

**SOURCE APPORTIONMENT OF AEROSOLS IN
GHAZIABAD USING ADVANCED RECEPTOR
MODELLING TOOLS**

LOVLEEN GUPTA



**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2022**

© **Indian Institute of Technology Delhi (IITD), New Delhi, 2022**

**SOURCE APPORTIONMENT OF AEROSOLS IN
GHAZIABAD USING ADVANCED RECEPTOR
MODELLING TOOLS**

by

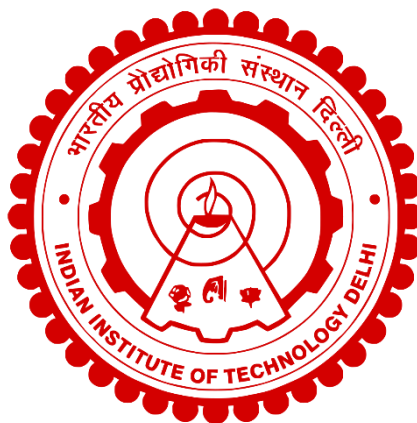
LOVLEEN GUPTA

DEPARTMENT OF CIVIL ENGINEERING

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2022**

Dedicated to

THE CAUSE OF CLEAN AIR & HUMAN HEALTH

CERTIFICATE

This is to certify that the thesis entitled “**Source Apportionment of Aerosols in Ghaziabad using Advanced Receptor Modelling Tools**” being submitted by **Mrs. Lovleen Gupta** to the **Indian Institute of Technology Delhi**, for the award of the degree of **Doctor of Philosophy** is a record of the original bonafide research work carried out by her under my guidance and supervision. The thesis work, in my opinion, has reached the requisite standards fulfilling the requirement for the Degree of Doctor of Philosophy.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

(Prof. Gazala Habib)

Associate Professor

Department of Civil Engineering,

Indian Institute of Technology Delhi,

Hauz Khas, New Delhi-110016, INDIA.

E-mail: gazala@civil.iitd.ac.in



(Prof. Ramya Sunder Raman)

Professor

Department of Earth and Environmental Sciences,

Indian Institute of Science and Education Research, Bhopal

Bhopal Bypass Road, Bhauri, Bhopal – 462066, INDIA.

E-mail: ramyasr@iiserb.ac.in

ACKNOWLEDGEMENT

The past few years at IIT Delhi have been an excellent learning experience, and it would not have been possible without the constant guidance, encouragement, and scientific inputs of my advisors Prof. Gazala Habib and Prof. Ramya Sunder Raman. I express my sincere gratitude to my advisors. In addition, there were many people/organizations who have supported me in different ways throughout my PhD. Therefore, I would like to thank:

- Uttar Pradesh Pollution Control Board for funding this research (Grant No.: H05539/CL/205/Source Apprt. Study/2014-17).
- My Research Committee (Prof. J. T. Sahu, Prof. Geetam Tiwari and Dr. Shaikh Z. Ahammad) for their scientific inputs throughout.
- Dr. Jai Prakash for scientific inputs and fruitful discussions.
- The heads and supporting staff of the locations where sampling was carried out.
- Mr. Kumail Zaidi, Mr. Rishabh and Mr. Imam Hussain of IIT Delhi for assisting with the sampling. Dr. Mahak Bansal, Ms. Swati Joshi, Mr. Kashish Jain, Ms. Jyoti Kumari at IIT Delhi and Mr. Ankur Bhardwaj, Mr. Priyabrata Nandi and Ms. Anusmita Das at IISER Bhopal for the support in the laboratories. Rest of the members of ARC lab at IIT Delhi for their unconditional support.
- Engineers and experts of Thermo Fischer Scientific India Private Limited, and MARS Bioanalytical for their prompt support for the instrument upkeep.
- Department of Civil Engineering at IITD and Dr. Sanjay Gupta, Mr. Ishwar, Mr. Deepak in the Environmental Laboratory at IIT Delhi for providing me with the necessary support required from the lab from time to time.
- All India Council of Technical Education, Government of India for sponsoring me to pursue my PhD.
- Delhi Technological University for relieving me full time to focus on my PhD.

And as life is not only about science, I am indebted to my late mother who with her dedication and hard work brought me to the platform I am on today. My sincere thanks go to my father for encouraging me during the lows. I am grateful to my husband for motivation, trust and love. My little daughter and son also deserve a mention here, who are the driving force to give my best to whatever I do. Last but not the least, I thank God for everything.

ABSTRACT

Atmospheric aerosols consist of a wide range of solid or liquid particles suspended in air. These aerosols contribute to air pollution and are termed as Particulate Matter (PM). In addition to the climate effects by scattering and absorption of solar and terrestrial radiation and inducing changes in the cloud properties, PM is known to have acute and chronic human health effects. While it's accepted that higher the ambient PM concentration higher is the health risk, the gravity of health risk depends on the chemical composition of ambient PM. Also, to devise effective strategies, the quantification of emission sources is an essential precondition. Based on the aerodynamic diameter of the particle, PM is classified as PM₁₀ (diameter <10 µm) and PM_{2.5} (diameter < 2.5 µm). While the PM_{2.5} and PM₁₀ concentrations are routinely monitored across India by the government, the information on the likely sources which impact the air quality is scarcely available. Most of the studies which quantify the sources impacting the air quality in India focuses on the metropolitan cities like Mumbai, Delhi, Chennai and Kolkata, very few have been carried out in other locations. Ghaziabad is an industrial city bordering on one side with Delhi, where the PM concentration have been reported to be exceeding the World Health Organization standards throughout the year and no detailed source apportionment study exists for it. The objective of this work is to understand:

1. Mass and chemical composition of PM_{2.5} and PM₁₀ over Ghaziabad;
2. Identification and quantification of sources responsible for ambient PM_{2.5} and PM₁₀ in Ghaziabad; and
3. Identification of probable regional and local source locations.

To achieve the above stated objectives, PM_{2.5} and PM₁₀ samples and in-situ meteorological parameters were collected over two locations (hereafter called as “site A” and “site B”) in Ghaziabad throughout the year from June 2018 - May 2019 (both months inclusive). 24-hour integrated samples (9:00AM – 9:00AM) were collected every third day on multiple filter substrates using medium volume samplers at both locations. PM_{2.5} and PM₁₀ mass and chemical constituents (viz., organic, elemental and pyrolytic carbon, thirteen water soluble inorganic ions and twenty-six trace elements) were measured for the entire sampling duration and at both locations. USEPA PMF5 was used to apportion PM_{2.5} and PM₁₀ sources at both locations. Finally, probable source locations (and/or preferred transport pathways) were inferred using two well-established probability functions: (a) the Conditional Bivariate Probability Function (CBPF), to correlate the

output of PMF model with local wind directional data, and (b) the Potential Source Contribution Function (PSCF), to correlate the output of PMF model with 120 h air-mass back-trajectories, arriving at the receptor sites during sampling duration. The key findings of the thesis are:

1. The annual average $PM_{2.5}$ and PM_{10} concentrations were found to be $142 \pm 82 \mu g m^{-3}$ and $252 \pm 135 \mu g m^{-3}$ at site A and $157 \pm 95 \mu g m^{-3}$ and $278 \pm 151 \mu g m^{-3}$ at site B respectively. Both of which are orders of magnitude higher than the World Health Organization standards for ambient air quality. PM (both $PM_{2.5}$ and PM_{10}) concentrations at the two sites were also compared with the third site maintained by the Central Pollution Control Board and across the three sites, no statistically significant variability was seen, indicating rapid mixing in the city's airshed.
2. Temporally, the PM concentration (both size fractions) followed post-monsoon > winter > pre-monsoon > monsoon. The average $PM_{2.5}$ concentration in Ghaziabad during the monsoon, post-monsoon and pre-monsoon season were ~ 1.2 times higher than the $PM_{2.5}$ observed in Delhi during the same period. For winter, the concentrations were comparable. The PM_{10} concentration during the monsoon season were ~ 1.2 times higher than those observed for Delhi during the same period. For the other three seasons, the PM_{10} concentration were comparable. This indicated more combustion sources in Ghaziabad.
3. The relative contribution of $PM_{2.5}$ to PM_{10} was observed to be highest (~ 0.70 across the three sites) during the winter season and lowest (~ 0.4 across the three sites) during the monsoon season. This may be attributed to enhanced heating requirements during winter and windy meteorological conditions during the monsoon.
4. Spearman rank correlation revealed that ventilation coefficient (VC), temperature and relative humidity were the main local factors influencing the PM concentration, with the magnitude of association varying seasonally.
5. MLR revealed that the variability in local meteorological parameters accounted for $\sim 50\%$ of the variability (maximum) in $PM_{2.5}$ and PM_{10} mass during monsoon and post-monsoon respectively.
6. Cluster and CWT analysis revealed influence from regional sources during winter, post-monsoon and pre-monsoon, while the monsoon season had air-masses transporting dust aerosols as they passed over the African desert and western states in India.

7. Premature mortality estimates attributable to ambient PM_{2.5} in Ghaziabad was ~873 per million, which is ~ 70% higher than Delhi.
8. The average distribution of chemical components of PM_{2.5} over the year was ~50% carbonaceous mass; ~32-33% ionic mass; and ~16-19% elemental mass at both sites. For PM₁₀, carbonaceous mass was ~30%; WSII mass was ~16-22% and elemental mass was ~21-26% at both sites.
9. Major WSII's contributing to the PM mass were: NO₃⁻, SO₄²⁻, Cl⁻ and NH₄⁺ contributing on average ~ 90% of the PM_{2.5} ionic mass and ~ 82% of the PM₁₀ ionic mass across both sites. Aerosols were found to be acidic/moderately acidic (pH ~ 4) throughout the year with lower pH in monsoon compared to the other seasons. PM_{2.5} mass (including water) doubled at RH ~90% due to high AWC
10. Major trace elements that contributed on average >90% total elemental mass were Al, Si, Fe, Mn, K, Zn and Pb across both PM size fractions and sites.
11. Eight sources were resolved using USEPA PMF5. The sources in decreasing order of their contribution to the PM_{2.5} mass were: vehicular emissions (22%), secondary formation (21%), combustion aerosol (18%), resuspended dust I (14%), resuspended dust II (10%), brick manufacturing (9%), mixed metal processing (5%) and copper smelter (4%). Source contribution to the PM₁₀ mass were: resuspended dust I (25%), resuspended dust II (24%), combustion aerosol (24%), secondary formation (12%), vehicular emissions (7%), copper smelter (5%), brick manufacturing (3%) and mixed metal processing (1%).
12. On days when 24-hour average PM_{2.5} concentration was >90 µgm⁻³, brick processing and vehicular were mainly responsible. In case of PM₁₀, when the 24-hour average concentration was >250 µgm⁻³, mixed combustion and resuspended dust (I&II) were the main contributors.
13. The probable source regions were local as well as regional in nature, with states in the upper Indo Gangetic Plain namely Punjab, Haryana, Delhi being important source regions for PM_{2.5} and PM₁₀ measured at the receptor site. Also, specifically, for resuspended dust II which is one of the main contributors to PM₁₀ during high PM₁₀ days, the probable source is the construction, prevailing in the city.

The outcomes of this study are expected to strengthen the air quality management plans for Ghaziabad. The results from this study can be used by the regulatory bodies for devising appropriate control strategies. Also, given its proximity to Delhi, it is expected that improvements in air quality management over Ghaziabad will benefit the entire National Capital Region in India. Further, it is hoped that the results of this study will provide inputs to validate emission inventories as well as climate model outputs over the region.

सार

वायुमंडलीय एरोसोल में हवा में विद्यमान ठोस या तरल कणों की एक विस्तृत श्रृंखला होती है। ये एरोसोल वायु प्रदूषण में योगदान करते हैं और इन्हें पार्टिकुलेट मैटर (पीएम) कहा जाता है। सौर और स्थलीय विकिरण के प्रकीर्णन और अवशोषण और बादल के गुणों में परिवर्तन को प्रेरित करके जलवायु प्रभावों के अलावा, पीएम को मानव स्वास्थ्य पर विकट और दीर्घकालिक प्रभावों के लिए जाना जाता है। हालांकि यह माना जाता है कि बाहरी पीएम सांद्रता जितनी अधिक होती है, स्वास्थ्य जोखिम उतना ही अधिक होता है, स्वास्थ्य जोखिम की गंभीरता बाहरी पीएम की रासायनिक संरचना पर निर्भर करती है। इसके अलावा, प्रभावी रणनीति तैयार करने के लिए, उत्सर्जन स्रोतों की मात्रा का निर्धारण एक आवश्यक शर्त है। कण के वायुगतिकीय व्यास के आधार पर, पीएम को पीएम₁₀ (व्यास <10 µm) और पीएम_{2.5} (व्यास <2.5 µm) के रूप में वर्गीकृत किया गया है। हालांकि सरकार द्वारा पूरे भारत में पीएम_{2.5} और पीएम₁₀ सांद्रता की नियमित रूप से निगरानी की जाती है, परन्तु वायु गुणवत्ता को प्रभावित करने वाले संभावित स्रोतों की जानकारी अत्यंत दुर्लभ है। भारत में वायु गुणवत्ता को प्रभावित करने वाले स्रोतों को मापने वाले अधिकांश अध्ययन मुंबई, दिल्ली, चेन्नई और कोलकाता जैसे महानगरीय शहरों पर केंद्रित हैं, बहुत कम अन्य स्थानों पर किए गए हैं। गाजियाबाद एक औद्योगिक शहर है जो दिल्ली के साथ जुड़ा हुआ है, और जहां पूरे वर्ष पीएम सांद्रता विश्व स्वास्थ्य संगठन के मानकों से अधिक होने सम्बन्धी सूचना उपलब्ध है परन्तु इसके लिए कोई विस्तृत विनियोजित स्रोत अध्ययन मौजूद नहीं है। इस कार्य का उद्देश्य यह समझना है कि:

1. गाजियाबाद के ऊपर पीएम_{2.5} और पीएम₁₀ का द्रव्यमान और रासायनिक संरचना
2. गाजियाबाद में बाहरी पीएम_{2.5} और पीएम₁₀ के लिए जिम्मेदार स्रोतों की पहचान और परिमाणीकरण तथा
3. संभावित क्षेत्रीय और स्थानीय स्रोत स्थानों की पहचान।

उपर्युक्त उद्देश्यों को प्राप्त करने के लिए जून 2018 से मई 2019 (दोनों महीने शामिल) तक पूरे वर्ष में गाजियाबाद में दो स्थानों (इसके बाद में इन्हे साइट ए और साइट बी लिखा गया है) पर पीएम_{2.5} और पीएम₁₀ नमूने और इन सीटू मौसम संबंधी मापदंडों को एकत्र किया गया था। 24 घंटे एकीकृत नमूने 9:00 पूर्वाह्न से 9:00 पूर्वाह्न, प्रत्येक तीसरे दिन, दोनों स्थानों पर मध्यम मात्रा के नमूनों का उपयोग करके कई फिल्टर सबस्ट्रेट्स पर एकत्र किए गए थे। पीएम_{2.5} और पीएम₁₀ के द्रव्यमान और रासायनिक घटक (अर्थात्, जैविक, तात्विक और पाइरोलाइटिक कार्बन, तेरह पानी में घुलनशील अकार्बनिक आयन और छब्बीस ट्रेस तत्व) पूरे नमूने की अवधि के लिए और दोनों स्थानों पर मापा गया। USEPA पीएम_{एफ}5 का उपयोग दोनों स्थानों पीएम_{2.5} और पीएम₁₀ स्रोतों को विभाजित करने के लिए किया गया था। अंत में, संभावित स्रोत स्थानों (और/या पसंदीदा परिवहन मार्ग) को दो सुस्थापित प्रायिकता फलन का उपयोग करके अनुमान लगाया गया था: अ) कंडीशनल बाईवैरिएट प्रोबैबिलिटी फंक्शन - स्थानीय पवन दिशात्मक डेटा के साथ पीएम_{एफ} मॉडल के आउटपुट को सहसंबंधित करने के लिए, ब) पोटेंशियल सोर्स कॉन्ट्रिब्यूशन फंक्शन - नमूना अवधि के दौरान रिसेप्टर साइटों पर पहुंचने वाले 120 एच एयर-मास बैक-ट्रैजेक्टरी के साथ पीएम_{एफ} मॉडल के आउटपुट को सहसंबंधित करने के लिए। थीसिस के प्रमुख निष्कर्ष हैं:

1. वार्षिक औसत पीएम_{2.5} और पीएम₁₀ सांद्रता साइट ए पर क्रमशः $142 \pm 82 \mu\text{gm}^{-3}$ और $252 \pm 135 \mu\text{gm}^{-3}$ और साइट बी पर $157 \pm 95 \mu\text{gm}^{-3}$ और $278 \pm 151 \mu\text{gm}^{-3}$ पाए गए। ये दोनों बाहरी वायु गुणवत्ता के लिए विश्व स्वास्थ्य संगठन के मानकों से अधिक हैं। दोनों स्थलों पर पीएम (पीएम_{2.5} और पीएम₁₀ दोनों) की सांद्रता की तुलना केंद्रीय प्रदूषण नियंत्रण बोर्ड द्वारा बनाए गए तीसरे स्थल से भी की गई और तीनों स्थलों पर कोई सांख्यिकीय रूप से महत्वपूर्ण परिवर्तनशीलता नहीं देखी गई, जो शहर के एयरशेड में तेजी से मिश्रण का संकेत देती है।
2. अस्थायी रूप से, पीएम सांद्रता रूझान (दोनों आकार के अंश) मानसून के बाद > सर्दी > ग्री-मानसून > मानसून के बाद है। गाजियाबाद में मानसून, पोस्ट-मानसून और ग्री-मानसून सीजन के दौरान औसत पीएम_{2.5} सांद्रता इसी अवधि के दौरान दिल्ली में देखे गए पीएम_{2.5} की तुलना में ~1.2 गुना अधिक थी। सर्दियों के लिए, सांद्रता तुलनीय थी। मानसून के मौसम के दौरान पीएम₁₀ की सांद्रता इसी अवधि के दौरान दिल्ली में देखी गई तुलना में ~1.2 गुना अधिक थी। अन्य तीन मौसमों के लिए, पीएम₁₀ सांद्रता तुलनीय थी। इसने गाजियाबाद में अधिक दहन स्रोतों का संकेत दिया।
3. पीएम_{2.5} और पीएम₁₀ का सापेक्षिक योगदान सर्दियों के मौसम के दौरान उच्चतम (तीन स्थलों में ~0.70) और मानसून के मौसम के दौरान सबसे कम (तीन स्थलों में ~0.4) देखा गया। यह सर्दियों के दौरान बढ़ी हुई ऊष्मा आवश्यकताओं और मानसून के दौरान हवा की मौसम संबंधी स्थितियों के कारण हो सकता है।
4. स्पीयरमैन रैंक कौरीलेशन से पता चला कि वेंटिलेशन गुणांक (वीसी), तापमान और सापेक्ष आर्द्रता पीएम सांद्रता को प्रभावित करने वाले मुख्य स्थानीय कारक थे, जो की मौसम के अनुसार बदलते रहते हैं।
5. एमएलआर द्वारा परिणाम निकला कि स्थानीय मौसम संबंधी मापदंडों में परिवर्तनशीलता क्रमशः पीएम_{2.5} और पीएम₁₀ द्रव्यमान में परिवर्तनशीलता; अधिकतम का 50% मानसून और मानसून के बाद के दौरान होती है।
6. क्लस्टर और सीडब्ल्यूटी विश्लेषण ने सर्दियों, मानसून के बाद और पूर्व-मानसून के दौरान क्षेत्रीय स्रोतों से प्रभाव का खुलासा किया जबकि मानसून के मौसम वायु में धूल के एरोसोल विद्यमान थे क्योंकि वे भारत में अफ्रीकी रेगिस्तान और पश्चिमी राज्यों से गुजरते थे।
7. गाजियाबाद में बाहरी पीएम_{2.5} के कारण समय से पहले समाप्त होने की दर का अनुमान ~873 प्रति मिलियन था, जो दिल्ली की तुलना में ~ 70% अधिक है।
8. दोनों स्थलों पर वर्ष के दौरान पीएम_{2.5} के रासायनिक घटकों का औसत वितरण ~ 50% कार्बनयुक्त द्रव्यमान; ~32-33% आयनिक द्रव्यमान; और ~16-19% तात्विक द्रव्यमान था। दोनों स्थलों पर पीएम₁₀ के लिए, कार्बनयुक्त द्रव्यमान ~ 30%; WSII द्रव्यमान ~ 16-22% तात्विक द्रव्यमान ~ 21-26% था।
9. दोनों जगहों पर पीएम द्रव्यमान में विद्यमान प्रमुख WSII थे: NO_3^- , SO_4^{2-} , Cl^- और NH_4^+ जो की पीएम_{2.5} आयनिक द्रव्यमान का औसतन ~ 90% और पीएम₁₀ आयनिक द्रव्यमान का ~ 82% हिस्सा रखते हैं। अन्य मौसमों की तुलना में मानसून में कम पीएच के साथ एरोसोल पूरे वर्ष अम्लीय/मध्यम

अम्लीय (पीएच ~ 4) पाए गए। उच्च एडब्ल्यूसी के कारण पीएम_{2.5} द्रव्यमान (पानी सहित) RH ~90% पर दोगुना हो गया।

10. दोनों पीएम आकार के अंशों और स्थलों में कुल मौलिक द्रव्यमान के औसतन > 90% योगदान देने वाले प्रमुख ट्रेस तत्व Al, Si, Fe, nwsK, Zn और Pb थे।
11. USEPA PMF5 का उपयोग करके आठ स्रोतों का पता किया गया। पीएम_{2.5} द्रव्यमान में उनके योगदान के घटते क्रम में स्रोत थे: वाहन उत्सर्जन (22%), द्वितीयक गठन (21%), दहन एयरोसोल (18%), resuspended धूल I (14%), resuspended धूल II (10) %, ईंट निर्माण (9%), मिश्रित धातु प्रसंस्करण (5%) और कॉपर स्मेल्टर (4%)। पीएम₁₀ द्रव्यमान में स्रोत योगदान थे: resuspended धूल I (25%), resuspended धूल II (24%), दहन एयरोसोल (24%), माध्यमिक गठन (12%), वाहन उत्सर्जन (7%), कॉपर स्मेल्टर (5%)), ईंट निर्माण (3%) और मिश्रित धातु प्रसंस्करण (1%)।
12. उन दिनों जब 24 घंटे की औसत पीएम_{2.5} सांद्रता >90 μgm^{-3} थी, ईंट प्रसंस्करण और वाहन उत्सर्जन मुख्य रूप से जिम्मेदार थे। पीएम₁₀ के मामले में, जब 24 घंटे की औसत सांद्रता >250 μgm^{-3} थी, मिश्रित दहन और resuspended धूल (I&II) मुख्य योगदानकर्ता थे।
13. संभावित स्रोत क्षेत्र स्थानीय होने के साथ-साथ क्षेत्रीय प्रकृति के थे, रिसेप्टर साइट पर मापे गए पीएम_{2.5} और पीएम₁₀ के लिए ऊपरी इंडो गंगा क्षेत्र के राज्य, पंजाब, हरियाणा, दिल्ली महत्वपूर्ण स्रोत क्षेत्र हैं। इसके अलावा, विशेष रूप से, resuspended धूल II के लिए, जो उच्च पीएम₁₀ दिनों के दौरान पीएम₁₀ में मुख्य योगदानकर्ताओं में से एक है, संभावित स्रोत शहर में चल रहा निर्माण है।

इस अध्ययन के परिणामों से गाजियाबाद के लिए वायु गुणवत्ता प्रबंधन योजनाओं को मजबूत करने की उम्मीद है। इस अध्ययन के परिणामों का उपयोग नियामक निकायों द्वारा उचित नियंत्रण रणनीति तैयार करने के लिए किया जा सकता है। साथ ही, दिल्ली से इसकी निकटता को देखते हुए, यह उम्मीद की जाती है कि गाजियाबाद में वायु गुणवत्ता प्रबंधन में सुधार से भारत में पूरे राष्ट्रीय राजधानी क्षेत्र को लाभ होगा। इसके अलावा, यह आशा की जाती है कि इस अध्ययन के परिणाम उत्सर्जन सूची के साथ-साथ क्षेत्र में जलवायु मॉडल आउटपुट को मान्य करने के लिए इनपुट प्रदान करेंगे।

TABLE OF CONTENTS

Certificate	i
Acknowledgement	ii
Abstract.....	iii
Table of Contents	vii
List of figures.....	xii
List of tables.....	xvii
List of Abbreviations	xxi
Chapter 1: Introduction	1
1.1 Atmospheric aerosols – definition, concentration, impacts, chemical composition and sources.....	1
1.1.1 Definition	1
1.1.2 Aerosol concentration in India.....	2
1.1.3 Aerosol health impacts.....	3
1.1.4 Aerosol climate impacts.....	4
1.1.5 Variability of chemical composition and sources	5
1.2 Motivation and objective of the current study	6
1.2.1 Gaps in existing knowledge.....	24
1.2.2 Objectives	24
1.2.3 Thesis Organization	25
Chapter 2 : Methodology.....	27
2.1 Measurement campaign	28
2.1.1 Site selection and sampler location.....	28
2.1.2 Ambient aerosol sampling devices	30

2.1.3 Sampling protocol.....	30
2.1.4 Filter substrate preparation and sample storage.....	31
2.2 PM mass measurement	33
2.3 Chemical analysis methodology	34
2.3.1 Carbonaceous fractions.....	35
2.3.2 Water soluble inorganic ions (WSIIs).....	36
2.3.3 Elements.....	38
2.4 Data screening and analysis methodology.....	40
2.5 Coefficient of Divergence.....	41
2.6 Estimation of PM _{2.5} related premature deaths	41
2.7 Indicators for the transformation of NO ₂ and SO ₂ : SOR and NOR.....	44
2.8 Calculation of Aerosol acidity (pH) and water content (AWC) using ISORROPIA-II	44
2.9 Source apportionment	46
2.9.1 Choice of the source apportionment model	46
2.9.2 Application of Positive Matrix Factorization (PMF) for source apportionment	48
2.10 Probable source locations	49
2.10.1 Conditional Bivariate Probability Function (CBPF).....	50
2.10.2 Concentration-Weighted Trajectory (CWT).....	50
2.10.3 Potential source contribution function (PSCF).....	51
Chapter 3 :	52
Spatio-temporal variability of PM ₁₀ and PM _{2.5} and associated health effects	52
3.1 Data screening and statistical analysis.....	53
3.2 General meteorology over the study area	53
3.3 Temporal and spatial variability of PM ₁₀ and PM _{2.5} over Ghaziabad	54

3.3.1 PM ₁₀ concentration	54
3.3.2 PM _{2.5} concentration.....	57
3.4 Relative contribution of PM _{2.5} to PM ₁₀	62
3.5 Coefficient of Divergence	63
3.6 Effect of meteorology	63
3.6.1 Correlation with meteorological parameters.....	63
3.6.2 Role of local wind speed and wind directions	68
3.6.3 Cluster analysis and CWT	70
3.7 Premature mortality estimates.....	73
3.8 Summary	74
Chapter 4 : Chemical composition of Aerosols.....	76
4.1 Data pre-processing	77
4.1.1 Carbonaceous fractions.....	77
4.1.2 Water soluble inorganic ions	78
4.1.3 Trace Elements.....	78
4.2 Overall chemical composition	78
4.2.1 Descriptive statistics and mass reconstruction.....	78
4.2.2 Spatial and temporal variation	85
4.3 Carbonaceous fractions.....	87
4.3.1 Spatial and temporal variability	88
4.3.2 Correlation between OC and EC.....	91
4.4 Water Soluble Inorganic Ions (WSIIs)	91
4.4.1 Spatial and temporal variability	92
4.4.2 Role of relative humidity and temperature in WSII formation.....	97

4.4.3 Statistical difference between concentrations	99
4.4.4 Sea salt contribution of ions.....	100
4.4.5 Ammonium Neutralization and key salts present	100
4.4.6 Formation path of SO_4^{2-} and NO_3^- : SOR and NOR	103
4.4.7 Ambient aerosol water content and acidity (pH)	104
4.5 Trace Elements.....	106
4.5.1 Spatial and temporal variability	106
4.6 Summary	110
Chapter 5 : source apportionment of $\text{PM}_{2.5}$ and PM_{10} and their geographical locations.....	112
5.1 Data preparation for USEPA PMF5	113
5.1.1 Input files for PMF5.....	113
5.2 PMF5 solution interpretation	115
5.3 Detailed factor description and probable regional and local source locations.....	118
5.3.1 Combustion aerosol	118
5.3.2 Secondary formation.....	120
5.3.3 Vehicular emissions	122
5.3.4 Resuspended dust I	123
5.3.5 Resuspended dust II	125
5.3.6 Brick Manufacturing.....	126
5.3.7 Copper Smelter	128
5.3.8 Mixed metal processing	130
5.4 Temporal variation of aerosol sources	131
5.5 Major sources responsible for high PM concentration	133
5.6 Ghaziabad PM sources compared to Delhi	134

5.7 Summary	136
Chapter 6 Conclusion and scope of future work	138
References	141
Appendix A: Supporting data	160
Supporting Tables	161
Supporting Figures.....	172
Appendix B: Publications and Conference Presentations.....	184
Appendix C: Curriculum Vitae.....	186

LIST OF FIGURES

Figure 1.1: Schematic of the atmospheric particle size distribution (Barbara Finlayson-Pitts James Pitts, 2000)	2
Figure 1.2: Mortality rate ratio vs. PM _{2.5} concentration in six cities of USA (from (Laden et al., 2006)). The letters on the graph represents different cities in the study.....	4
Figure 1.3: Global distribution of mortality attributed to air pollution (from (Lelieveld et al., 2015)	4
Figure 2.1: Outline of the entire study	27
Figure 2.2: Map of India locating New Delhi and Ghaziabad City (upper right panel) and location of sites in Ghaziabad (bottom right panel). Ghaziabad map has been taken from the state government's website (https://ghaziabad.nic.in/); Yearly wind rose plot (2.2a, 2.2b, 2.2c); five-year back trajectories from HYSPLIT during winter (2.2d), pre-monsoon (2.2e), monsoon (2.2f) and post-monsoon (2.2g).	29
Figure 2.3: Picture of PM sampler, weather station and inverter installed at Site A (left) and Site B (right).....	31
Figure 2.4: Schematic of the filter placement in the PM sampler	31
Figure 2.5: Pictures during sample collection	33
Figure 2.6: Typical thermogram from DRI carbon analyzer	35
Figure 2.7: Typical chromatogram of anions.....	37
Figure 2.8: Typical sample chromatogram of anions	37
Figure 2.9: Predicted particle concentration using ISORROPIA-II vs. measured particle concentration.....	45
Figure 2.10: Approaches for estimating pollution source contributions using receptor models. Specific models are shown in italics and with dotted arrows [Taken from (Viana et al., 2008)].	48

Figure 3.1: Map of India locating New Delhi and Ghaziabad City (left) and location of three sites in Ghaziabad (bottom). Ghaziabad map has been taken from state government's website (https://ghaziabad.nic.in/)	54
Figure 3.2: Variation of PM _{2.5} and PM ₁₀ ; Temperature and Relative Humidity; Wind Speed and Wind Direction; Planetary Boundary Layer Height (PBLH) and Precipitation at Site A during the sampling duration.....	55
Figure 3.3: Time series of PM _{2.5} and PM ₁₀ ; Temperature and Relative Humidity; Wind Speed and Wind Direction; Planetary Boundary Layer Height (PBLH) and Precipitation at Site B.	56
Figure 3.4: Time series of PM _{2.5} and PM ₁₀ ; Temperature and Relative Humidity; Wind Speed and Wind Direction; Planetary Boundary Layer Height (PBLH) and Precipitation at Site C.	56
Figure 3.5: Annual and seasonal variation in PM ₁₀ and PM _{2.5} concentration at the three sites. Box enclosed by the 25th and 75th percentile limits, the median (solid line) and mean (cross) within the box, whiskers indicating the maximum and minimum and outliers are shown by circles outside the whiskers	57
Figure 3.6: PM ₁₀ (left panel) and PM _{2.5} (right panel) CBPF plots at the three sites for all four seasons	70
Figure 3.7: Seasonal air mass trajectory clusters. The black dot represents location of Ghaziabad.	72
Figure 3.8: Seasonal CWT plots of PM ₁₀ (left panel) and PM _{2.5} (right panel) in Ghaziabad. The black dot represents Ghaziabad's location.....	73
Figure 3.9: Deaths attributable to ambient PM _{2.5} by disease cause. LRI = Lower respiratory infection; TBLC = Tracheal, bronchus and lung cancer (TBLC); IHD = Ischemic heart disease; COPD = Chronic obstructive pulmonary disease (COPD) and DMT2 = Diabetes mellitus Type 2 in Ghaziabad (left panel) and comparison of per million mortality estimates in Ghaziabad and Delhi (right panel).....	74
Figure 4.1: Chemical constituent plot. Top panel is for PM _{2.5} and bottom panel is for PM ₁₀ . Left panel shows the mass concentration, and the right panel shows the mass fraction.	83
Figure 4.2: Reconstructed mass vs. gravimetric mass for a)PM _{2.5} and b) PM ₁₀	85

Figure 4.3: Day-to-day and monthly variability of OC, EC and OC/EC at both sites for both size fractions.....	90
Figure 4.4: Scatter plots between OC and EC for PM _{2.5} [(a) Site A and (b) Site B]; for PM ₁₀ [(c) Site A and (d) Site B.	91
Figure 4.5: Annual mean WSII mass concentration (left) and %age of the total measured ionic mass of each ion (right) for PM _{2.5} and PM ₁₀ at both sites.	92
Figure 4.6: Day-to-day and monthly variability of WSIIs.....	93
Figure 4.7: Seasonal variability in the concentration of WSII for PM _{2.5} and PM ₁₀ at both sites. Concentration is represented in μgm^{-3}	94
Figure 4.8: Variation of concentration of NO_3^- , SO_4^{2-} , Cl^- and NH_4^+ under different weather regimes for both sites and both PM size fractions. Concentration expressed in μgm^{-3}	98
Figure 4.9: Aerosol Neutralization Ratio (ANR) for PM _{2.5} (a) and PM ₁₀ (b) and Total NH_x vs Required NH_x for both PM fractions (c).....	101
Figure 4.10: Aerosol Water Content (AWC) derived from ISORROPIA-II. (a) Boxplots: Distribution of estimated AWC across seasons, Scatterplots – Relationship between (b) AWC & RH and (c) Fit of growing PM _{2.5} mass with RH. (d) Distribution of estimated pH across seasons (e) Relationship between pH and ambient temperature, and (d) Relationship between pH and AWC. Data refer to the average results.	105
Figure 4.11: Elemental mass concentration (left) and mass fraction (right) for PM _{2.5} and PM ₁₀ at both locations during the sampling period.....	106
Figure 4.12: Time series of trace elements in PM _{2.5} and PM ₁₀ at both sites.	107
Figure 4.13: Elemental concentration in PM _{2.5} / Elemental concentration in PM ₁₀ at both sites	109
Figure 4.14: Seasonal and spatial variation in trace elements for PM _{2.5} . and PM ₁₀ . The box is outlined by 25 th and 75 th percentile values; bottom and top whiskers represents minimum and maximum respectively; solid bar in the box represents median and cross represents mean.	110
Figure 5.1: Modelled vs measured PM _{2.5} and PM ₁₀ concentrations.	116

Figure 5.2: PMF5 resolved factor profiles for combustion aerosol	120
Figure 5.3: PMF5 resolved factor profiles for secondary formation	121
Figure 5.4: PMF5 resolved factor profiles for vehicular emissions	123
Figure 5.5: PMF5 resolved factor profiles for resuspended dust I.....	124
Figure 5.6: PMF5 resolved factor profiles for resuspended dust II	126
Figure 5.7: PMF5 resolved factor profiles for brick processing.....	128
Figure 5.8: PMF5 resolved factor profiles for copper smelter	130
Figure 5.9: PMF5 resolved factor profiles for mixed metal processing	131
Figure 5.10: Overall average contribution (in % both sites together) of PMF5 resolved factors to PM _{2.5} and PM ₁₀ ; % source contribution season wise and month wise for PM _{2.5} (top panel) and PM ₁₀ (bottom panel) at both sites	133
Figure 5.11: Average % contribution of sources to mean PM _{2.5} (top panel) and PM ₁₀ (bottom panel) at Site A during the entire year	134
Figure A.1: Photographs of various directions from Site A.	172
Figure A.2: Photographs of various directions from Site B.	173
Figure A.3: PM concentration and accumulated precipitation at three sites during monsoon ..	174
Figure A.4: Location of CPCB monitoring stations in Delhi	174
Figure A.5: SO ₄ ²⁻ /S plots for both sites and both size fractions	175
Figure A.6: Variation in temperature, humidity, PBLH and precipitation during sampling period	175
Figure A.7: Seven (left panel) and nine factor (right panel) profile for PM _{2.5}	176
Figure A.8: Seven (left panel) and nine factor (right panel) profile for PM ₁₀	177
Figure A.9: Average percentage contribution of PMF5 resolved factors to mean PM _{2.5} mass at a) site A and b) site B.....	178

Figure A.10: Average percentage contribution of PMF5 resolved factors to mean PM ₁₀ mass at a) site A and b) site B.....	178
Figure A.11: Brick kiln mapping in and around Ghaziabad using Google Earth Pro overlapped with wind rose plots at site A and B.	179
Figure A.12: Windrose plots for Site A and Site B during post-monsoon and winter season ..	179
Figure A.13: Industrial mapping for Ghaziabad city (boundary highlighted in red).....	180
Figure A.14: Average % contribution of sources to mean PM _{2.5} (top panel) and PM ₁₀ (bottom panel) at Site B during the entire year	181
Figure A.15: Error estimation summary for PM _{2.5}	182
Figure A.16 Error estimation summary for PM ₁₀	183

LIST OF TABLES

Table 1.1: PM ₁₀ and PM _{2.5} annual and 24-hour standards suggested by WHO, EU, USEPA and India	3
Table 1.2: Details of the source apportionment studies carried out since 2000 till date in Delhi and neighboring cities in the IGP	8
Table 2.1: Summary of instruments used for specific chemical analysis	34
Table 2.2: QA-QC parameters for carbon analysis.....	36
Table 2.3: QA-QC parameters for ion analysis.....	38
Table 2.4: Epsilon 5 setup for Ghaziabad PM ₁₀ and PM _{2.5} samples.....	39
Table 2.5: QA-QC parameters for analyzed elements	39
Table 2.6: Baseline mortality data for Uttar Pradesh (https://vizhub.healthdata.org/gbd-compare/india)	43
Table 3.1: Summary statistics of PM (PM ₁₀ and PM _{2.5}) and meteorological parameters for the three sites throughout the study period.	59
Table 3.2: Comparison of PM concentration from the current study to literature. 24-hour integrated samples collected in all the studies	61
Table 3.3: Mann-Whitney U test on the three sites for PM ₁₀ and PM _{2.5}	63
Table 3.4: Spearman rank correlations (ρ) between PM fractions and key meteorological parameters (only ρ values significant at the 95% confidence level are shown)	65
Table 3.5: MLR for PM ₁₀ and PM _{2.5} . N is the number of observations in the data set; NS indicates a non-significant parameter.....	67
Table 4.1: Summary statistics of PM _{2.5} and associated chemical species mass concentration at both Sites A and B. BDL (%) corresponds to the %age of samples whose concentration is lower than the detection limit of the instrument/method by which the analytes were detected. NA	

indicates Not Applicable. Outliers (Mean $\pm$ 3SD) were not considered while presenting the summary statistics. The rows in italics represents species where >60% values were BDL. 79

Table 4.2: Summary statistics of PM₁₀ and associated chemical species mass concentration at both Sites A and B. BDL (%) corresponds to the %age of samples whose concentration is lower than the detection limit of the instrument/method by which the analytes were detected. NA indicates Not Applicable. Outliers (Mean $\pm$ 3SD) were not considered while presenting the summary statistics..... 81

Table 4.3: Average WSII concentration in PM_{2.5} and PM₁₀ during different seasons at both sites 87

Table 4.4: Carbonaceous fractions seasonal summary for both sites and both size fractions 89

Table 4.5: Average WSII concentration in PM_{2.5} and PM₁₀ during different seasons at both sites 94

Table 4.6: Seasonal ratios for the dominant WSII in PM_{2.5} and PM₁₀ at both sites..... 96

Table 4.7: Classification of combinations of temperature and relative humidity in different weather regimes in Ghaziabad 98

Table 4.8: Mann-Whitney U test on WSII concentration in PM_{2.5} and PM₁₀ for site A and site B 99

Table 4.9: Ratio of vital ions and their comparison to the ratios in seawater 100

Table 4.10: R² values between (a) [NH₄⁺] and [SO₄²⁻], (b) [ns-NH₄⁺] and [Cl⁻], (c) [ns-NH₄⁺] and [NO₃⁻], and (d) [ns-NH₄⁺] and [Cl⁻ + NO₃⁻] through different seasons 103

Table 4.11: Sulphur Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR) in different seasons for PM_{2.5} and PM₁₀ 104

Table 5.1: Summary statistics of identified factors (sources) of PM_{2.5} mass 118

Table 5.2: Summary statistics of identified factors (sources) of PM₁₀ mass 118

Table 5.3: PM mass concentration bins to examine source contribution on high PM days 134

Table 5.4: Factor approximate average mass contribution (%) to PM_{2.5} and PM₁₀ at Ghaziabad resolved by this study compared with estimates at Delhi 136

Table A.1: Relative risks (RRs) used by age and sex for each outcome for the particulate matter integrated exposure response curve. LRI is Lower Respiratory Infection, TBLC is Tracheal, Bronchus and Lung Cancer, IHD is Ischaemic Heart Disease, COPD is Chronic Obstructive Pulmonary Disease, DMT2 is Diabetes Mellitus Type 2 against PM _{2.5} concentration of 150 µgm ⁻³	161
Table A.2: Baseline mortality data for Dehi (https://vizhub.healthdata.org/gbd-compare/india). LRI is Lower Respiratory Infection, TBLC is Tracheal, Bronchus and Lung Cancer, IHD is Ischaemic Heart Disease, COPD is Chronic Obstructive Pulmonary Disease, DMT2 is Diabetes Mellitus Type 2	161
Table A.3: Relative risks (RRs) used by age for each outcome for the particulate matter integrated exposure response curve against PM _{2.5} concentration 135 µgm ⁻³ (annual average PM _{2.5} in Delhi during June 2018-May 2019). LRI is Lower Respiratory Infection, TBLC is Tracheal, Bronchus and Lung Cancer, IHD is Ischaemic Heart Disease, COPD is Chronic Obstructive Pulmonary Disease, DMT2 is Diabetes Mellitus Type 2	162
Table A.4: Seasonal average concentration of chemical components (OC, EC, WSIs and elements) in µgm ⁻³ at both sites for PM ₁₀ and PM _{2.5} in Ghaziabad	163
Table A.5: ANR values as reported in literature	165
Table A.6: Coefficient of determination between anions and cations for PM _{2.5}	165
Table A.7: Coefficient of determination between anions and cations for PM ₁₀	166
Table A.8: S/N ratio of PM _{2.5} and PM ₁₀ chemical constituents	166
Table A.9: Constraints imposed on base run for PM _{2.5} and PM ₁₀	167
Table A.10: Bootstrap mapping for constrained eight factor solution with minimum correlation ($r^2=0.6$) for PM _{2.5}	167
Table A.11: Bootstrap mapping for constrained eight factor solution with minimum correlation ($r^2=0.6$) for PM ₁₀	168
Table A.12: Scaled residuals beyond ±3 standard deviations for eight factors constrained run as site and sampling dates for PM _{2.5}	169

Table A.13: Scaled residuals beyond ± 3 standard deviations for eight factors constrained run as site and sampling dates for PM_{10}	170
---	-----

LIST OF ABBREVIATIONS

Acronyms	Expanded Form
<i>AE</i>	Anion Equivalents
<i>BC</i>	Black Carbon
<i>CBPF</i>	Conditional Bivariate Probability Function
<i>CE</i>	Cation Equivalents
<i>CMB</i>	Chemical Mass Balance
<i>CoD</i>	Coefficient of Divergence
<i>COPD</i>	Chronic Obstructive Pulmonary Disease
<i>COPREM</i>	Constrained Physical Receptor Model
<i>CPCB</i>	Central Pollution Control Board
<i>CWT</i>	Concentration Weighted Trajectory
<i>DRI</i>	Desert Research Institute
<i>EC</i>	Elemental Carbon
<i>EF</i>	Enrichment Factor
<i>EU</i>	European Union
<i>IGP</i>	Indo Gangetic Plain
<i>IHD</i>	Ischemic Heart Disease
<i>IMPROVE</i>	Interagency Monitoring for Protected Visual Environments
<i>INDOEX</i>	Indian Ocean Experiment
<i>LRI</i>	Lower respiratory infection
<i>MDL</i>	Method Detection Limit
<i>ME</i>	Multilinear Engine
<i>MLR</i>	Multiple Linear Regression
<i>MSA</i>	Methane Sulfonic Acid
<i>NAAQ</i>	National Ambient Air Quality
<i>NAAQS</i>	National Ambient Air Quality Standards
<i>NCR</i>	National Capital Region
<i>NH</i>	National Highway
<i>NS</i>	Non-significant

Acronyms	Expanded Form
<i>OC</i>	Organic Carbon
<i>PBLH</i>	Planetary Boundary Layer Height
<i>PCA</i>	Principle Component Analysis
<i>PM</i>	Particulate Matter
<i>PMF</i>	Positive Matrix Factorization
<i>PSCF</i>	Potential Source Contribution Function
<i>QBQ</i>	Quartz Behind Quartz
<i>QBT</i>	Quartz Behind Teflon
<i>RCM</i>	Reconstructed Mass
<i>RTI</i>	Research Triangle Institute
<i>TSP</i>	Total Suspended Particles
<i>TTFA</i>	Target Transformation Factor Analysis
<i>USEPA</i>	United States Environmental Protection Agency
<i>VC</i>	Ventilation Coefficient
<i>WHO</i>	World Health Organization
<i>WSIIs</i>	Water Soluble Inorganic Ions