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 $\mu g/m^3$ to 152 $\mu g/m^3$) 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 (K, OA, 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 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.