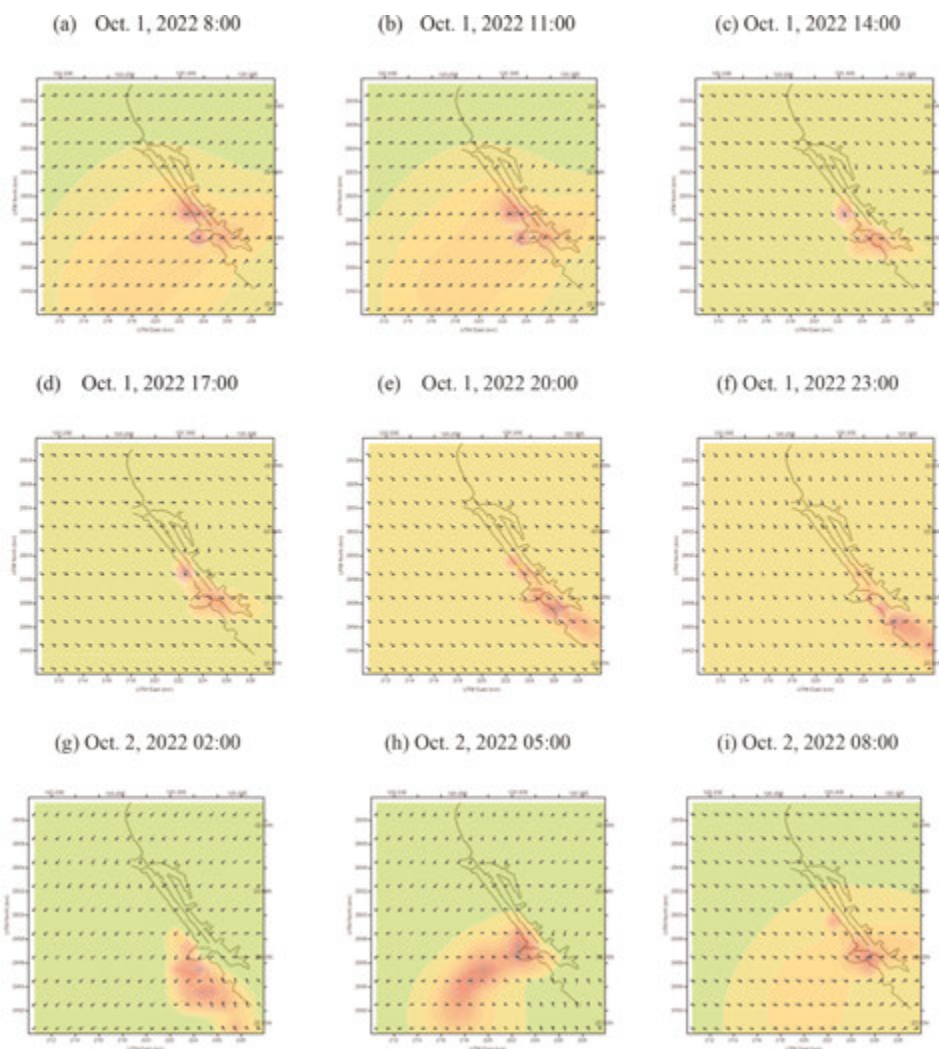


Figure 25.
Pollution dispersion of $PM_{2.5}$ in the Kaohsiung Area on October 1–2, 2022.

by atmospheric photochemical reactions, while moderate correlations between levoglucosan and K^+ suggest that wintertime biomass burning is one of the major $PM_{2.5}$ sources.

In Metro Kaohsiung, mobile sources play a dominant role in $PM_{2.5}$ concentrations, with concentrations closely correlated to those in Kaohsiung Harbor, indicating strong port-urban interactions. Higher concentrations of SO_4^{2-} than NO_3^- in the port area show the dominance of industrial emissions and ship exhausts, whereas mobile sources influenced the chemical composition of $PM_{2.5}$ in urban areas. The V/Ni ratios in the port areas exceed those in the urban areas, underlining the notable impacts of ship emissions on Kaohsiung Harbor and Metro Kaohsiung's air quality. SOAs originally blown from long-range transport during the winter and spring seasons contribute significantly to $PM_{2.5}$ in both areas, further compounded by higher atmospheric

stability and lower mixing layer heights. The wind wake effect from the Central Mountain Range inhibited the dispersion of air pollutants, intensifying PM_{2.5} accumulation.

The contributions of PM_{2.5} in Kaohsiung Harbor included secondary sulfates, heavy fuel oil boilers, and ship emissions. Main engines contribute 2.9–5.3%, while auxiliary engines contribute 3.8–8.3%, with higher contributions mainly attributed to longer operating times during berthing. The port areas experience more pronounced impacts from sea breeze in the afternoon, which transports air pollutants toward inland. In summer weather, characterized by few clouds, high solar radiation, and thermal convection, amplifies SLB effects, further increase maritime emissions' impact on Metro Kaohsiung.

The study identified critical policy recommendations to mitigate PM_{2.5} emissions in the Kaohsiung region. Firstly, stricter controls on auxiliary engine emissions are essential, given their extended operation and substantial contribution to the degradation of ambient air quality. Additionally, port management and traffic control should focus on reducing emissions from vehicles and ships. Moreover, promoting cleaner fuels, such as low-sulfur options, alongside alternative propulsion systems and shore power, can significantly reduce emissions. A comprehensive PM_{2.5} control strategy targeting both port and urban sources is required to address the region's unique pollution dynamics. Finally, international collaboration on reducing ship emissions globally is also vital for improving ambient air quality in the coastal regions.

By implementing the control strategies obtained from this study, Kaohsiung City can reduce its PM_{2.5} emissions, mitigate the impacts of port activities on urban air quality, and enhance environmental sustainability. Shore power systems (SPS) should be prioritized to replace auxiliary engine operations during berthing, significantly reducing emissions from maritime activities. These measures could not only improve particulate air quality in Kaohsiung Harbor and Metro Kaohsiung but also set a benchmark for other industrial port cities facing similar environmental challenges.

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Assessment of Air Pollution and Its Mitigation Potential Using Tolerant Plant Species in Rivers State, Nigeria

Patrick Amaibi, Emmanuel Iyor and Oladapo Akinfolarin

Abstract

The use of plant species to assess air pollutant levels from industrial and non-industrial areas in Rivers State has been investigated. The biochemical parameters (relative water content (RWC), leaf extract pH, total chlorophyll, and ascorbic acid) of six plant species growing within the study sites were collected and analysed to estimate the air pollution tolerance index (APTI) of each plant in two seasons (dry and wet). Air quality analyses were undertaken using hand-held equipment to measure the levels of PM_{2.5}, PM₁₀, VOCs, and other pollutants from the selected areas. Statistical correlation was conducted to find the relationship between APTI and the pollution source for both seasons. Based on the APTI values, there was a significant difference ($p < 0.05$) between the wet season and the dry season. The source apportionment indicates that the major air pollutants are PM_{2.5} and PM₁₀. These pollutants correlate strongly with the APTI values ($R = 0.9989$), suggesting that the air pollution is likely caused by particulate matter (PM_{2.5} and PM₁₀) from vehicular emissions. Since some plant species, such as mangoes, showed a relatively high tolerance response to air pollutants, they can be planted along roads within industrial areas to serve as a sink in the environment.

Keywords: particulate matter, air pollution tolerance index, biochemical parameters, air pollutant, seasonal variations

1. Introduction

Increased urbanisation and industrialisation have become a great concern due to their adverse impacts on human health and the environment. The growing urban population in recent times, along with air pollution, is considered to have drawn much attention in several studies [1, 2]. Air pollution is one of the major environmental problems confronting most developing and industrialised nations [3–6].

The release of air pollutants such as SO₂, VOCs, CO, particulate matter (PM), and heavy metals into the atmosphere affects the ambient air quality. These pollutants are usually monitored to ascertain the level of atmospheric pollution.

Hence, monitoring specific stations may not be sufficient to cover an entire area. To monitor a fixed location by a technological approach, a representation of the whole area can be expensive to implement [7], whereas, vegetation has been studied to provide a cost-effective and simpler method to monitor air quality across urban areas [8].

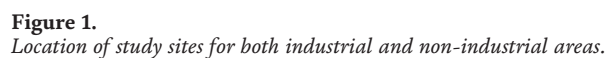
In recent studies, various parts of plant species, including tree bark, tree rings, and leaves, have been widely used as bioindicators of air pollutants [9–12]. Plants respond differently to air pollutants according to the locations in which they are found, most especially in densely populated urban and industrial areas [8, 13]. The plants growing at polluted sites have shown an overall effect of a mixture of pollutants on them [14, 15]. Plant leaves act as sinks, providing a large surface area for the deposition of pollutants [15]. Air pollutants can affect plant growth by altering the biochemical compositions, such as chlorophyll, pH of the leaf, ascorbic acid, and relative water content (RWC) [16]. These parameters provide the physiological and morphological characteristics of the plants and can be combined to estimate the air pollution tolerance index (APTI) of a particular species. The APTI helps to express and identify the ability of plants to resist the adverse conditions of air pollution. APTI can be categorised based on the sensitivity, intermediate tolerance, and tolerance of plant species towards air pollutants [17, 18]. However, studies suggest that using local plant species, the levels of air pollution can be assessed by their APTI values [19]. Although previous studies have used different parts of plant species, mostly conducted on leaves, the outcome remains unclear.

Therefore, it is important to prioritize the source of the pollutants in a given location. Source apportionment helps attribute air pollutants and their relative levels to various sectors (residential, industrial), activities (traffic, biomass burning), and climatic conditions (rainy, summer). This approach has been demonstrated to study several sources of pollutants [20]. Typically, the APTI determination not only provides information on air pollutants but also identifies their sources. As such, there is a need to adopt source identification of the pollutants using a hand-held air sensor system. An important part of this study was to assess the pollutant levels in the sampling areas and correlate them with the APTI values for each season in order to identify the causes of air pollution in a particular area. However, industrial areas with heavy traffic are expected to have particulate matter (PM₁₀ and PM_{2.5}) as the dominant pollutants responsible for atmospheric pollution [20]. Therefore, it is of interest to compare the APTI values from both industrial and non-industrial areas according to seasonal variations. Hence, the objective of this paper is to assess air pollution and its mitigation potential using tolerant plant species in Rivers State, Nigeria.

2. Materials and methods

2.1 Sampling and study sites

For a number of reasons, our study focused on industrial areas, whereas a non-industrial area was chosen as a control sample. The study areas selected are: Eleme Petrochemical (4°48'47.4"N and 7°05'48.9"E); Eleme Refinery (4°46'26.2"N and 7°06'24.6"E); Fertilizer (Notore) (4°44'01.2"N and 7°07'54.5"E); and Rivers State University (RSU) (4°48'06.6"N and 6°58'37.8"E) (**Figure 1**). In this investigation, the study led to the basis for comparison between the two sites — industrial and



non-industrial areas. However, we acknowledge that there may be other anthropogenic activities, such as construction work and, sometimes, high traffic movements, apart from industrial emissions, going on within the non-industrial site. Improving our understanding of the role different plant species play in acting as sinks and bioindicators of air pollutants will also allow urban planners and regulators to choose trees that can serve as green belts across highly polluted urban environments.

2.2 Biochemical parameters of plant species

All plant species [mango (*Mangifera indica*, family Anacardiaceae), guava (*Psidium guajava*, family Myrtaceae), papaya (*Carica papaya*, family Caricaceae), Siam weed (*Chromolaena odorata*, family Asteraceae), plantain (*Musa paradisiaca*, family Musaceae), and *Pennisetum pedicellatum* (family Poaceae)] collected for this study were commonly found within the four sampling locations. The selected species have different leaf textures, are widely grown, and were obtained 15 m away from the edge of the main roads. Fresh leaf samples were taken in triplicate ($n = 3$) from the six different plants, then immediately transferred to the laboratory for determination of biochemical parameters such as RWC, total chlorophyll, leaf extract pH, and ascorbic acid. All weight-based measurements (RWC, ascorbic acid) are reported on a fresh weight basis.

2.3 Relative water content (RWC)

Fresh leaf samples were collected in triplicate ($n = 3$) and weighed to determine the fresh weight (FW). Then, the leaf samples were weighed after being immersed in water overnight to obtain the weight of the turgid sample (TW). The blotted leaf samples were then placed in an oven to dry at 105°C for 2 hours and reweighed to obtain the dry weight (DW). The %RWC was calculated as expressed by Eq. (1) [21].

$$\%RWC = \frac{FW - DW}{TW - DW} \times 100 \quad (1)$$

where FW = fresh weight, DW = dry weight, TW = turgid weight.

2.4 Total chlorophyll

The absorbance of the leaf extract was measured at 650 nm using a DD-LAB 195–1,000 nm after instrument calibration against a reagent blank. Ten millilitres of acetone (80%) was added to a crushed leaf sample (5 g) and allowed for 15 minutes. After decanting using centrifuge at 2,500 rpm for 10 minutes, sample extract was subjected to spectrophotometer analysis to determine total chlorophyll, according to the procedure described by [22]. Measurements were performed in triplicate ($n = 3$).

2.5 pH of leaf extract

Aliquot of the crushed leaf sample (5 g) was homogenised in 50 ml of distilled water. The sample was filtered to obtain a suspension, in which the pH was measured using a pH meter (Extech PH100), in accordance with the method described elsewhere [23].

2.6 Ascorbic acid

A crushed leaf sample (1 g fresh weight) was placed in a test-tube and treated with 4 ml oxali-ethylenediaminetetraacetic acid, followed by the addition of 1 ml orthophosphoric acid, 1 ml sulphuric acid (5%), 2 ml ammonium molybdate (5%), and 3 ml distilled water to form the solution [24]. The sample solution was then allowed to stand for 15 minutes, and the absorbance was measured at 760 nm using

a spectrophotometer. The concentration of ascorbic acid present in each sample was extrapolated from the calibration curve. Each analysis was performed in triplicate (n = 3).

2.7 APTI calculation

The APTI values of the six plant species collected from four sampling sites were calculated based on biochemical parameters. The samples were taken during two seasons (dry and wet) to investigate the impact of climatic conditions on the dispersion of air pollutants around industrial and non-industrial vicinities. APTI for the studied plant species was calculated in triplicate (n = 3) according to the season, based on their parameters, including relative water content (R; %), total chlorophyll (T; mg/g), leaf-extract pH (P), and ascorbic acid (A; mg/g). The APTI was calculated using Eq. (2) [25].

$$APTI = \frac{A \times (T + P) + R}{10} \quad (2)$$

The APTI values were categorised into four groups (**Table 1**) [25].

2.8 Hand-held air analyser

In this study, the particulate matter (PM10 and PM2.5), including other air pollutants (CO₂, VOCs, NO₂, and SO₂), was measured using a hand-held air analyser (AEROCET 531S and Aeroqual Series 500, respectively). The data were collected between May and August, 2021 and December and February, 2022, representing the wet and dry seasons, respectively, and averaging the data obtained for PM10 PM2.5, and other pollutants for all sampling locations. Measurements were taken in triplicate (n = 3) at each site during each season.

2.9 Statistical analysis

A robust statistical test to evaluate the variation in the dataset was performed. The seasonal variation in terms of the APTI was analysed for significant difference by t-test using Microsoft Excel. The normality of the dataset was assessed using the Shapiro–Wilk test. Homogeneity of variances was confirmed using Levene’s test, confirming the suitability of parametric tests.

The APTI for each plant species was presented in a bar chart according to the season. A visual plot showing the air quality index from the sampling locations with respect to the season was illustrated using a bar chart.

APTI value	Evaluated response
>30	Tolerant
17–29	Intermediate
1–16	Sensitive
<1	Very sensitive

Table 1.
APTI categories based on plant biochemical parameters.

Furthermore, the relationship between APTI values and other air pollutants was assessed by Pearson's correlation analyses, which assumes a linear relationship and normal distribution of data. During the statistical analyses, the following packages were employed: Minitab version 18, Microsoft Excel, and GraphPad.

3. Results and discussion

3.1 Evaluation of APTI of selected plant species

APTI was derived from experimentally determined biochemical parameters using selected plant species collected from both industrial and non-industrial areas. The biochemical parameters and APTI for plant species from both industrial and non-industrial areas are presented in **Table 2**.

In all the studied plant species analysed according to seasonal variations for the APTI, the wet season was significantly higher ($p < 0.05$) than the dry season. The plants were more tolerant to weather conditions during the wet season. Plants collected from the non-industrial area showed a slightly lower APTI in all the seasons compared to that of the industrial areas. In the non-industrial area, the APTI ranged from 20.6 to 31.2, and the maximum was observed in mangos during the wet season. Meanwhile, the APTI values for each plant collected from the industrial areas showed an increase, ranging from 21.5 to 42.0, with the maximum value also found in mangos during the wet season. This finding aligns with studies in other urban environments, where mango has consistently been identified as a tolerant species suitable for green belt development [2, 26].

The APTI was estimated using four biochemical characteristics, such as RWC, chlorophyll, ascorbic acid, and pH, obtained from plant leaves. Plants with higher APTI have more tolerance, while plants with low APTI values are more sensitive, which can be used to predict the air quality within the areas.

The biochemical parameters showed RWC ranging from 49.4% to 100%, with the maximum value observed in guavas during the wet season.

Water content in plant leaves from the industrial areas was higher than that of the non-industrial areas.

High water content in plant leaves helps maintain their physiological balance when under stress conditions, such as severe exposure to air pollutants, in order to avoid total dryness. However, the maintenance of RWC by plants may suggest their relative tolerance level towards air pollution [27]; the higher the RWC in a plant leaf, the greater its tolerance capacity to drought.

Hence, the relatively high RWC in plant samples from the industrial area may be responsible for the normal functioning of the biological processes even in the presence of air pollutants [28]. The chlorophyll content, ranging from 9.90 to 17.03 mg/g, was found to be higher in the non-industrial area than in industrial areas during the two seasons (**Table 2**). The Siam weed obtained from the non-industrial area had the highest chlorophyll content among all the plant samples. Although the chlorophyll content varies amongst all the investigated plant species, it is an indication of the pollution status of the area as well as the age of the plant species [29]. It has been observed that the lower the pollution level, the higher the chlorophyll content, since certain pollutants can greatly affect the chlorophyll content in plants [26].

Plant species	Parameter	^a RSU		^b Petrochemical		^b Refinery		^b Fertilizer	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Siam weed	pH	5.9	8.2	5.5	5.6	5.5	5.6	5.6	5.6
	Chlorophyll	14.07	17.03	10.67	10.16	11.8	12.61	13.45	13.69
	RWC	49.37	83.98	52.31	93.46	50.19	90.89	48.67	86.65
	Ascorbic acid	7.84	6.12	10.3	10.72	10.06	9.94	8.86	8.2
	APTI	20.6	23.8	22.1	26.2	22.5	27.2	21.7	24.5
Guava	pH	5.8	6.7	5.5	5.6	5.6	5.7	5.7	5.8
	Chlorophyll	14.07	13.53	9.9	11.6	10.78	12.1	12.09	13.08
	RWC	52.05	90.52	65.52	101.11	58.82	98.77	54.65	93.99
	Ascorbic acid	8.38	7.66	11.44	11.26	10.96	10.48	9.7	8.14
	APTI	21.9	24.6	24.4	31.8	23.8	28.5	22.8	24.8
Papaya	pH	7.1	9.3	6.6	7	6.5	7	7	7.1
	Chlorophyll	14.07	12.85	9.96	12.29	9.2	12.31	12.36	12.49
	RWC	50.94	89.65	60.23	96.37	58.27	94.13	51.1	91.69
	Ascorbic acid	7.84	7.66	11.2	11.02	10.18	9.76	8.5	8.08
	APTI	21.7	23.3	24.6	30.9	22.4	28.3	21.5	25
Plantain	pH	7	9.8	6.7	7.1	6.3	7.6	7	8.1
	Chlorophyll	14.12	16.28	9.98	12.38	11.9	12.63	12.54	14.02
	RWC	52.03	86.3	62.7	94.65	56.83	96.84	52.47	91.53
	Ascorbic acid	8.68	8.44	12.87	11.5	11.74	11.2	10.36	10.12
	APTI	25.8	30.7	27.8	34.3	27	32.3	25.7	31.5
Poaceae	pH	6.4	7.7	5.9	6.2	6	6.1	6.1	6.2
	Chlorophyll	14.28	16.9	10.97	12.12	12.69	13.82	13.01	14.49
	RWC	47.95	86.48	52.13	88.08	49.13	87.73	47.44	84.75
	Ascorbic acid	7.66	7.78	12.99	11.08	11.62	11.44	10.54	10.06
	APTI	24.3	27.8	27.2	30.4	26.7	31.3	24.9	28.5
Mango	pH	5.8	6.3	5	5.2	5	5.2	5.5	5.9
	Chlorophyll	14.02	16.92	10.85	12.2	11.98	12.8	13.68	13.98
	RWC	60.84	98.8	81.71	124.35	66.83	109.43	61.49	99.51
	Ascorbic acid	10.52	9.16	14.43	14.31	13.47	12.99	11.62	11.18
	APTI	27	31.2	31.6	42	29.6	34.2	28.4	31.8

^aa (non-industrial area), ^bb (industrial areas).

Table 2.
 Biochemical parameters of plant species (n = 18) found around industrial and non-industrial areas.

The ascorbic acid in plant leaves acts as an antioxidant to help resist adverse environmental conditions. The results obtained from this study showed that the ascorbic acid content varied from 6.12 to 14.43 mg/g, with the highest

value exhibited by mangos, followed by Siam weed as the lowest. The ascorbic acid content in plant leaves from industrial areas was higher compared to those from non-industrial areas. Ascorbic acid, generally, is a stress-reducing factor expected to be higher in industrial areas in order to pose a high tolerance to air pollutants [30]. It was reported [28] that an increase in the pollution load causes a corresponding increase in the ascorbic acid content by increasing the rate of production of reactive oxygen species (ROS) during the photo-oxidation process in all plants.

The pH of the plant extract collected from both industrial and non-industrial areas varied from 5.0 to 9.0 during the wet and dry seasons. In the industrial areas, the pH observed was slightly acidic, while in the non-industrial areas, the pH tended to be slightly alkaline in nature. The acidic condition of the pH from the leaf extracts in the industrial areas may be caused by the release of SO₂, NO₂, and other acidic pollutants from industrial emissions into the ambient air. Plant species with good sensitivity to air pollution show low pH in their leaf extracts; this may reduce the photosynthesis process in the plant. When the observed pH is high, it indicates a good tolerance level against air pollution [31].

The APTI value from the industrial areas showed an increase when compared to that of the non-industrial area. These results indicate that plants found in the industrial areas are mostly exposed to higher pollution compared to those in the non-industrial area. Out of the six plant species studied, the results revealed that mangos had the highest APTI, and these findings are consistent with those reported previously for some tree species in an urban area [2]. From this study, it shows that the plant species collected from the industrial areas have the highest APTI, which can be used to reduce air pollution within the area, whereas the lowest APTI can be used as an indication to measure the level of air pollution. The wet season showed higher APTI values than the dry season in all the locations, as presented in **Figure 2**. The weather conditions may cause this during the wet season; rainfall cleanses particulate matter from the air and leaf surfaces, while higher humidity facilitates better plant physiological functioning and dilution of gaseous pollutants [26, 31].

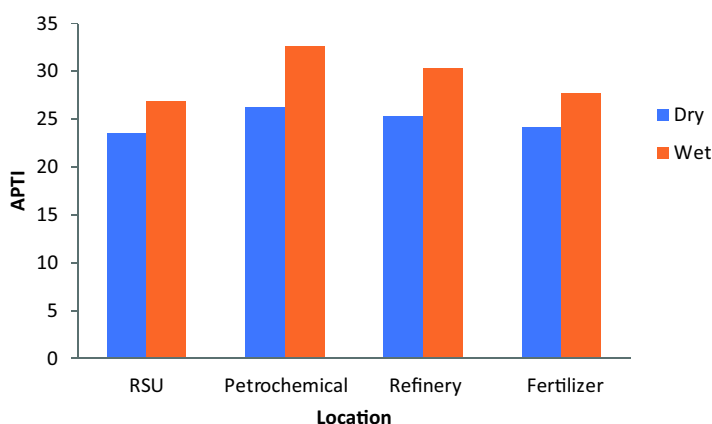


Figure 2.
Seasonal variations of APTI values across the study areas.

3.2 Correlation analysis between APTI and other pollutants

A Pearson correlation analysis was performed on the dataset obtained from the hand-held air analyser and the APTI data according to seasonal variations. **Table 3** presents the correlation analysis between APTI and the ambient air pollutants. During each of the seasons, the APTI strongly correlated with VOC, PM₁₀, PM_{2.5}, and CO₂ having the following correlation coefficient values (*r*): 0.914, 0.957, 0.950, and 0.968, respectively. Particulate matter from both PM₁₀ and PM_{2.5} appeared to be the major contributing factors in the determination of APTI. Although the APTI correlates more strongly with CO₂ (*r* = 0.968), the available plant species may not have been able to mop up the excess atmospheric CO₂ caused by population density, industrial emissions, and heavy vehicular traffic.

As expected, the results suggest that high APTI estimated within the industrial areas may be linked to anthropogenic activities. It is important to note that in the wet season, there is an increase in CO₂ due to dispersive wind, especially across the industrial areas. These results are consistent with previous studies conducted [32, 33] on air quality in an urban environment.

In the dry season, the APTI data correlate strongly with VOC (*R* = 0.990) and CO₂ (*R* = 0.955). Data obtained from the different seasons exhibited a stronger correlation between APTI and VOC, PM₁₀, PM_{2.5}, and CO₂ during the wet season as compared to the dry season. The difference in the results may be due to the weather conditions (low humidity and high temperature) observed during the dry season. Plant species may have low RWC, which is not sufficient enough to dissolve the ambient air pollutants for plant leaf uptake.

APTI data from the wet season was found to be higher than that of the dry season, as observed in **Table 2**. From the correlation analysis, the results showed that there are four major factors (VOC, PM₁₀, PM_{2.5}, and CO₂) that correlate strongly with the APTI dataset in the wet season, whereas only two major air pollutants (VOC and CO₂) have a stronger correlation with APTI in the dry season when conducted separately. These major pollutants may not only be released from

APTI	VOC	PM ₁₀	PM _{2.5}	CH ₄	H ₂ S	O ₃	NO ₂	CO ₂	
APTI	1								
VOC	0.914	1							
PM ₁₀	0.957 [*]	0.759	1						
PM _{2.5}	0.950	0.744	0.992 ^{**}	1					
CH ₄	0.639	0.645	0.611	0.510	1				
H ₂ S	^b	^b	^b	^b	^b				
O ₃	-0.030	0.157	-0.107	-0.226	0.721	^b	1		
NO ₂	-0.412	-0.024	-0.627	-0.676	0.071	^b	0.647	1	
CO ₂	0.968 [*]	0.934	0.879	0.897	0.471	^b	-0.169	-0.352	1

*Significant correlation (*p* < 0.05); **Highly significant correlation (*p* < 0.01); ^bValue could not be determined/calculated due to lack of variance.

Table 3.
Correlation between APTI and air indicators (VOC, PM₁₀, PM_{2.5}, H₂S, CH₄, O₃, and NO₂) across study areas.

industrial activities but can also be derived from other diffuse sources, including unpaved roads, construction activities, and heavy vehicular movements. The results revealed that particulate matter (PM₁₀ and PM_{2.5}) also correlates strongly in both seasons, and these findings correspond to those observed for the assessment of particulate air pollution in Romania by [33].

Although no significant difference was observed between PM₁₀ and PM_{2.5}, PM₁₀ was higher than PM_{2.5} in both seasons, whereas the highest levels were recorded during the dry season due to drought in the atmosphere. Further studies need to be considered to assess the air quality index from the particulate matter data set obtained using the portable sensor system.

4. Conclusion

This present study showed the APTI values of six plant species determined using the biochemical parameters such as RWC, chlorophyll, ascorbic acid, and pH of the leaf extract. The results revealed that the seasonal variation of plants' response to air pollutants may be caused by geographical and environmental conditions. In the industrial areas, the plant species collected for this study exhibited a higher APTI compared to those found in the non-industrial area, indicating their adaptation to chronic pollution stress. Out of the six plant species, the APTI values can be arranged in the order of Siam weed < papaya leaf < Poaceae < guava leaf < plantain leaf < mango leaf.

A strong correlation between the APTI and particulate matter (PM₁₀ and PM_{2.5}) further suggests that different plant species can respond differently to air pollutants. The identification of mango and plantain as highly tolerant species provides a clear practical implication for urban planning: these species are recommended for planting as green belts along roadsides and within industrial estates in Rivers State, Nigeria, to mitigate particulate pollution. Conversely, sensitive species like Siam weed could serve as effective bioindicators for monitoring air quality. Hence, air pollution management should be practiced in all designated industrial areas, incorporating phytoremediation strategies using tolerant native species. Future studies should focus on long-term monitoring of these species' health and their specific particulate matter (PM) deposition capacities to optimize green space planning.

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Perspective Chapter: Exploring Ultrafine Particle Emission Sources and Predictions – Recent Case Studies from South Asian Urban Areas in Taiwan

Tse-Lun Chen, Ta-Chih Hsiao, Tzu-Chi Lin and Po-Kai Chang

Abstract

This chapter investigates the emission sources and characteristics of ultrafine particles (UFPs) in Taiwan's metropolitan areas, as well as their potential health risks. The research team established mobile air quality monitoring stations in Taipei, New Taipei, and Taichung, employing advanced instruments to collect data on UFP size distribution, chemical composition, and meteorological conditions. The findings show the UFP emissions in urban areas, revealing that traffic is the primary source. Due to complex meteorological conditions and high vehicle density, monitoring airborne UFPs is particularly challenging and necessary in subtropical, traffic-heavy cities like those in Taiwan. Understanding the characteristics of UFPs from various emission sources is essential for formulating effective air pollution control strategies. Additionally, lung-deposited surface area (LDSA) concentrations can be utilized to assess health risks associated with UFPs, contributing to the development of more precise air quality management policies. The research should focus on the chemical composition of various UFP sources for a comprehensive health risk assessment, as well as the development of accurate UFP monitoring and prediction models, potentially using machine learning techniques. Effective traffic management and emission control strategies are necessary to abate UFP emissions and their impact on public health. Overall, this chapter provides critical information on the sources, characteristics, and health risk assessments of UFPs in Taiwan's metropolitan areas, serving as a reference for formulating air pollution prevention policies and protecting public health.

Keywords: ultrafine particles, particle size number distribution, urban traffic area, source apportionment, lung-deposited surface area, tree-based machine learning model

1. Introduction

Inhaling airborne particulate pollutants is linked to health threats, mainly including respiratory diseases [1–3]. Current global air quality standards for particulate matter (PM) focus on mass concentration ($\mu\text{g}/\text{m}^3$), often overlooking the impact of

submicron ($PM_{1.0}$) and ultrafine particles (UFPs, $<0.1\ \mu m$ in aerodynamic diameter) [4, 5]. Research indicates that increased exposure to UFP concentrations may enhance the risk of respiratory illnesses [6–8], cardiovascular diseases [9, 10], and neurological disorders [11]. The World Health Organization (WHO) recognizes the importance of UFPs in its air quality guidelines, emphasizing health impacts, environmental effects, real-time and long-term measurement, control strategies, and epidemiological assessment [12].

The particle size is crucial for their dynamic behavior in the atmospheric environment and the human respiratory system. Smaller particles can remain airborne longer and travel further distances [13, 14]. Health risks from particles are more closely linked to the amount deposited in the lungs rather than the ambient concentrations [15, 16]. Results from lung deposition show that UFPs smaller than 10 nm tend to deposit in the head and nose rather than reaching the alveolar region. Therefore, understanding particle number size distribution (PNSD) is crucial for assessing health risks and identifying emission sources, especially for UFPs [17–19]. UFPs can penetrate the bloodstream and accumulate in the brain *via* the olfactory route, posing risks because their large surface area can carry toxic substances [20–22]. This raises concerns about their potential link to neurodegenerative diseases [23–27]. While this study does not cover these aspects, PNSDs are considered important climate monitoring parameters within the Global Climate Observing System [28].

Traffic emissions are a significant source of UFPs, accounting for about half of the urban particle number concentration (PNC) [23, 29]. PNSDs with peaks in the nucleation mode ($<20\ nm$) and Aitken mode (20–100 nm) indicate traffic-related pollution [24–27]. However, UFPs also originate from sources such as cooking, industry, and secondary formation [30–32]. Therefore, health risks from UFP exposure should not be solely attributed to traffic emissions. Understanding the sources, characteristics, and health risks of UFPs is essential for policymakers. In this chapter, we present recent case studies of UFP measurements at three urban sites in Taiwan to explore the characteristics, source analysis, health risks, and prediction of UFP emissions.

2. Methodology

2.1 Site description

This research involved setting up a specialized air quality monitoring station within an air-conditioned trailer, named the Integrated Measurement of Pollution and Aerosol Composition & Transformation (IMPACT), across three distinct locations and campaigns. As illustrated in **Figure 1a**, the first monitoring site was situated in the northeastern part of the National Taiwan University campus in Taipei (25.2°N, 121.54°E), next to a major north-south traffic corridor that sees approximately 90,000 vehicles daily in the heart of Taipei. Data collection at this site took place from December 2019 to November 2020, with a specific focus on the COVID-19 third alert period from April to August 2021.

The second measurement site was positioned at an intersection in New Taipei City (24.6°N, 121.29°E), as shown in **Figure 1b**. The station is located 5 and 80 meters south of a major traffic route and an elevated expressway, respectively, with a national highway 500 meters to the southwest, handling around 85,700 vehicles each



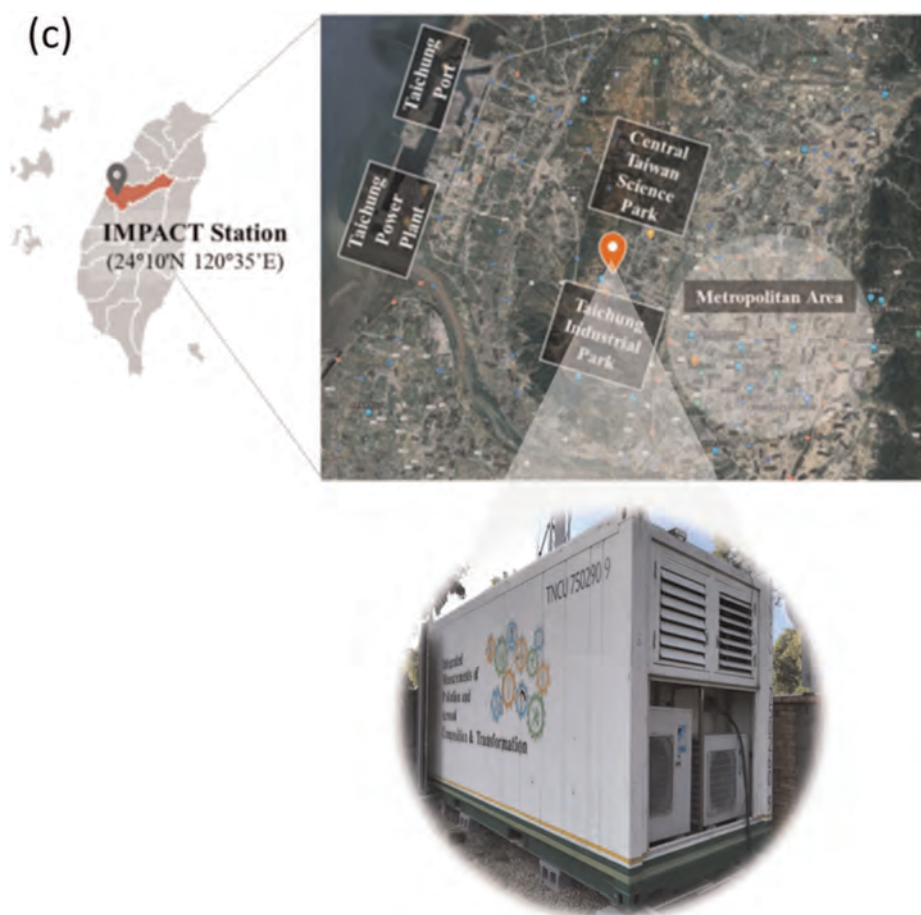


Figure 1.

Geological site of IMPACT air quality station in (a) Taipei (adopted from [34]), (b) New Taipei city (adopted from [33]), and (c) Taichung.

day. This campaign study was conducted from November 2016 to June 2017, during which a notable decline in traffic flow was observed on weekends, especially in motorcycle traffic, leading to nearly a 50% drop during peak hours [33]. Additionally, traffic volume was assessed using the You Only Look Once (YOLO) model, with video recordings captured at city measurement sites in Taipei and New Taipei [33, 34].

The third site was located at Tunghai University in Taichung, Taiwan (24.1°N, 120.35°E), as shown in **Figure 1c**, where measurements were taken from August 2020 to September 2021. This urban area is characterized by a high population density and substantial vehicular traffic, nestled in a basin and flanked by the mountains to the west, which rise to about 300 meters, and the central mountain range to the east. The urban center of Taichung faces significant air quality issues due to nearby pollution sources, including a coal-fired power plant and various industrial zones.

2.2 Instrumentations

The key instruments used in the IMPACT trailer are detailed in **Table 1**. $PM_{1.0}$ mass concentrations were continuously monitored with a Tapered Element Oscillating

Measurement	Instrument (model)	Time resolution	Unit
PM ₁	Tapered Element Oscillating Microbalance (TEOM, Thermo Fisher Scientific, 1405-F)	6 min	µg/m ³
BC	Seven-wavelength dual-spot Aethalometer (AE33, Magee, Scientific)	1 min	ng/m ³
PNSD (11.8–593.5 nm)	Scanning Mobility Particle Sizer (SMPS Model 3936, TSI Corp.)	6 min	#/cm ³
PNC (#/cm ³)	Differential mobility analyzer (DMA, Model 3081, TSI Corp.)		
GMD (nm)	Condensation particle counter (CPC, Model 3772, TSI Corp.)		
PNSD (626 ~ 19,810 nm)	Aerodynamic particle sizer (APS, Model 3321, TSI Corp.)	6 min	#/cm ³
PNC (#/cm ³)			
LDSA	Nanoparticle surface area monitor (NSAM, Model 3550; TSI Corp.)	5 min	µm ² /cm ³

Table 1.
Specifications of instrumentations in IMAPCT air quality station at three different measurement sites.

Microbalance (TEOM, R&P 1405-F, Thermo Scientific™), while black carbon (BC) levels were tracked using a seven-wavelength Aethalometer (Model AE33, Magee Scientific, Berkeley, CA, USA). Particle sizes from 11.8 to 593.5 nm and 0.52 to 19.81 µm were measured every 6 minutes using a scanning mobility particle sizer (SMPS, Model 3936, TSI Corp.) and an aerodynamic particle sizer (APS, Model 3321, TSI Corp.), respectively. The SMPS includes a long differential mobility analyzer (DMA, Model 3081, TSI Corp.) and a condensation particle counter (CPC, Model 3772, TSI Corp.). The PNSD from the SMPS and APS was categorized into four size ranges: (a) nucleation mode (11.8–25 nm), (b) Aitken mode (25–100 nm), (c) accumulation mode (100–593.5 nm), and (d) coarse mode (600–2500 nm). Combining data from the APS and SMPS provides a comprehensive view of the dynamic evolution of aerosol size distribution, although merging aerodynamic and electrical diameters is challenging. We established a custom Python code to combine PNSD data using a method from the literature [35]. Both instruments were calibrated with certified polystyrene latex (PSL) particles before deployment. Additionally, a nanoparticle surface area monitor (NSAM, Model 3550; TSI Corp.) was used to assess the lung-deposited surface area (LDSA) concentration in the alveolar region at measurement sites in Taipei and New Taipei City. For more information on additional monitoring parameters—such as meteorological factors (ambient temperature, relative humidity, wind speed, and wind direction), water-soluble inorganic ions, metals, and trace gaseous pollutants—please refer to our previous study [5, 33, 36].

3. Source-oriented health risk assessment of UFPs

3.1 PMF model with PNSD input

In this research, the US EPA PMF 5.0 model was utilized to apportion sources, integrating data from both SMPS and APS within the size range of 11–2.5 µm. The data were averaged dynamically at a one-hour interval, employing a t-test for variance

analysis to eliminate outlier values exceeding the 95% confidence interval, thus ensuring a normal distribution. Visualizations of the PNSD profile, time series, and wind rose diagrams were created. As expressed in Eq. (1), it is proposed that p factors influence the receptor through a linear combination of a broad array of variables:

$$x_{i,j} = \sum_{k=1}^p g_{i,k} \cdot f_{k,j} + e_{i,j} \quad (1)$$

where $x_{i,j}$ refers to the measured concentration or size bins of species j at time i , $g_{i,k}$ indicates the contribution of the k_{th} factor to the receptor at that time, $f_{k,j}$ represents the concentration or fraction of the k_{th} factor contributing to species j , and $e_{i,j}$ is the residual for species j at time i . According to guidance from the U.S. EPA PMF 5.0 user manual, the residuals are expected to be within ± 3 . The known values of $x_{i,j}$ are used within the PMF framework to estimate contributions $g_{i,k}$ and fractions $f_{k,j}$. The optimal solution is determined by evaluating the residuals and the objective function Q , as described in Eq. (2) [23]:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{e_{ij}}{u_{ij}} \right]^2 \quad (2)$$

In this context, Q serves as a measure of goodness-of-fit for the PMF outcomes, while u_{ij} denotes the uncertainty associated with the i_{th} sample of the j_{th} species. The uncertainties (u_{ij}) in PNSD-PMF are determined using Eqs. (3) and (4):

$$\sigma_{i,j} = \begin{cases} \alpha(N_{i,j} + \bar{N}_j) & N_{i,j} > 0 \\ 2\bar{N}_j & N_{i,j} = 0 \end{cases} \quad (3)$$

$$u_{ij} = \sigma_{i,j} + \beta \times N_{i,j} \quad (4)$$

In these equations, $\sigma_{i,j}$ represents the error for the j_{th} size bin at time i , $N_{i,j}$ is the pPNC for the j_{th} size bin and i_{th} time, $\bar{N}_j$ is the arithmetic average for the j_{th} size bin, α is a constant set at 0.01, and β varies between 0.01 and 0.5, adjusted based on the distribution of scaled residuals and the ratio of uncertainty to concentration [37]. To ensure accurate source identification, a hybrid approach integrating the PMF model for both PNSD and PM_{2.5} chemical compositions has proven effective in interpreting relevant factors. We conducted separate source apportionments for PNSD and PM_{2.5} chemical compositions and compared their statistical properties to identify the specific chemical fingerprints for each aerosol size mode. This hybrid PMF strategy is particularly beneficial for UFPs, as traditional PMF models that rely solely on PM_{2.5} chemical compositions may not adequately capture sources based on chemical fingerprints [38, 39]. We reported the following cases in coupling physical and chemical source profiles allows for the extraction of detailed information, such as the potential abundance of specific chemical species within certain size ranges.

3.2 Interpretation of PNSD-PMF profiles

Figure 2 illustrates the PNSD-PMF profile from the IMPACT study in the Taipei case during winter time. This profile reflects various factors, including sources influencing the measurement site, daily patterns, and the relationships between PNSD and air pollutants, chemical compositions, and meteorological conditions. Factor 1 is

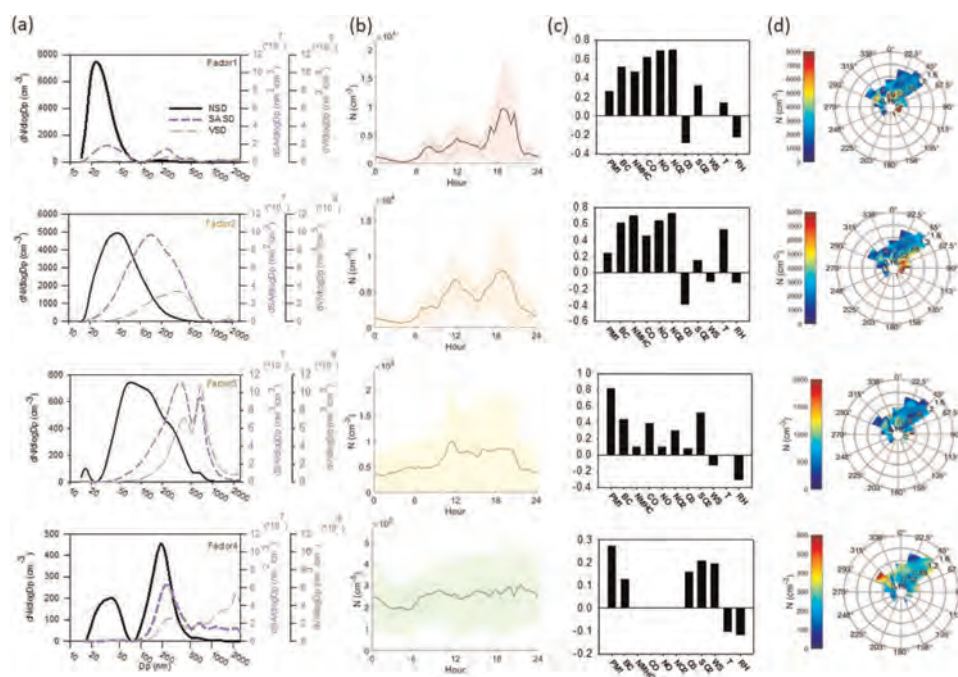


Figure 2. Four PMF factor profiles of (a) PNSD (black solid line), surface area size distribution (blue dashed line), volume size distribution (gray dashed line), (b) diurnal patterns (the shaded area represents the range of standard deviation), (c) the histogram of Spearman correlation coefficients for auxiliary variables (only statistically significant coefficients are shown), and (d) the wind rose diagram with factor concentrations at Taipei IMPACT air quality station (adopted from [36]).

identified by peaking in the range of 25–30 nm, displaying a distinct diurnal pattern with peaks in the early morning, around noon time, and in the late afternoon. Medium-high Spearman correlations are noted for Factor 1 (F1-P) with traffic emission indicators such as CO ($r = 0.62$, $p < 0.01$) and NO_x ($r = 0.73$, $p < 0.001$). Additionally, significant correlations were observed with vehicle counts, including cars ($r = 0.69$, $p < 0.01$), motorbikes ($r = 0.63$, $p < 0.01$), and buses/trucks ($r = 0.60$, $p < 0.01$). The polar plot shows PNC levels reaching up to 8000 cm^{-3} from the east wind direction, along with low wind speeds ($WS < 0.3 \text{ m s}^{-1}$), which align closely with traffic flow on major roads. Similar PNSD patterns have been reported in studies from a UK highway, London's international airport, and a major traffic route in Beijing, suggesting emissions from “fresh road traffic” [29, 39, 40].

Factor 2 exhibits a diurnal pattern similar to Factor 1, with high values during peak traffic hours and pronounced peaks at noon. This factor shows significant correlations with traffic-related air pollutants (TRAPs) and traffic volume, indicating its association with traffic emissions. Compared to Factor 1, Factor 2's PNSD profile is broader, with its peak shifting to a larger size range of 45–50 nm. Factor 2 reaches its peak concentration at noon and shows a medium correlation with temperature ($r = 0.52$, $p < 0.05$). High temperatures combined with low relative humidity may enhance secondary aerosol formation through photochemical reactions, similar to patterns observed in Singapore from aged traffic emissions [23, 41].

Factor 3 accounts for a significant portion of total surface area and volume concentrations. The wind rose plot shows no significant variations in PNC, with a plateau

level in the afternoon. High correlations exist between Factor 3 and $PM_{1.0}$ ($r = 0.82$, $p < 0.001$) and coarse particles ($r = 0.93$, $p < 0.001$). A robust linear relationship with secondary aerosol species, including sulfate (SO_4^{2-}), ammonium (NH_4^+), and nitrate (NO_3^-), indicates this factor primarily represents “secondary aerosol.” Factor 4 displays bimodal peaks in the PNSD profile at 40 and 200 nm. No significant correlations were found between Factor 4 and other TRAPs ($p > 0.05$). PNC remains stable throughout the day, with higher concentrations associated with increased wind speeds, suggesting Factor 4 represents “urban background and/or regional transport” [23, 29, 37, 39].

The second case of PNSD-PMF analysis took place in the trailer in New Taipei. This analysis utilized PNSD profiles and conditional probability (CPF) results to interpret various factors. As illustrated in **Figure 3**, factor 1 emerged as the primary

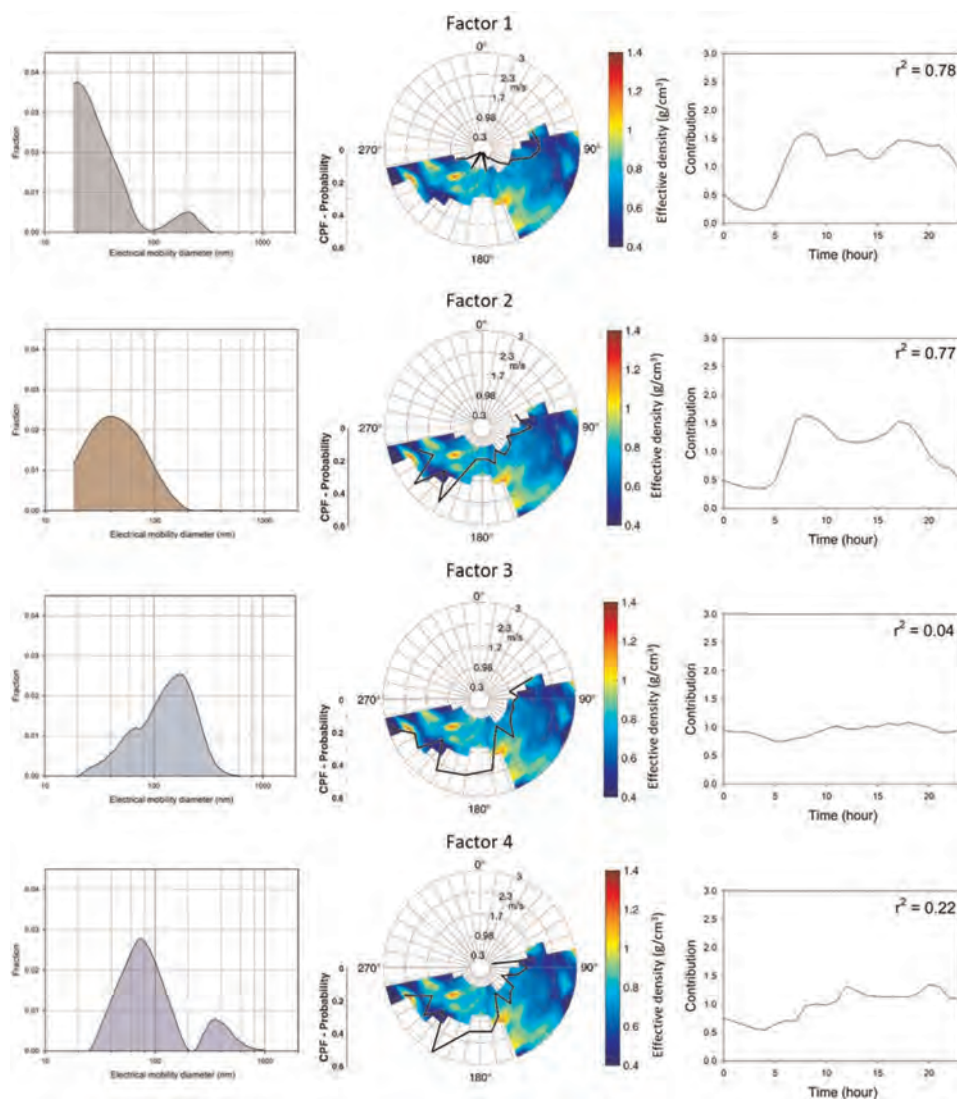


Figure 3. Factor profiles resolved from PSDs using PMF (left) and the CPF plots of each factor (black line) combined with the effective density (right) at the New Taipei IMPACT air quality station (adopted from [33]).

contributor to PNC in the nucleation range, peaking at 20 nm. This finding aligns with previous studies that have associated similar particle size distributions with road traffic [42]. The CPF analysis suggested that factor 1's source was located at the east of the measurement site, near a highway intersection, correlating with particles of low effective density, indicative of fresh traffic emissions. Established research indicates a strong correlation between BC and traffic emissions, with peaks typically occurring during morning and evening rush hours [43]. The correlation coefficient (r^2) between the diurnal patterns of factor 1 contributions and traffic flow exceeded 0.78, classifying this factor as representative of fresh traffic pollution.

Factor 2 was characterized by UFPs within the size range of 18–100 nm, with a modal peak at 40 nm, merely larger than that of factor 1. The CPF analysis revealed elevated probabilities for wind directions between 210 and 260°, linked with particles of higher effective density. The diurnal contribution pattern for this factor closely mirrored traffic flow, showing increased concentrations during peak traffic hours. The average concentration of BC from the southwest cluster was notable in the morning. This area, adjacent to national highways and a recreational park, suggests that traffic-related pollutants may mix with VOCs from biogenic sources, leading to a partially aged air mass at the measurement site. These findings indicate a link between this factor and aged traffic emissions.

Factor 3 showed a single mode at 175 nm. Particles smaller than 100 nm generally have short lifetimes due to rapid coagulation and condensational growth, while particles larger than 1000 nm are quickly removed by gravitational settling [44]. As a result, regional transport aerosols primarily consist of accumulation mode particles, peaking around 100–200 nm [45]. The diurnal contribution pattern for factor 3 showed minimal variation, suggesting it was less influenced by urban activities, thus classifying it as representative of urban background levels. Factor 4 demonstrated dual peaks at 74 and 359 nm. Cooking emissions typically show an unimodal size distribution, peaking between 20 and 70 nm [45].

The CPF analysis indicated that factor 4 was mainly associated with winds from the southeast. The patterns of BC in this cluster were consistent, with increased concentrations during daily meal times. Research shows that organic aerosols from cooking can lead to significant concentration spikes around lunchtime and in the evening [46]. Therefore, the initial peak for factor 4 is likely due to cooking emissions, while the secondary peak can be ascribed to secondary aerosols. Thus, factor 4 represents a mixing of cooking emissions and secondary aerosol.

The third case of the PNSD-PMF profile from the Tunghai IMPACT air quality station identifies five resolved factors, detailed in **Figure 4**. Factor 1 primarily encompasses nucleation mode particles and Aitken mode particles. It contributes significantly to number concentration (47.8%) but minimally to volume (1.9%) and surface area concentrations (7.0%). Diurnal trends show a pronounced peak during morning and evening commuting hours. Correlation analysis reveals a strong association with TRAPs (NO, NO₂, CO, and BC). The measurement site's proximity to the east-west Taiwan Boulevard, coupled with wind rose data, indicates that Factor 1 represents “fresh traffic emissions,” especially under moderate to low northwest winds.

Factor 2 also includes nucleation and Aitken mode particles, peaking at 20–30 nm and 105–300 nm. Its contributions to volume and surface area are 6.7 and 16.1%, respectively. Similar to Factor 1, it peaks during commuting hours but has a lower overall concentration. A wind rose analysis suggests that northeast winds may transport particles from nearby traffic.

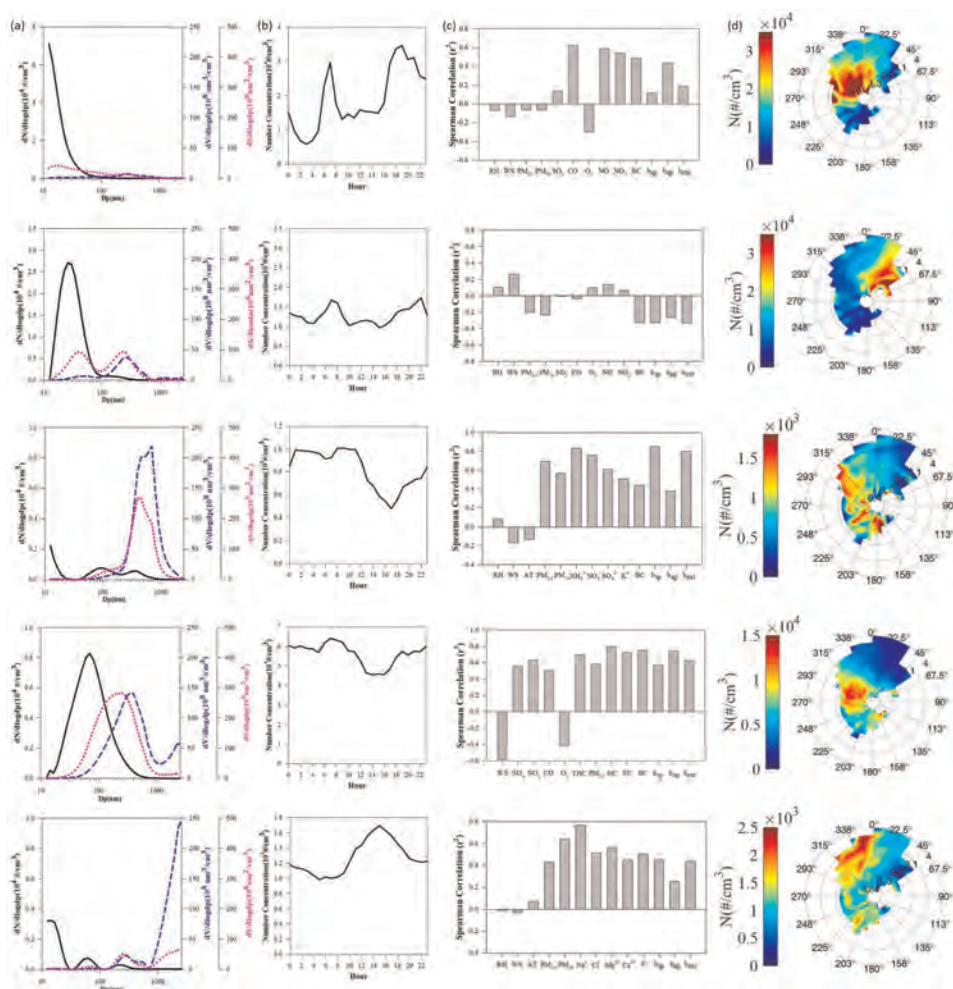


Figure 4.

Five PMF factor profiles of (a) PNSD (black solid line), surface area size distribution (purple dashed line), and volume size distribution (blue dashed line), (b) diurnal patterns of contribution of number concentrations, (c) the histogram of Spearman correlation coefficients for auxiliary variables (only statistically significant coefficients are shown), and (d) the wind rose diagram with factor concentration at Tunghai IMPACT air quality station.

Factor 3, representing secondary aerosols, contributes 2.2% to number concentration but significantly impacts volume (32.1%) and surface area (23.9%) concentrations, peaking at 300–700 nm. It shows higher concentrations at night and early morning, correlating moderately to highly with $PM_{2.5}$, PM_{10} , NH_4^+ , NO_3^- , and SO_4^{2-} . This suggests that nighttime increases may be linked to secondary inorganic aerosol formation. Wind rose data indicates elevated concentrations during higher northwest winds and moderate southwest winds.

Factor 4, associated with combustion-related pollution, features a broad particle size distribution with a primary peak from 20 to 600 nm and a secondary peak at 10–106 μm . It accounts for 14.7% of number concentration, with the highest contributions to volume and surface area. It correlates with NO_x , NO_2 , CO, total hydrocarbons (THC), organic carbon (OC), elementary carbon (EC), and BC, indicating its link to

combustion sources like traffic and industry. Higher concentrations are observed in the early morning and at night, with a moderate to high negative correlation with wind speed, suggesting local emissions accumulate due to lower mixing layer heights at night.

Factor 5, dominated by micrometer-sized particles ($dp > 1 \mu\text{m}$), contributes 2.9% to number concentration and 24.9 and 8.2% to volume and surface area concentrations, respectively. It correlates well with $\text{PM}_{2.5}$, PM_{10} , Na^+ , Cl^- , and crustal elements like Mg^{2+} and Ca^{2+} , indicating it represents “crustal elements and sea salt”. Diurnal trends show elevated concentrations between 2 and 4 PM, likely due to higher temperatures and wind speeds facilitating dust suspension and sea salt transport. Wind rose data further supports this, showing increased concentrations during high north-west winds, likely due to the station’s coastal location.

3.3 UFP sources during COVID-19 soft lockdown period

In 2020, the global implementation of urban lockdowns and restrictions aimed at controlling the spread of SARS-CoV-2 (COVID-19) led to a marked decline in many human activities [47]. This downturn resulted in substantial and declined air pollutants, including $\text{PM}_{2.5}$, PM_{10} , BC, SO_2 , and NO_x , primarily due to decreased vehicular traffic [47–50]. The lockdowns created a unique opportunity to examine urban air quality in relation to diminished anthropogenic air pollutant emissions [51]. However, some researchers caution against attributing the reduction in traffic emissions solely to these measures, as factors like weekend and holiday effects, varying lockdown regulations, and different meteorological conditions also played a role [52].

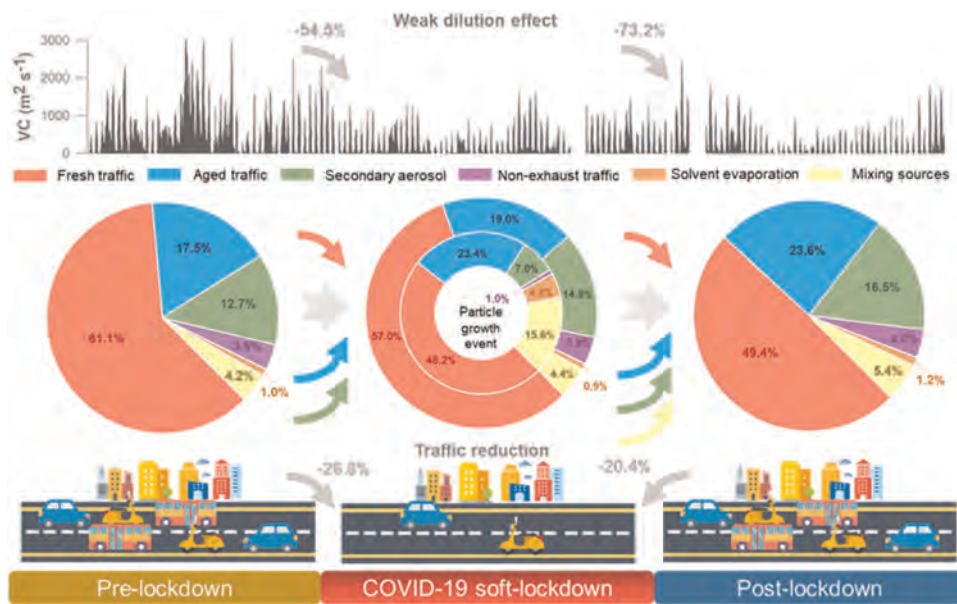
During this period, an intriguing increase in surface O_3 concentrations was observed, mainly due to the weak titration effect from reduced NO_x levels in urban areas [53–57]. PNSD, PNCs, and new particle formation (NPF) were reported in heavily polluted megacities around the world [58, 59]. Although UFP concentrations decreased by 30–40% during the lockdown, the frequency of NPF events increased, alongside enhancements in the Aitken and accumulation modes [60, 61]. This phenomenon is largely attributed to elevated levels of condensing vapors, including sulfuric acid, as well as increased concentrations of key oxidants and radicals affecting VOCs [62, 63]. Additionally, the particle growth and formation rate improved due to a rise in oxygenated organic molecules resulting from increased atmospheric oxidation capacity [59]. As lockdown policies were gradually lifted and traffic volumes returned to normal conditions, there was a corresponding rise in the condensation sink. This suggested potential losses of gaseous precursors and newly formed particles due to increased primary emissions [60]. While many studies have concentrated on PNSD changes during strict lockdowns, the summer of 2021 marked Taipei’s emergence as Taiwan’s COVID-19 epicenter, albeit with less severity than in many other countries. During the “soft lockdown” phase, authorities enacted a Level 3 COVID-19 alert, imposing moderate restrictions on human and industrial activities, which could serve as a model for future transitions toward widespread electric vehicle adoption.

Table 2 indicated significant reductions in N_{coa} , $\text{PM}_{1.0}$, and BC by 36–49, 21–37, and 27–31% during the soft lockdown, respectively, compared to periods before and after the lockdown. Notably, N_{nuc} decreased by 16 and 34% during the soft lockdown compared to the preceding and following periods. Interestingly, both N_{Aitk} and N_{acc} experienced increases during this phase, with N_{acc} reaching up to 1.34 times higher than in the post-lockdown period. As shown in **Figure 5**, a 20.4–26.8% reduction in traffic volumes before and after the soft lockdown period was observed, indicating

Items (units)	P1	P2	P3	Comparison	
	Mean/SD	Mean/SD	Mean/SD	P2/P1	P2/P3
N_{nuc} (cm^{-3})	$1.37 \times 10^{-4} \pm 1.33 \times 10^{-4}$	$1.14 \times 10^{-4} \pm 9.48 \times 10^{-5}$	$1.73 \times 10^{-4} \pm 1.56 \times 10^{-4}$	0.84	0.66
N_{Aitk} (cm^{-3})	$5.94 \times 10^{-3} \pm 4.52 \times 10^{-3}$	$6.77 \times 10^{-3} \pm 4.55 \times 10^{-3}$	$7.73 \times 10^{-3} \pm 5.24 \times 10^{-3}$	1.14	0.88
N_{acc} (cm^{-3})	$1.5 \times 10^{-3} \pm 9 \times 10^{-2}$	$1.73 \times 10^{-3} \pm 1.19 \times 10^{-3}$	$1.29 \times 10^{-3} \pm 7.05 \times 10^{-2}$	1.15	1.34
N_{coa} (cm^{-3})	2.8 ± 2.65	1.43 ± 0.9	2.25 ± 1.37	0.51	0.64
GMD (nm)	39.3 ± 23.5	36.30 ± 11.07	30.65 ± 6.94	0.92	1.18
PM_{10} ($\mu g m^{-3}$)	11.6 ± 7.73	7.32 ± 4.01	9.23 ± 4.83	0.63	0.79
BC ($ng m^{-3}$)	1556.7 ± 982.5	1133.92 ± 681.67	1635.70 ± 958.25	0.73	0.69

Table 2.

Specifications of instrumentations at three different measurement sites.

**Figure 5.**

The traffic-induced shift of source apportionment was resolved from the PNSD and UFP measurement data before, during, and after the COVID-19 third alert period in Taipei City (Apr. 2021 to Aug. 2021). The ventilation coefficient (VC) was calculated using the boundary layer height multiplied by the surface wind speed to describe the potential for air pollutants to be diluted per unit time (adopted from [34]).

that decreased primary traffic-related UFP emissions contributed to a higher presence of aged particles and secondary aerosols.

Additionally, we calculated the ventilation coefficient (VC), which represents the ratio between wind speed and mixing layer height, to evaluate the dispersion effect of air masses on air pollutant concentrations. The VC values at the observation site decreased by 54.5% from the pre-lockdown phase to the soft lockdown period and by 73.2% in the post-lockdown period, indicating a significantly weak dilution effect throughout the campaign. This decline, combined with increased contributions from sources like solvent evaporation, worsened air quality upon the return to normal traffic levels. During this traffic-induced shift, contributions from the resolved factors “aged traffic,” “solvent evaporation,” and “mixing sources” increased, while those

from factors “fresh traffic,” “non-exhaust traffic,” and “secondary aerosol” declined. This observation suggested that additional emissions sources and an enhanced frequency of photochemical reactions during the particle aging process were particularly influential in the soft lockdown phase, especially during the particle growth events shown in the inner circle [34]. The case study in Taipei underscores the significant impact of local traffic reductions on PNSD in urban environments, suggesting that effective traffic management can play a crucial role in lowering primary UFP emissions, especially under unfavorable dilution conditions.

3.4 Lung-deposited surface area (LDSA) concentration

LDSA is a critical index for evaluating particle interactions with lung tissue and acts as a key indicator of health risks from UFP exposure [64, 65]. It takes into account the potential chemical interactions on the particle-lung surface, which can enhance the toxicity of inhaled particles [66]. Previous research evidenced the interactions between LDSA, UFPs, and health effects [67] by using the International Commission on Radiological Protection (ICRP) lung deposition model. It further defined the theoretical LDSA (LDSA_{SMPS}) can be calculated from the PNSD data provided by the SMPS. The difference between LDSA_{NSAM} and LDSA_{SMPS} is mainly due to the assumption that particles are spherical. The LDSA ratio (α) is employed to quantify the extent of fractal characteristics: a ratio near 1 indicates a predominance of spherical particles, while higher values suggest a greater degree of fractal structures:

$$\text{LDSA ratio } (\alpha) = \frac{\text{LDSA}_{\text{NSAM}}}{\text{LDSA}_{\text{SMPS}}} \quad (5)$$

Urban areas typically exhibit higher LDSA concentrations [68, 69]. A study by Reche et al. [70] in Barcelona, Spain, examined the variability, sources, and processes affecting particle surface area by analyzing LDSA data alongside particle number concentration, particle size distribution, and BC [70]. They found a strong correlation between hourly LDSA and BC concentrations ($r^2 = 0.82$), with the highest correlation between LDSA and particle number concentration (PNC) in the 50–200 nm size range ($r^2 = 0.78$). Although traffic emissions are major contributors to LDSA in urban areas, other sources, such as long-range transported pollution and cooking aerosols, also play significant roles. In Helsinki and Delhi, Salo et al. found the different median particle sizes of LDSA, attributing the differences to transport sources rather than local traffic [71]. These findings underscore the need for a comprehensive analysis of the factors influencing LDSA concentrations.

In our recent study, we demonstrated the weekend effect on changing the LDSA fractions and their measured concentrations using PNSD-PMF data (see **Figure 6a** and **b**) at Taipei urban roadside [36]. On both weekdays and weekends, contributions from fresh road traffic to LDSA concentrations became less significant. Instead, factors of secondary aerosols and aged road traffic emerged as the dominant sources, as depicted in **Figure 6c**. LDSA ratios peaked during rush hours, indicating the presence of freshly emitted, irregular particles. Aged particles, located at Aitken and accumulation modes, significantly contributed to LDSA at heavy traffic sites. When considering volume concentration, urban background, and secondary aerosols were the main contributors. As shown in **Figure 6d**, the factor of fresh road traffic emissions primarily deposited in the head region (42.6%), whereas the factor of aged road traffic shifted deposition to the pulmonary/alveolar region (48.4%). Therefore, considering

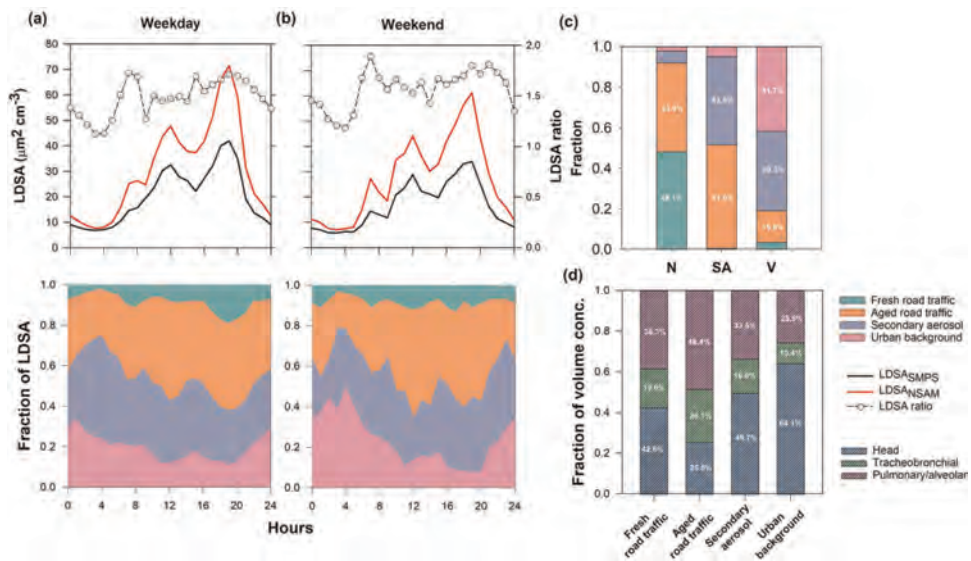


Figure 6.

Diurnal patterns of $\text{LDSA}_{\text{SMPS}}$, $\text{LDSA}_{\text{NSAM}}$, the LDSA ratio, and the fraction of LDSA for different PNSD-PMF sources on (a) weekdays and (b) weekends. (c) Fraction of number (N), surface area (SA), volume (V) concentration, and (d) fraction of the lung deposition dose on volume concentration for different PNSD-PMF (adopted from [36]).

size distribution and chemical characteristics is important in urban air pollution mitigation and health risk assessments, as changes in PM composition during atmospheric aging can influence health risks.

In our second case study in New Taipei City, we observed that the diurnal variation of $\text{LDSA}_{\text{NSAM(traffic)}}$ mirrored traffic flow, peaking at 8:00 AM (weekday: $54.4 \mu\text{m}^2/\text{cm}^3$; weekend: $41.9 \mu\text{m}^2/\text{cm}^3$) (Figure 7a and b) [33]. The difference in peak $\text{LDSA}_{\text{NSAM(traffic)}}$ concentrations between weekdays and weekends was significantly larger than for non-apportioned $\text{LDSA}_{\text{NSAM}}$ (difference $< 3.4 \mu\text{m}^2/\text{cm}^3$), likely due to variations in traffic flux and greater influences of $\text{LDSA}_{\text{NSAM(non-traffic)}}$ on weekends. Figure 8 illustrates the diurnal diagram of α for each factor, highlighting distinct outcomes of traffic and non-traffic sources. Generally, the α for factor 1 (fresh traffic

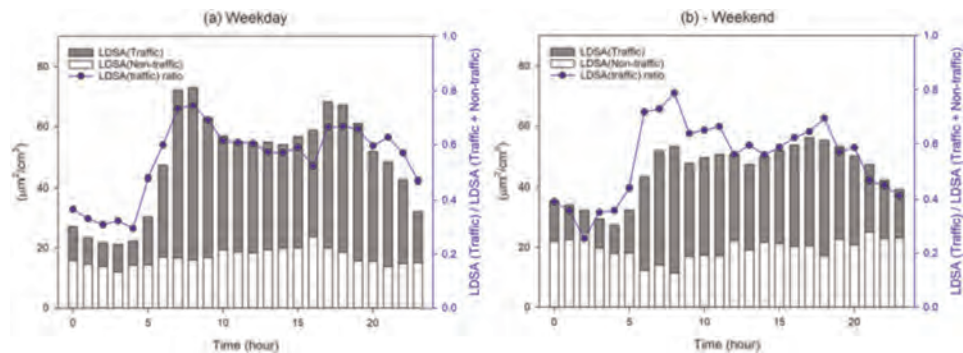


Figure 7.

Diurnal variations of $\text{LDSA}_{\text{NSAM}}$ contributed by traffic emission (a) on weekdays and (b) on weekends. The white column represents the $\text{LDSA}_{\text{NSAM (non-traffic)}}$, and the gray column represents the $\text{LDSA}_{\text{NSAM (traffic)}}$. The blue line represents the ratio of $\text{LDSA}_{\text{NSAM (traffic)}}$ to total $\text{LDSA}_{\text{NSAM}}$ (adopted from [33]).

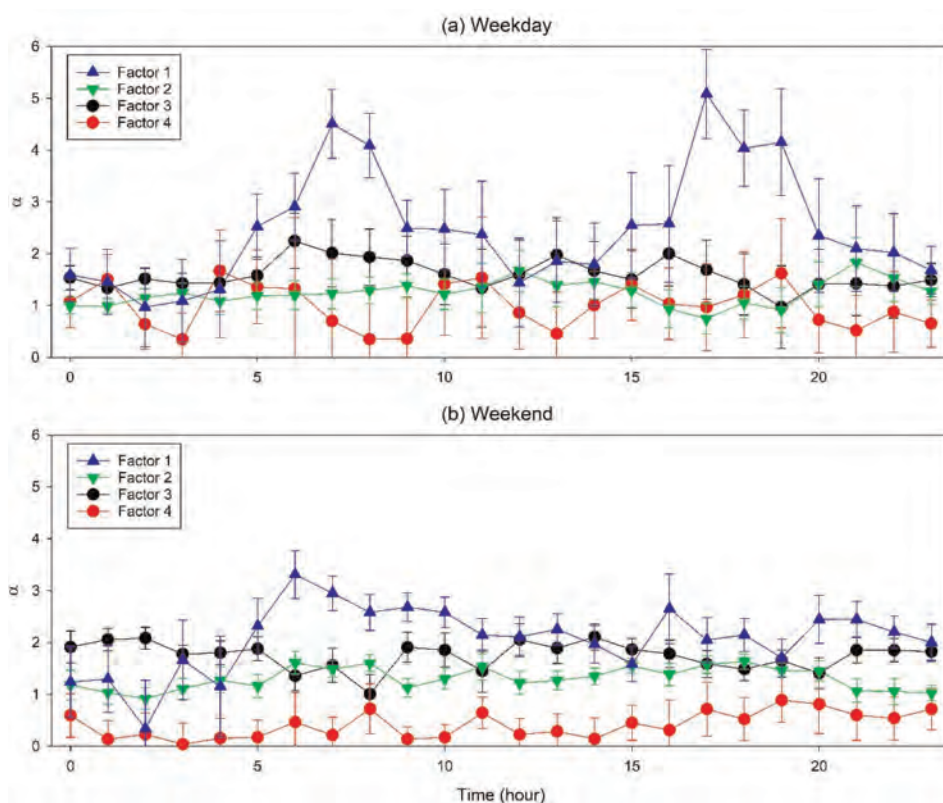


Figure 8.
 The diurnal patterns of the fitted LDSA ratio (α) on (a) weekdays and (b) weekends (adopted from [33]).

pollution) was higher, showing clear dual peaks during rush hours and emphasizing the fractal nature of freshly emitted traffic particles. On average, $\text{LDSA}_{\text{NSAM}(\text{traffic})}$, including factors 1 (fresh traffic pollution) and 2 (aged traffic emissions), accounted for about 57% of the total $\text{LDSA}_{\text{NSAM}}$, increasing to 74% during traffic rush hour.

4. Machine-learning-assisted estimation of UFP observation

4.1 Current challenges

Traditional physical-chemical models are widely applied in environmental science, but their accuracy in analyzing the sources and behaviors of UFPs and other pollutants is often limited by uncertainty. These models also heavily rely on the precise quantification of environmental variables, which in the real world are subject to significant spatial and temporal variability, making it difficult for physical-chemical models to fully capture this complexity. Moreover, these models face high computational costs and efficiency issues when handling large-scale datasets, which limits their practical application. Machine learning (ML) models provide new perspectives and deeper insights into the formation, transport, and control of ultrafine particles. They surpass traditional models by handling nonlinear relationships, offering flexibility in isolating complex influencing factors, enhancing model interpretability, and capturing subtle patterns in time series data.

4.2 Advanced machine learning model

With the advancement of big data and ML technologies, ML has become a powerful tool in UFP monitoring and analysis, offering more precise capabilities to capture and predict UFP behavior, as well as to deepen the understanding of how environmental factors and human activities influence their concentration changes. Our latest study performed the PNSD from 2018 to 2023, applying tree-based models such as Random Forest (RF), Gradient Boosting Regression Trees (GBRT), and eXtreme Gradient Boosting (XGB) to predict UFP concentrations (PNC) across different modes. The study successfully differentiated baseline fluctuations from contributions due to human activities, analyzing the specific contributions of various factors, including meteorological conditions (wind speed, temperature, humidity, etc.) and human activities (such as different time markers) [72]. In this study, a de-weathering method to separate the effects of meteorological variables from UFP observations was proposed, allowing for the precise identification of fluctuations caused by human activities. By controlling the influence of meteorological variables, this method clearly distinguishes the contribution of human activities to the fluctuations in UFP concentrations. Particularly during peak traffic hours, the changes in traffic flow significantly affected the concentration of UFPs in Aitken and nucleation modes, as shown in **Figure 9**. This indicates that, even under relatively stable meteorological conditions, human activities strongly influence UFP concentrations.

In addition to forecasting UFPs, compared with other common pollutants, such as NO_x , PM_{10} , and $\text{PM}_{2.5}$. The comparison revealed that UFP concentrations are more sensitive to changes during peak traffic hours, while traditional pollutants like $\text{PM}_{2.5}$ are more influenced by meteorological conditions and seasonal variations. This finding suggests that while traditional pollutants are affected by multiple factors, the variation patterns of UFPs are more reflective of human activities, especially changes in traffic flow and precursor substances. By analyzing SHAP values, which provide an interpretable analysis of the contributions of various factors, the specific contribution of each meteorological parameter to UFP concentrations can be quantified. The study

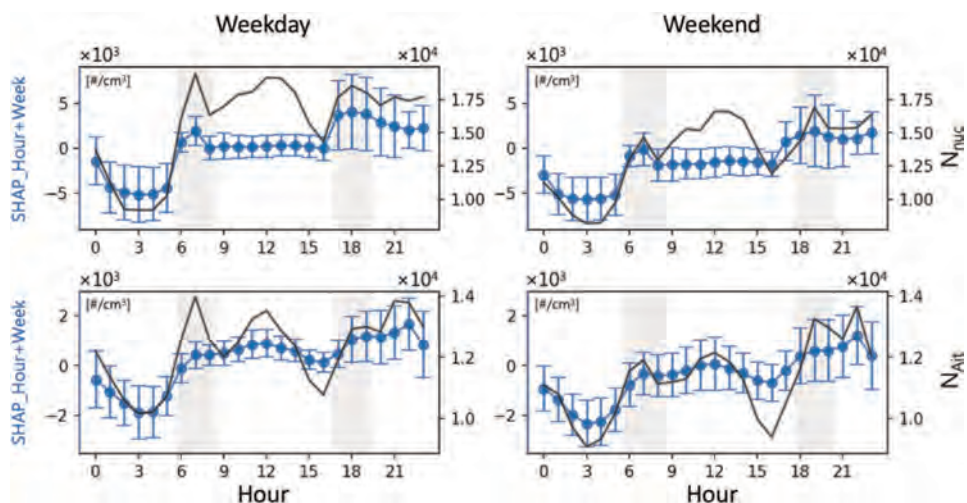


Figure 9. Normalized short-term human activities (hours and weeks represented by SHAP value), compared with observation in N_{nuc} and N_{Ait} . (The color shading in the background represents the traffic rush hours in the morning and evening.) (adopted from [72]).

results indicate that wind speed is a key factor influencing PNC, particularly under low wind conditions where local sources contribute the most to UFPs. This finding is consistent with existing studies and emphasizes the critical role of wind speed in affecting ultrafine particle concentrations. Additionally, temperature and humidity also exhibit significant effects across different particle size modes, indicating that under certain conditions, secondary formation processes (such as gas-to-particle conversion) may significantly alter UFP concentrations.

Through these ML models, we demonstrated how baseline weather fluctuations can be differentiated from human activities, which is crucial for future environmental policy development. This method not only aids in identifying and quantifying the primary sources of UFPs but also helps in understanding their variation patterns under different seasonal and meteorological conditions. As ML technologies continue to evolve, these methods will provide more accurate predictions and support more targeted pollution control and emission reduction strategies.

5. Perspective and prospects

Based on these three case studies in Taiwan urban areas, to effectively manage atmospheric particle growth and control emissions, establishing comprehensive long-term monitoring of UFPs is crucial. These particles exhibit significant spatial and temporal variability and originate from diverse sources such as traffic emissions, industrial activities, biomass burning, and atmospheric new particle formation events. Although they contribute minimally to the overall mass of aerosols, UFPs significantly impact total particle number concentration and can penetrate deeply into the lungs, posing cardiovascular and respiratory health risks. Understanding the spatiotemporal distribution of UFPs is vital for identifying their sources and developing effective emission control strategies. Long-term data collection not only tracks trends in UFP concentrations but also evaluates the success of emission reduction measures [73]. This monitoring is essential for understanding particle growth dynamics through processes like condensation and coagulation, which influence the overall aerosol size distribution.

Research into UFP toxicity further underscores the importance of sustained monitoring. Studies indicate that semi-volatile organic compound UFPs (SVOC UFPs) from diesel engines exhibit higher neurotoxic potency than solid UFPs [74]. These particles can enter the brain *via* the olfactory pathway, raising significant health concerns. Reducing the aromatic content in fuels, such as using hydrogenated vegetable oil, can mitigate these neurotoxic effects, highlighting the need for continuous monitoring and regulation to reduce associated health risks.

Moreover, the role of gaseous pollutants in air pollution toxicity should not be underestimated [75]. While UFPs primarily originate from combustion processes, gaseous pollutants have diverse sources, including industrial activities and natural emissions. These pollutants can interact with UFPs, enhancing their harmful effects. UFPs and gaseous pollutants impact health through different pathways; UFPs deposit deep in the respiratory tract, while gaseous pollutants may enter the bloodstream directly. More *in vivo* studies are needed to understand these interactions fully.

Future studies should focus on integrating long-term and real-time UFP monitoring with an appropriate PM_{2.5} toxicity evaluation platform to gain insights into the effectiveness of emission control strategies and facilitate health risk assessment. This approach emphasizes the need for advanced measurement techniques to evaluate

both particulate and gaseous pollutants, ultimately aiding the development of strategies to mitigate health and environmental risks and protect human health and the environment. Stakeholders are encouraged to take immediate action by investing in these technologies to drive significant improvements in air quality and public health.

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Air pollution research is rapidly expanding from compliance metrics to source-resolved, health-relevant evidence that supports action. This book presents international case studies and perspectives on key air pollutants, with emphasis on PM_{2.5}, ultrafine particles, and atmospheric ammonia. Chapters cover chemical characterization and source apportionment, toxicity potential and guideline benchmarking, and the analytical methods needed for accurate measurement of reactive species that drive secondary aerosol formation. The book discusses mitigation options, ranging from source-focused strategies to nature-based approaches such as tolerant plant species, and bridges atmospheric science with practical monitoring and control applications.

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