

**CHEMICAL CHARACTERIZATION AND SOURCE
APPORTIONMENT OF PM_{2.5} AT KERBSIDE LOCATIONS IN
DELHI CITY**

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DELHI CITY**

by

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Department of Civil Engineering

Submitted

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to the



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“what we do, echoes in eternity...”

- Gladiator

CERTIFICATE

This is to certify that the thesis entitled “**Chemical Characterization and Source Apportionment of PM_{2.5} at Kerbside Locations in Delhi City**”, being submitted by **Ms. Isha Khanna** has been prepared under our supervision in conformity with the rules and regulations of the **Indian Institute of Technology Delhi**. We further certify that the thesis has attained a standard required for the award of the degree of **Doctor of Philosophy** of the institute. The work, or any part thereof, has not been submitted elsewhere for the award of any other degree or diploma.

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ABSTRACT

Urban air pollution has been one of the major problems affecting public health and the environment around the globe. Due to urbanisation and fast-paced development, the problem has been more complex and severe in developing countries when compared to developed world particularly in terms of health impacts (Lanki *et al.*, 2006; Pope *et al.*, 2006; Wang *et al.*, 2017). One of the major causes is unplanned growth of the cities, exponential increase in population and number of motorized vehicles. These ultimately lead to increase in air pollutants, in particular, Particulate Matter (PM) in the ambient atmosphere. PM, one of the six criteria pollutants, is an important indicator of air quality. In a study in Delhi city, India, the annual average PM₁₀ and PM_{2.5} concentrations have been reported to be $232.1 \pm 131.1 \mu\text{g}/\text{m}^3$ (standard – $60 \mu\text{g}/\text{m}^3$) and $118.3 \pm 81.7 \mu\text{g}/\text{m}^3$ (standard – $40 \mu\text{g}/\text{m}^3$) (Tiwari *et al.*, 2015). These values have been much higher than the prescribed annual ambient average standards of Indian air quality (CPCB, 2011b). The characteristics of PM depend on sources of origin and their emission rates (Srimuruganandam and Nagendra, 2012b; Khanna, Khare and Gargava, 2015). It typically contains wide range of chemical species, ranging from metals to organic and inorganic compounds (Zhang *et al.*, 2006; Srivastava and Jain, 2008; Pindado and Perez, 2011; Sharma and Dikshit, 2016; Singh *et al.*, 2017). Identification and quantification of various sources has, therefore, become necessary to link them with existing air quality levels measured at certain locations as well as predict air quality at various locations. It helps in assessing the impact of nearby sources and also to evaluate the control strategies for some emission sources. The relationship between exposure to PM concentration and associated health effects have been linked with chemical characteristics of the PM, thereby making it important for air quality management in urban areas (Bonasoni *et al.*, 2008; Singh *et al.*, 2017). The present research aims to develop a more fundamental understanding of the chemical

characteristics of PM_{2.5} emitted from a large number of sources at two kerbside locations – one at a highway with predominantly vehicular emissions and one at an institutional area with mixed sources. The research aims to identify and apportion the dominant sources using receptor models. It also compares the performance of two widely used receptor models, Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF), to check their suitability and robustness in Indian conditions. The diurnal concentrations of PM_{2.5} and its constituents have been observed to be significantly different at both sites. It has been observed during the night time, the PM_{2.5} concentrations are 1.5 times higher than daytime in winter and summer seasons. This may be due to inter-city movements of diesel-fuelled (BS-III) heavy duty vehicles entering through the Delhi city and open biomass burning especially during winter season (CPCB, 2011a; Sharma and Dikshit, 2016). Chemical characterization of both organic and inorganic components has been carried out which has shown that the crustal elements to be non-enriched as they are emitted from natural sources, i.e. upper soil strata. The organic molecular marker analysis has found that coal and biomass combustion primarily contributes to organic carbon during winters; whereas, vehicular emissions are dominant sources of organic carbon during summers. The risk has been estimated using excess cancer risk by calculating the benzo(a)pyrene-equivalent concentrations of poly aromatic hydrocarbons which indicate higher values during winters than summers at both the sites. The comparative performance analysis of PMF and CMB have found satisfactory performance of both models having reasonable correlations between modelled and observed values. PMF has advantage over Principal Component Analysis due to its non-negativity constraint which provides solutions closer to real-world scenarios. The results have shown that in absence of locally available source profiles, PMF may preferably be used instead of CMB.

सार

शहरी वायु प्रदूषण दुनिया भर में सार्वजनिक स्वास्थ्य और पर्यावरण को प्रभावित करने वाली प्रमुख समस्याओं में से एक है। शहरीकरण और तेज गति से विकास के कारण, विकसित देशों की तुलना में स्वास्थ्य संबंधी समस्याओं की तुलना में समस्या अधिक जटिल और गंभीर हो गई है, विशेष रूप से स्वास्थ्य प्रभावों के मामले में (लंका आदि, २,००६; पोप आदि, २,००६; वांग आदि, २,०१७)। प्रमुख कारणों में से एक शहरों की अनियोजित विकास, आबादी में घातीय वृद्धि और मोटर वाहनों की संख्या ये अंततः वायु प्रदूषण में बढ़ जाती है, विशेष रूप से, परिवेशी वातावरण में पार्टिकुलेट मैटर (पीएम)। पीएम, छह मापदंड प्रदूषकों में से एक, हवा की गुणवत्ता का एक महत्वपूर्ण संकेत है। दिल्ली शहर, भारत में एक अध्ययन में, वार्षिक औसत पीएम_{१०} और पीएम_{२.५} सांद्रता २३२.१±१३१.१ माइक्रोग्राम/मी^३ (मानक- ६० माइक्रोग्राम/मी^३) और ११८.३±८१.७ माइक्रोग्राम/ मी^३ (मानक-४० माइक्रोग्राम/मी^३) (तिवारी आदि, २०१५)। ये मूल्य भारतीय वायु गुणवत्ता (सीपीसीबी, २,०११बी) के निर्धारित वार्षिक परिवेश औसत मानकों की तुलना में काफी अधिक है। पीएम की विशेषताएं मूल स्रोतों और उनके उत्सर्जन दर पर निर्भर करती हैं (श्रीमूर्गानन्दम और नागेंद्र, २०१२बी, खन्ना, खर और गारगाव, २०१५)। इसमें आम तौर पर रासायनिक प्रजातियों की व्यापक श्रेणी होती है, जिसमें धातुओं से लेकर कार्बनिक और अकार्बनिक यौगिकों (झांग आदि २,००६ तक, श्रीवास्तव और जैन, २००८; पिंडडो और पेरेज़, २,०११) शर्मा और दीक्षित, २,०१६, सिंह आदि, २,०१७)। इसलिए विभिन्न स्रोतों की पहचान और मात्रा का ठहराव, इसलिए, कुछ स्थानों पर मापा मौजूदा वायु गुणवत्ता के स्तर के साथ जोड़ने के साथ-साथ विभिन्न स्थानों पर वायु की गुणवत्ता का अनुमान लगाने के लिए आवश्यक हो गया है। यह पास के स्रोतों के प्रभाव का आकलन करने और कुछ उत्सर्जन स्रोतों के लिए नियंत्रण रणनीतियों का मूल्यांकन करने में भी सहायता करता है। पीएम एकाग्रता और संबद्ध स्वास्थ्य प्रभावों के संपर्क में पीएम के रासायनिक गुणों से

जुड़े हुए हैं, जिससे शहरी इलाकों में वायु गुणवत्ता प्रबंधन के लिए महत्वपूर्ण बना हुआ है (बोनसनी आदि, २००८; सिंह आदि, २,०१७)। वर्तमान अनुसंधान का उद्देश्य पीएम द्वारा 2 करब साइड स्थानों पर बड़ी संख्या में स्रोतों से उत्सर्जित पीएम_{२.५} की रासायनिक विशेषताओं की अधिक मूलभूत समझ विकसित करना है - मुख्य रूप से वाहन उत्सर्जन के साथ राजमार्ग पर एक और मिश्रित स्रोतों वाला एक संस्थागत क्षेत्र। रिसेप्टर मॉडल का उपयोग करके प्रमुख स्रोतों को पहचानने और उन्हें विभाजित करने के लिए अनुसंधान का लक्ष्य है। यह भारतीय परिस्थितियों में उनकी उपयुक्तता और मजबूती की जांच करने के लिए दो व्यापक रूप से प्रयुक्त रिसेप्टर मॉडल, केमिकल मास बैलेंस (सीएमबी) और पॉजिटिव मैट्रिक्स फैक्टोरिजेशन (पीएमएफ) के प्रदर्शन की तुलना भी करता है। पीएम_{२.५} और उसके घटकों की रोजमर्रा की सांद्रता को दोनों साइटों पर काफी अलग-अलग देखा जा रहा है। यह रात के समय के दौरान मनाया जाता है, पीएम_{२.५} सांद्रता सर्दियों में १.५ गुना अधिक है और गर्मी के मौसम। यह दिल्ली शहर के माध्यम से प्रवेश करने वाले डीजल-ईंधन वाले (बीएस-तृतीय) भारी शुल्क वाले वाहनों के अंतर शहर आंदोलनों और सर्दियों के मौसम (सीपीसीबी, २,०११ए; शर्मा और दीक्षित, २,०१६) के दौरान विशेष रूप से खुला बायोमास जल के कारण हो सकता है। जैविक और अकार्बनिक दोनों अवयवों के रासायनिक लक्षण वर्णन किया गया है, जिसमें पता चला है कि क्रस्टल तत्वों को गैर-समृद्ध होना चाहिए क्योंकि वे प्राकृतिक स्रोतों से उत्सर्जित होते हैं, अर्थात् ऊपरी मिट्टी की सतह। कार्बनिक आणविक मार्कर विश्लेषण में पाया गया है कि कोयले और बायोमास दहन मुख्य रूप से सर्दियों के दौरान कार्बनिक कार्बन में योगदान देता है; जबकि, ग्रीष्म ऋतु के दौरान वाहन उत्सर्जन कार्बनिक कार्बन के प्रमुख स्रोत हैं। बेंज़ो(ए)पाइरीन-बराबर पॉलि सुगंधित हाइड्रोकार्बन की सांद्रता की गणना करके जोखिम का अतिरिक्त कैंसर जोखिम का अनुमान लगाया गया है जो दोनों साइटों पर ग्रीष्मकाल की तुलना में सर्दियों के दौरान उच्च मूल्यों को दर्शाता है। पीएमएफ और सीएमबी के तुलनात्मक निष्पादन विश्लेषण दोनों मॉडलों के संतोषजनक प्रदर्शन को मिला है जो मॉडलिंग और मनाया मूल्यों के बीच उचित

सहसंबंध रखता है। पीएमएफ ने अपनी गैर-नकारात्मकता बाधा के कारण प्रधान घटक विश्लेषण पर लाभ प्राप्त किया है जो वास्तविक दुनिया परिदृश्यों के करीब समाधान प्रदान करता है। परिणाम दिखाते हैं कि स्थानीय रूप से उपलब्ध स्रोत प्रोफाइल के अभाव में, पीएमएफ को सीएमबी के बजाय अधिमानतः उपयोग किया जा सकता है।

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Abbreviations

ALA	American Lung Association
CMB	Chemical Mass Balance
CNG	Compressed Natural Gas
DPCC	Delhi Pollution Control Committee
EC	Elemental Carbon
EPA	Environmental protection Agency
GC-MS	Gas Chromatogram- Mass Spectrometer
IC	Ion Chromatogram
LCV	Light Commercial Vehicles
OC	Organic Carbon
PCA	Principal Component Analysis
PM	Particulate Matter
PM ₁	Particulate Matter with diameter less than 1 micron
PM _{2.5}	Particulate Matter with diameter less than 2.5 microns
PM ₁₀	Particulate Matter with diameter less than 10 microns
PMF	Positive Matrix Factorization
SIA	Secondary Inorganic Aerosols
SOA	Secondary Organic Aerosol
SPM	Suspended Particulate Matter
TOT	Thermal Optical Treatment
TSP	Total Suspended Particulate matter
WHO	World Health Organization
XRF	X-ray Diffraction