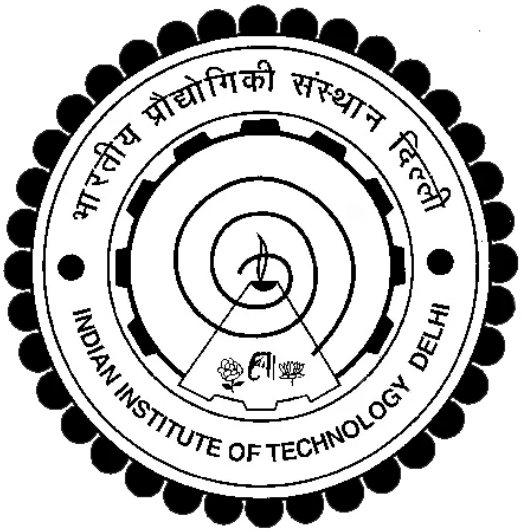
FROM NUCLEATION TO HAZE: AEROSOL EVOLUTION IN POLLUTED ENVIRONMENTS

UMER ALI



DEPARTMENT OF CHEMICAL ENGINEERING

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FROM NUCLEATION TO HAZE: AEROSOL EVOLUTION IN POLLUTED ENVIRONMENTS

By

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Submitted

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"And do not cause corruption upon the earth after its reformation."

(Qur'an 7:56)

With deep gratitude and reverence, I dedicate this work:

To Allah, the Most Gracious, the Wisest, the Giver of knowledge and the Sustainer of all that exists.

To all His noble Messengers, who illuminated the world with guidance, truth, and compassion.

And to the priceless gift of clean air, an unseen blessing that sustains life and reminds us of our sacred duty to protect and cherish the Earth.

Certificate

This is to certify that the thesis entitled “From Nucleation to Haze: Aerosol Evolution in Polluted Environments”, submitted by Umer Ali 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.

Prof. Vikram Singh
Department of Chemical Engineering,
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Prof. Mayank Kumar
Department of Mechanical Engineering,
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Abstract

Fine particulate matter ($PM_{2.5}$) adversely impacts human health, climate, air quality, and visibility, necessitating effective mitigation strategies. Addressing these challenges requires a thorough understanding chemical composition, physical properties (e.g., hygroscopicity, phase state), and atmospheric interactions (e.g., gas-particle partitioning, secondary formation) of $PM_{2.5}$. However, persistent knowledge gaps, particularly in quantifying sources, formation pathways, and thermodynamic behaviour, hinder region-specific policy development, especially in pollution hotspots like the Indo-Gangetic Plain (IGP). This study investigates two critical aerosol processes in Delhi, a representative IGP megacity: (1) new particle formation (NPF) and (2) hygroscopic water uptake driving aerosol liquid water content (ALWC). Using real-time non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$) data from an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) and thermodynamic modelling (ISORROPIA II), we analysed ALWC dynamics for two winter periods (Dec 2019–Jan 2020 and Dec 2020–Feb 2021). A 50% increase in average NR-$PM_{2.5}$ concentrations (from 102 μg/m³ to 152 μg/m³) resulted in a 60% rise in ALWC, which exhibited exponential growth with relative humidity (RH), becoming significant at RH >80%. Ammonium sulphate dominated ALWC uptake at lower RH, while ammonium nitrate prevailed at higher RH. Elevated $PM_{2.5}$ and RH significantly reduced visibility, with light scattering efficiency increasing by more than 3.5 times at RH >85%. Chloride (Cl) concentrations in $PM_{2.5}$ have halved in recent years, reducing their contribution to ALWC. While nitrate and sulphate, the other major contributors to ALWC, are linked to power plants and vehicular emissions, the sources of chloride remain poorly understood. Source apportionment studies in Delhi have struggled to identify the exact sources of chloride due to weak correlations with primary tracers. This study investigated one potential source of chloride: crop residue (stubble) burning. Real-time $PM_{2.5}$ chemical composition data from stubble burning hotspots in rural Punjab during peak stubble burning demonstrated strong correlations between Cl and primary biomass burning tracers (potassium; K, organic aerosols; OA, black carbon; BC). Elemental source apportionment in Punjab attributed ~80% of chloride to stubble burning, supported by diagnostic Cl/K molar ratios (~2), indicative of gaseous chloride emissions beyond potassium chloride (KCl). In contrast, Delhi's chloride dynamics were predominantly governed by meteorological processes, with secondary chloride formation contributing 70–80% of total chloride and biomass burning accounting for only 10–20%. Diagnostic ratios (Cl/K, Cl/OA, Cl/BC) in Delhi revealed a complex mix of sources: post-monsoon chloride signatures aligned with Punjab's stubble burning, while elevated Cl/K ratios

in other seasons (summer, winter) pointed to non-biomass sources like waste burning or industrial emissions. We also investigated the seasonal characteristics of particle size distribution (PSD) in Delhi's atmosphere, with a special focus on NPF. Our findings reveal pronounced seasonal variations in particle number and mass concentration levels following the variations in atmospheric conditions and emission sources across different seasons. Condensation sink (CS) emerged as a primary factor governing NPF, with no NPF events observed when daytime CS exceeded 0.06 s^{-1}. NPF events were characterized by relatively high formation rates, high sulphuric acid concentrations, and a relatively large CS compared to cleaner and more pristine environments. The estimated formation rates were comparable to other polluted regions and could be explained by mechanisms involving H_2SO_4, ammonia and amines like dimethylamine (DMA). On days with comparable CS, chemical composition showed no significant variation between NPF and non-NPF days, with organics contributing ~50% of $PM_{2.5}$, emphasizing the dominance of physical processes. Higher atmospheric liquid water content, driven by elevated RH, inhibited NPF, highlighting the critical influence of relative humidity on particle formation. Additionally, simultaneous analysis of PSD and $PM_{2.5}$ mass composition revealed significant variations during daytime and night-time growth phases. Daytime growth of nucleated particles was associated with increases in sulphate and low-volatility oxygenated organics, suggesting the involvement of sulphuric acid and oxidized vapours in early particle growth. This study highlights the need for comprehensive, long-term monitoring of ALWC, PSD, and $PM_{2.5}$ chemical composition to address Delhi's air quality challenges. Mitigation strategies should prioritize reducing inorganic $PM_{2.5}$ concentrations to lower ALWC and improve visibility, while at the same time focus on controlling precursor gases such as sulphuric acid and organic vapours to limit the formation of ultrafine particles, which have significant health and climate impacts.

सारांश

सूक्ष्म कणिकीय पदार्थ (PM2.5) मानव स्वास्थ्य, जलवायु, वायु गुणवत्ता और दृश्यता पर प्रतिकूल प्रभाव डालता है, जिससे प्रभावी न्यूनीकरण रणनीतियों की आवश्यकता होती है। इन चुनौतियों का समाधान करने के लिए PM2.5 के रासायनिक संघटन, भौतिक गुणों (जैसे, जल-अवशोषण क्षमता, अवस्था) और वायुमंडलीय अंतःक्रियाओं (जैसे, गैस-कण विभाजन, द्वितीयक निर्माण) की गहन समझ आवश्यक है। हालांकि, विशेष रूप से स्रोतों, निर्माण मार्गों और ऊष्मागतिक व्यवहार के मात्रात्मक आकलन में ज्ञान की कमी, क्षेत्र-विशेष नीति निर्माण में बाधा उत्पन्न करती है, खासकर इंडो-गंगेटिक प्लेन (IGP) जैसे प्रदूषण हॉटस्पॉट में। यह अध्ययन दिल्ली, एक प्रतिनिधि IGP महानगर, में दो महत्वपूर्ण एरोसोल प्रक्रियाओं की जांच करता है: (1) नए कण निर्माण (NPF) और (2) जल-अवशोषण द्वारा एरोसोल द्रव जल सामग्री (ALWC) का निर्माण। एरोडाइन एरोसोल केमिकल स्पेशिएशन मॉनिटर (ACSM) से प्राप्त वास्तविक समय के गैर-दहनशील $PM_{2.5}$ (NR-$PM_{2.5}$) डेटा और ऊष्मागतिक मॉडलिंग (ISORROPIA II) का उपयोग करते हुए, हमने दो शीतकालीन अवधियों (दिसंबर 2019–जनवरी 2020 और दिसंबर 2020–फरवरी 2021) के लिए ALWC की गतिशीलता का विश्लेषण किया। NR-$PM_{2.5}$ की औसत सांद्रता में 50% की वृद्धि (102 $\mu g/m^3$ से 152 $\mu g/m^3$) के परिणामस्वरूप ALWC में 60% की वृद्धि हुई, जो सापेक्ष आर्द्रता (RH) के साथ घातीय रूप से बढ़ी और RH >80% पर महत्वपूर्ण हो गई। अमोनियम सल्फेट ने कम RH पर ALWC अवशोषण पर प्रभुत्व दिखाया, जबकि अमोनियम नाइट्रेट उच्च RH पर प्रभावी था। उच्च $PM_{2.5}$ और RH ने दृश्यता को काफी कम कर दिया, जहाँ RH >85% पर प्रकाश प्रकीर्णन दक्षता 3.5 गुना से अधिक बढ़ गई। हाल के वर्षों में $PM_{2.5}$ में क्लोराइड (Cl) सांद्रता आधी हो गई है, जिससे ALWC में उनका योगदान कम हुआ है। हालांकि, नाइट्रेट और सल्फेट, जो ALWC के अन्य प्रमुख योगदानकर्ता हैं, बिजली संयंत्रों और वाहन उत्सर्जन से जुड़े हैं, क्लोराइड के स्रोत अभी भी अस्पष्ट हैं। दिल्ली में स्रोत विभाजन अध्ययनों में क्लोराइड के सटीक स्रोतों की पहचान करने में कठिनाई हुई है क्योंकि यह प्राथमिक ट्रेसर्स के साथ कमजोर सहसंबंध दिखाता है। इस अध्ययन में क्लोराइड के एक संभावित स्रोत–फसल अवशेष (पराली) जलाने–की जाँच की गई। पंजाब के ग्रामीण क्षेत्रों में पराली जलाने के चरम समय के दौरान वास्तविक समय $PM_{2.5}$ रासायनिक संघटन डेटा ने Cl और प्राथमिक बायोमास जलने के ट्रेसर्स (K, OA, BC) के बीच मजबूत सहसंबंध दिखाया। पंजाब में तत्व-आधारित स्रोत विभाजन ने ~80% क्लोराइड को पराली जलाने से जोड़ा, जिसे Cl/K मोलर अनुपात (~2) द्वारा समर्थित किया गया, जो KCl से परे गैसीय क्लोराइड उत्सर्जन का संकेत देता है। इसके विपरीत, दिल्ली में क्लोराइड गतिशीलता मुख्यतः मौसम संबंधी प्रक्रियाओं द्वारा नियंत्रित थी, जहाँ द्वितीयक क्लोराइड निर्माण कुल

क्लोराइड का 70–80% योगदान देता है और बायोमास जलाने का योगदान केवल 10–20% है। दिल्ली में नैदानिक अनुपात (Cl/K, Cl/OA, Cl/BC) ने स्रोतों का एक जटिल मिश्रण दिखाया: मानसून के बाद के क्लोराइड संकेत पंजाब के पराली जलाने से मेल खाते थे, जबकि अन्य मौसमों (गर्मी, सर्दी) में उच्च Cl/K अनुपात ने गैर-बायोमास स्रोतों (जैसे कचरा जलाना या औद्योगिक उत्सर्जन) की ओर इशारा किया। हमने दिल्ली के वायुमंडल में कण आकार वितरण (PSD) की मौसमी विशेषताओं का भी अध्ययन किया, विशेष रूप से NPF पर ध्यान केंद्रित करते हुए। हमारे निष्कर्षों से पता चलता है कि वायुमंडलीय परिस्थितियों और उत्सर्जन स्रोतों में मौसमी परिवर्तनों के अनुसार कण संख्या और द्रव्यमान सांद्रता में स्पष्ट मौसमी भिन्नताएँ होती हैं। संघनन सिंक (CS) NPF को नियंत्रित करने वाला प्राथमिक कारक था, जहाँ दिन के समय CS >0.06 s^{-1} होने पर कोई NPF घटना नहीं देखी गई। NPF घटनाओं की विशेषता उच्च निर्माण दर, उच्च सल्फ्यूरिक अम्ल सांद्रता और उच्च CS थी। अनुमानित निर्माण दरें अन्य प्रदूषित क्षेत्रों के समान थीं और H2SO4 तथा एमाइन्स (डाइमिथाइलएमाइन (DMA) और अमोनिया सहित) से जुड़े तंत्रों द्वारा समझाई जा सकती हैं। CS की तुलनीय स्थितियों वाले दिनों में, NPF और गैर-NPF दिनों के बीच रासायनिक संघटन में कोई महत्वपूर्ण अंतर नहीं था, जहाँ कार्बनिक पदार्थ $PM_{2.5}$ का ~50% योगदान देते थे, जो भौतिक प्रक्रियाओं के प्रभुत्व को दर्शाता है। उच्च RH के कारण वायुमंडलीय द्रव जल सामग्री में वृद्धि ने NPF को रोका, जो कण निर्माण पर सापेक्ष आर्द्रता के महत्वपूर्ण प्रभाव को उजागर करता है। इसके अतिरिक्त, PSD और $PM_{2.5}$ द्रव्यमान संघटन का एक साथ विश्लेषण करने से दिन और रात के विकास चरणों के दौरान महत्वपूर्ण भिन्नताएँ देखी गईं। न्यूक्लिएटेड कणों का दिन के समय विकास सल्फेट और कम-वाष्पशील ऑक्सीजनयुक्त कार्बनिक पदार्थों में वृद्धि से जुड़ा था, जो सल्फ्यूरिक अम्ल और ऑक्सीकृत वाष्पों की भूमिका को प्रारंभिक कण विकास में दर्शाता है। यह अध्ययन दिल्ली की वायु गुणवत्ता चुनौतियों का समाधान करने के लिए ALWC, PSD और $PM_{2.5}$ रासायनिक संघटन की व्यापक, दीर्घकालिक निगरानी की आवश्यकता को रेखांकित करता है। न्यूनीकरण रणनीतियों को अकार्बनिक $PM_{2.5}$ सांद्रता को कम करके ALWC को कम करने और दृश्यता में सुधार करने पर ध्यान केंद्रित करना चाहिए, साथ ही सल्फ्यूरिक अम्ल और कार्बनिक वाष्पों जैसे पूर्वगामी गैसों को नियंत्रित करना चाहिए ताकि अति सूक्ष्म कणों के निर्माण को सीमित किया जा सके, जिनका स्वास्थ्य और जलवायु पर महत्वपूर्ण प्रभाव पड़ता है।

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