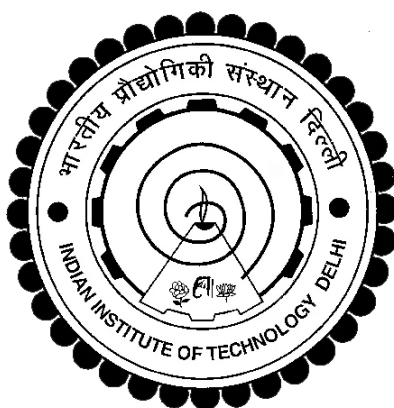


CHEMICAL CHARACTERIZATION, SOURCE APPORTIONMENT, AND FORMATION OF SECONDARY AEROSOLS

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Chemical characterization, source apportionment, and formation of secondary aerosols

by

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*Dedicated “To Allah, the Compassionate
and Merciful, and to His beloved
Messenger Muhammad (peace be upon
him), whose noble teachings illuminate
the path of truth and righteousness.*

Certificate

This is to certify that the thesis entitled “**Chemical characterization, source apportionment, and formation of secondary aerosols**”, submitted by **Mohd Faisal** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of the original, bonafide research work carried out by him under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

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 to the best of our knowledge.

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Abstract

The rapid growth of industrialization and increased energy demand have led to the deterioration of air quality in urban and peri-urban cities. Fine particulate matter, particularly atmospheric particulate matter (PM) with a diameter smaller than 2.5 μm (PM_{2.5}), significantly affects climate forcing and human well-being. At significant levels, prolonged contact with polluted air can lead to various human health-related problems. To expedite particulate matter removal strategies, sources contributing to the pollution need to be identified, apportioned, and removed. This study explored the highly time-resolved variation of the PM_{2.5} bound species sources contributing to both the inorganic and organic constituents, using state-of-the-art real-time online instruments in Delhi, India. We performed the detailed long-term source apportionment, including different components of PM_{2.5} (organics, elements, and black carbon), to provide valuable insights into Delhi's composition and particulate air pollution sources. We found that significant proportion of Delhi's ambient air particulate matter is attributed to the power plant (25-30%), biomass burning (BB) (25-35%), traffic emissions (20-30%), dust-related (5-15%) and industrial emissions (4-7%). Organic aerosol (OA) dominated mass fraction in all seasons, followed by other non-refractory species (SO_4^{2-} , NO_3^- , NH_4^+ , and Cl^-). We observed marked seasonal and diel variability in the concentration and composition of PM_{2.5} owing to the interactions of sources and atmospheric processes. Winter and post-monsoon were the most polluted periods of the year. The apportionment of organic aerosol (OA) yielded primary factors, hydrocarbon-like organic aerosol (HOA), biomass-burning organic aerosol (BBOA), and secondary factors, oxygenated organic aerosols, semi-volatile oxidized OA (SVOOA), low volatile oxidized OA (LVOOA1 and 2). On the other hand, eight sources are identified from the source apportionment of elements such as power plant dust, biomass burning, vehicular emission, secondary chloride, waste incineration, coal combustion, and industrial emission in all seasons. During the Diwali period, fireworks were identified as an additional source of pollution. The secondary chloride factor was dependent on the local wind direction (NW direction, 302–333°). Dust factor was found to dominate the elemental source apportionment in the summer season. Multiple high-loading dust storms were observed in the summer season. During the winter, power plant factors dominate the elemental source apportionment as the formation of sulfate particles was facilitated in the presence of higher RH and aerosol liquid water content (ALWC), indicating the role of rapid aqueous phase formation pathway in secondary aerosol haze formation. However, researchers have integrated data from multiple instruments to better understand PM sources and their chemical composition to

examine PM characteristics. Accordingly, in this study, source apportionment was also performed on a combined dataset consisting of non-refractory PM_{2.5} organic factors, elements, and BC; we evaluated two disparate factor analytic methodologies – namely, double-PMF (D-PMF) and Tracer-conjugate PMF (TC-PMF). The D-PMF, as well as TC-PMF, improved the interpretation of organic factor sources, such as apportioning considerable contributions of LVOOA2 (85%) to the power plant factor, which is often linked with regionally carried aged organic aerosols in the organics only PMF(O-PMF). Lastly, the D-PMF results significantly agreed with TC-PMF, indicating that either of the two techniques could be used to unmix the complex variety of PM_{2.5} sources in the Delhi-NCR region and, arguably, the larger Indo-Gangetic Plains also, since more than 50 % of that organic aerosol mass concentration is comprised of secondary organic aerosol (SOA). However, the underlying formation mechanism of SOA remains poorly understood in Delhi due to chemical complexities, numerous sources of organic precursors, and evolutionary processes. This study also examined the impacts of photochemical and aqueous-phase processing on factors related to SOA.

सारांश

औद्योगीकरण की तीव्र वृद्धि और ऊर्जा की बढ़ती मांग के कारण शहरी और उप-शहरी शहरों में वायु की गुणवत्ता में गिरावट आई है। $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) से छोटे व्यास वाले सूक्ष्म कण पदार्थ, विशेष रूप से वायुमंडलीय कण पदार्थ (PM), जलवायु परिवर्तन और मानव कल्याण को महत्वपूर्ण रूप से प्रभावित करते हैं। महत्वपूर्ण स्तरों पर, प्रदूषित हवा के साथ लंबे समय तक संपर्क से मानव स्वास्थ्य संबंधी विभिन्न समस्याएं हो सकती हैं। पार्टिकुलेट मैटर हटाने की रणनीतियों में तेजी लाने के लिए, प्रदूषण में योगदान देने वाले स्रोतों की पहचान करने, उनका विभाजन करने और उन्हें हटाने की आवश्यकता है। इस अध्ययन ने दिल्ली, भारत में अत्याधुनिक वास्तविक समय ऑनलाइन उपकरणों का उपयोग करके अकार्बनिक और कार्बनिक दोनों घटकों में योगदान देने वाले पीएम_{2.5} बाध्य प्रजातियों के स्रोतों की अत्यधिक समय-समाधान विविधता का पता लगाया। हमने दिल्ली की संरचना और कणिकीय वायु प्रदूषण स्रोतों में मूल्यवान अंतर्दृष्टि प्रदान करने के लिए, $\text{PM}_{2.5}$ (जैविक, तत्व और ब्लैक कार्बन) के विभिन्न घटकों सहित विस्तृत दीर्घकालिक स्रोत विभाजन का प्रदर्शन किया। हमने पाया कि दिल्ली के परिवेशीय वायु कणों का महत्वपूर्ण हिस्सा बिजली संयंत्र (25-30%), बायोमास जलने (बीबी) (25-35%), यातायात उत्सर्जन (20-30%), धूल से संबंधित (5) के लिए जिम्मेदार है। -15%) और औद्योगिक (4-7%)। सभी मौसमों में कार्बनिक एरोसोल (OA) का बड़े पैमाने पर प्रभुत्व रहा, इसके बाद अन्य गैर-दुर्दम्य प्रजातियों (NO_3 , SO_4 , NH_4 , Cl) का स्थान रहा। हमने स्रोतों और वायुमंडलीय प्रक्रियाओं की परस्पर क्रिया के कारण $\text{PM}_{2.5}$ की सांद्रता और संरचना में मौसमी और दैनिक परिवर्तनशीलता देखी। सर्दी और मानसून के बाद की अवधि वर्ष की सबसे प्रदूषित अवधि थी। कार्बनिक एरोसोल (OA) के विभाजन से प्राथमिक कारक, हाइड्रोकार्बन जैसे कार्बनिक एरोसोल (HOA), बायोमास जलाने वाले कार्बनिक एरोसोल (BBOA), और द्वितीयक कारक, ऑक्सीजन युक्त कार्बनिक एरोसोल, अर्ध-वाष्पशील ऑक्सीकृत OA (SVOOA), कम वाष्पशील ऑक्सीकृत प्राप्त हुए। OA (LVOOA1 और 2)। स्रोतों और उनकी रासायनिक संरचना को बेहतर ढंग से समझने के लिए कई उपकरणों से डेटा को एकीकृत किया है। तदनुसार, इस अध्ययन में, गैर-दुर्दम्य $\text{PM}_{2.5}$ कार्बनिक कारकों, तत्वों और बीसी से युक्त एक संयुक्त डेटासेट पर स्रोत विभाजन भी किया गया था; हमने दो असमान कारक विश्लेषणात्मक पद्धतियों का मूल्यांकन किया - अर्थात्, डबल-पीएमएफ (डी-पीएमएफ) और ट्रेसर-संयुग्म पीएमएफ (टीसी-पीएमएफ)। डी-पीएमएफ, साथ ही टीसी-पीएमएफ ने कार्बनिक कारक स्रोतों की व्याख्या में सुधार किया, जैसे कि बिजली संयंत्र कारक में एलवीओओ 2 (85%) के महत्वपूर्ण योगदान को विभाजित करना, जो अक्सर क्षेत्रीय रूप से ले जाए गए वृद्ध कार्बनिक एरोसोल से जुड़ा होता है। केवल ऑर्गेनिक्स पीएमएफ (ओ-पीएमएफ)। अंत में, डी-

पीएमएफ के नतीजे टीसी-पीएमएफ से काफी हद तक सहमत हैं, जो दर्शाता है कि दिल्ली-एनसीआर क्षेत्र और यकीनन, बड़े सिंधु-गंगा के मैदानों में पीएम_{2.5} स्रोतों की जटिल विविधता को अलग करने के लिए दोनों तकनीकों में से किसी एक का उपयोग किया जा सकता है। . इसके अलावा, चूंकि उस कार्बनिक एरोसोल द्रव्यमान सांद्रता का 50% से अधिक भाग द्वितीयक कार्बनिक एरोसोल (एसओए) से बना होता है। हालाँकि, रासायनिक जटिलताओं, कार्बनिक अग्रदूतों के कई स्रोतों और विकासवादी प्रक्रियाओं के कारण दिल्ली में SOA के अंतर्निहित गठन तंत्र को कम समझा जाता है। इस अध्ययन में, हमने SOA से संबंधित कारकों पर फोटोकैमिकल और जलीय-चरण प्रसंस्करण के प्रभावों की भी जांच की।

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