

Aerosol hygroscopicity and photodegradation in the polluted Indo-Gangetic Plain compared with the clean Himalayas examined using a quartz crystal microbalance

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Abstract

Reducing climate uncertainty requires a better understanding of the influence of aerosols on clouds and precipitation, particularly their hygroscopicity under subsaturated conditions, which affects their water uptake, associated optical properties, and radiative impacts. To investigate this, PM_{2.5} aerosol samples were analyzed from two contrasting locations: Leh, a high-altitude clean desert plateau in the Himalayas, and Delhi, a heavily polluted urban megacity in the Indo-Gangetic Plain (IGP). A quartz crystal microbalance was used to evaluate hygroscopic growth, including mass loss induced by ultraviolet irradiation. The findings show that Himalayan aerosols have a distinct deliquescence phase transition and high hygroscopicity. In contrast, IGP aerosols have delayed or absent deliquescence and low hygroscopicity. These differences highlight the significant role of chemical composition, particularly the organic fraction, in aerosol behavior. Furthermore, the greater photolytic mass loss observed in Himalayan aerosols suggests the presence of more photolabile components. These results underscore the importance of relative humidity history, chemical composition, and photochemistry in aerosol properties, which are crucial for developing accurate atmospheric models.

Introduction

Aerosols significantly influence climate dynamics by directly affecting the climate through the scattering and absorption of incoming solar radiation, as well as indirectly by serving as cloud condensation nuclei (CCN) or ice nuclei (IN). This interaction modifies cloud albedo, alters cloud lifetimes, and impacts the overall radiation balance of the Earth^{1,2}. The characteristics of aerosols, such as their size distribution, chemical reactivity, atmospheric lifetime, real and imaginary refractive indices, are strongly influenced by their hygroscopic properties and atmospheric aging processes, including photochemical processing^{3–6}. The significant differences in the hygroscopic nature, aging processes, and composition of both organic and inorganic particles in atmospheric aerosols lead to a diverse range of growth factors and phase transitions that must be accurately assessed for inclusion in climate models^{7,8}. The effects of hygroscopicity are particularly important under subsaturated conditions, where aerosol particles continuously interact with atmospheric water vapor, influencing their mass, size, phase state, and optical properties⁹. In this study, we employ a quartz crystal microbalance (QCM) to examine the hygroscopicity based on mass, changes in physical properties, and mass alterations that occur during the photodegradation of ambient aerosols. During photodegradation, organic aerosols (OA) typically break down into smaller, more volatile compounds that can evaporate into the gas phase, resulting in a reduction of OA mass^{4,10}. These photodegradation processes influence the Earth's climate by decreasing mass concentration and particle size, which in turn reduce the efficiency of organic aerosols in scattering sunlight^{4,11}.

The QCM has a significant history of use in atmospheric chemistry, such as examining the degree of water uptake by aerosols, OA evaporation rates, the oxidative aging of organic aerosols, and photosensitized reactions^{3,4,7}. Unlike other methods that are limited to specific particle size ranges and

have restricted relative humidity (RH) resolution, the QCM technique overcomes these challenges^{12,13}. It provides direct measurements of mass changes in the sub-microgram range, allowing precise quantification of aerosol particle behavior in relation to humidity and their degradation when exposed to UV light, all while being deposited on an inert QCM crystal in real time^{3,7}. QCM serves as an instrument for quantifying precise changes in the mass of particles adhered to a piezoelectric crystal by monitoring the frequency of oscillation. Variations in the frequency shift (Δf) are attributable to multiple mechanisms, including the adsorption and desorption of water vapor, as well as changes in the phase state of particulate matter, particularly during transitions between crystalline solids and aqueous phases. Additionally, the release of volatile photoproducts can further modulate the frequency response. Due to the QCM's sensitivity to mass changes at its sensor surface, it provides crucial real-time insights into phenomena such as hygroscopic growth, deliquescence, and efflorescence, in addition to quantifying the mass fraction remaining after photodegradation of ambient or laboratory-generated aerosols^{1,3,4,7,14}.

The Indian subcontinent's unique topographical and geographical characteristics result in a variety of climatic zones¹⁵. A key aspect of the regional climate is the Indian Summer Monsoon (ISM), which occurs from June to September. This period is marked by notable seasonal shifts in tropical rain bands linked to the Intertropical Convergence Zone (ITCZ) and significant wind reversals^{16–18}. The inaugural climate change assessment report of India, released in 2020, indicates that the country has encountered substantial challenges, including rising temperatures and increased frequency of extreme weather events, since the mid-20th century¹⁶. A key obstacle in addressing these challenges is the insufficient systematic measurement of aerosol characteristics within subsaturated regimes¹⁹. The selected sampling locations represent contrasting environments, including a relatively pristine area in the Himalayan region and a polluted environment in the IGP region dominated by anthropogenic emissions. It is anticipated that aerosol particles collected from the pristine location predominantly consist of aged secondary aerosols resulting from long-range transport, while those from the polluted area are primarily composed of locally and regionally sourced primary aerosols. Moreover, the atmospheric processing of complex aerosols complicates the understanding of their phase state and other pertinent properties^{7,20}. This study employs QCM measurements to investigate the relationships among aerosol hygroscopicity, photodegradation, relative humidity, and chemical composition of ambient aerosols collected at these two distinct locations in India. These contrasting environments provide an opportunity to examine how differences in aerosol sources, chemical composition, and atmospheric processing influence hygroscopicity and photochemical transformation.

Results

QCM-derived deliquescence behavior of PM_{2.5}

The study examined the phase transition behaviors, water uptake characteristics, and mass loss of ambient aerosol particles collected at two distinct locations: Leh in the climate-sensitive Himalayas and

Delhi in the heavily polluted Indo-Gangetic Plain. Figure 1 illustrates the sampling locations alongside aerosol optical depth (AOD) retrieved from MERRA-2²¹ across India, averaged over Jun – Aug 2024, highlighting Leh's relatively pristine conditions in contrast to the more polluted environment of Delhi. The prevailing air-mass transport pathways, derived from ERA5 reanalysis data^{22,23}, indicate that air masses predominantly arrived from the west and southwest during the sampling period. This observation underscores the significance of meteorological conditions prevailing over the two contrasting locations in assessing aerosol characteristic properties and their implications for air quality, which is essential for developing effective strategies to manage urban pollution and reduce its impacts on health and the environment. To further investigate the hygroscopic behavior and phase transitions of aerosols from these contrasting environments, the QCM-derived frequency response was analyzed as a function of RH.

The normalized frequency shift (Δf_N) was used to characterize the hygroscopic response of the deposited aerosol particles while accounting for differences in initial particle loading. The Δf_N response reflects changes in particle mass associated with water uptake, with a decrease in frequency corresponding to an increase in mass^{1,7,24,25}. The derivative of Δf_N with respect to RH, $d(\Delta f_N)/d(RH)$, was used to identify distinct changes in the frequency response with increasing RH. The RH at which $d(\Delta f_N)/d(RH) \geq 1$ was considered the deliquescence relative humidity (DRH), providing an indication of the onset of deliquescence in the aerosol particles^{1,7}.

The characteristic hygroscopic behavior of aerosol particles sampled from Leh and Delhi is shown in Fig. 2. In the case of aerosol particles from Leh (Fig. 2a), a pronounced increase in Δf_N is observed at a specific RH, signifying the phase transition from solid particles to liquid droplets due to deliquescence. Conversely, such a behavior for aerosol particles from Delhi (Fig. 2b) was absent over the entire measured range of RH. As can be seen from Figs. 2c and 2d, aerosol particles from Leh exhibit deliquescence at an average RH of $\sim 68\%$, referred to as the deliquescence relative humidity (DRH), while those from Delhi did not exhibit any deliquescence behavior up to 86% RH, which is the maximum RH that can be reached in our experimental setup. This limitation arises because, at higher RH, the liquid deposit forms discrete droplets rather than a uniform film. Under these conditions, viscous effects become more pronounced as the droplets' center of mass moves farther from the crystal surface. Consequently, the reduced mean velocity and kinetic energy of the liquid droplets result in a diminished QCM response²⁶. The contrasting hygroscopic behavior of the Himalayan and IGP aerosols suggests differences in their initial particle phase states. The Leh samples exhibited a distinct deliquescence transition at approximately 68% RH and efflorescence at approximately 40% RH (Figure S1), resulting in a pronounced hysteresis loop that is characteristic of predominantly crystalline particles^{27–30}. Crystalline, water-soluble particles undergo a first-order deliquescence transition at a characteristic DRH, while efflorescence occurs at a lower RH due to the persistence of metastable supersaturated solution droplets, resulting in hysteresis^{27–29}. The presence of a single DRH value in Leh also suggests that the aerosols are mostly internally mixed, positioning their DRH between that of the constituent materials, which contrasts with the multiple DRH values expected from externally mixed aerosols^{7,28}. In addition to

the contribution of the crystalline phase to the early onset of DRH observed in Leh, compared to Delhi, this is also likely attributable to the significant contribution of water-soluble organic compounds before the actual DRH threshold is met^{31,32} (Figs. 2c and 2d). The 68% DRH measured in Leh is significantly lower than that of pure inorganic salts like $(\text{NH}_4)_2\text{SO}_4$ (DRH = 75–80%)^{33,34} (Figure S3), indicating the sampled particles contain mixed salts and/or soluble organic compounds. Previous research confirms this complexity: organics can either reduce the DRH of the inorganic component or have no effect at all^{7,31,35–37}. Therefore, Leh particles primarily represent a complex mixture of inorganic salts and highly water-soluble organic compounds, as evident from the chemical composition data presented in Figure S4.

In contrast, the Delhi aerosol particles showed no distinct deliquescence (Fig. 2d) or hysteresis (Figure S2), with only a slight increase in frequency at very high RH (Fig. 2b). The absence of a distinct deliquescence transition and hysteresis suggests that the particles were predominantly amorphous or remained in a metastable liquid-like state, resulting in continuous water uptake rather than first-order phase transitions^{30,38,39}. The water uptake at high RH in Delhi suggests a different mixture of organic and inorganic compounds, as reflected in the chemical composition data presented in Figure S4, where the organic fraction may be composed of less water-soluble species. This limited solubility could either delay or completely prevent the clear appearance of a DRH. Furthermore, organic aerosols can sometimes take up water gradually without a distinct phase transition,^{31,40} existing in a non-crystalline state^{31,41–44}. Nonetheless, a slight but noticeable increase in frequency was observed for the Delhi particles at approximately 86% RH, which may be attributed to continued water uptake by the particles. This gradual uptake of water could transform the initially amorphous particles into concentrated aqueous solution droplets that remain metastable with respect to the crystalline phase while maintaining equilibrium with the surrounding relative humidity, potentially indicating the onset of a phase transition²⁸. Thus, the contrasting behavior of the Himalayan and IGP aerosols is likely governed by differences in particle phase state and chemical composition.

Mass-Based Hygroscopic Growth and κ Characterization

The QCM measurements, detailed in Fig. 3, reveal significant differences in the mass-based hygroscopic growth factors (gf_m) and corresponding hygroscopicity parameters (κ_m) between the aerosol particles from Leh and Delhi when exposed to a wide range of RH. The gradual increase in film mass with increasing RH, reflected by the corresponding increase in gf_m , defined as the ratio of film mass at a given RH, from < 5% to 81% RH, to that at < 5% RH, confirms continuous water uptake^{7,25,45} (Figs. 3a and b), which is dominated by absorption after subtracting the baseline surface adsorption measured on a clean QCM crystal^{7,25}. The observed gf_m values are highly consistent with the κ -Köhler parametrization, shown by the solid lines (green for Leh in Fig. 3a; red for Delhi in Fig. 3b). A cross-site comparison is achieved using the dashed lines: the fit using Delhi's κ is shown in Fig. 3(a) together with the Leh data, and vice versa in Fig. 3(b), clearly demonstrating that the hygroscopic behavior is significantly different between

the sampling locations. A maximum RH was reached (due to the QCM's inability to accurately measure mass past deliquescence)^{1,7}, yielding a maximum gf_m of 1.2 at 75.8% RH for Leh and 1.08 at 80.7% RH for Delhi. These pronounced variations in gf_m at given RH values strongly indicate different chemical compositions and hygroscopicities across the two sampled environments.

Figures 3c and 3d present the calculated average κ_m values for Leh and Delhi, derived directly from the hygroscopic growth factors (gf_m) shown in Figs. 3a and 3b. Across the investigated RH range, the average κ_m values, indicated by the dashed lines, showed a significant difference: 0.03 for Delhi and 0.05 for Leh. These consistently low κ_m values strongly suggest a substantial contribution of organics to the hygroscopic growth until deliquescence, as organics typically have lower κ_m values ranging from 0.01 to 0.5 for slightly to very hygroscopic organic species^{46,47}. This variation in κ_m between sites clearly demonstrates that the hygroscopicity parameter in the subsaturated region is highly dependent on the chemical composition of the aerosol particles^{7,46}. The chemical composition of the sampled aerosol particles, presented in Figure S4, shows contributions from both water-soluble inorganic ions and organic material at both sites. The relatively low κ_m values observed for Leh and Delhi, despite the substantial contribution of water-soluble inorganic ions to their chemical composition, indicate that aerosol hygroscopicity cannot be inferred from the inorganic fraction alone. Pöhlker et al. (2023) demonstrated that effective aerosol hygroscopicity depends on the relative contributions of organic and inorganic components, which exhibit substantially different intrinsic hygroscopicities⁴⁶. Moreover, the hygroscopic behavior of internally mixed organic-inorganic particles can be influenced by the composition ratio, organic–inorganic interactions, and particle phase state, resulting in water uptake that differs from that expected based solely on the individual components³¹. Specifically, the aerosols in IGP exhibited a very low average κ_m (0.03), likely due to the strong influence of less soluble primary organic species, a finding supported by the previously observed delayed or complete absence of the DRH in investigated samples^{8,31,46,48–51}. Conversely, the Himalayan aerosol particles exhibited a slightly higher average κ_m (0.05), reflecting a greater contribution from more soluble secondary organic species⁴⁸.

Photolytic Mass Loss of Ambient Aerosols

Figure 4 illustrates the experimental results from the UV photolysis experiments, indicating that aerosol particles from both locations experience notable mass loss due to photodegradation when exposed to UV irradiation at 300 nm and 340 nm, representing atmospherically relevant UV-B and UV-A radiation, respectively. The figure presents the time profiles of mass fraction remaining for Himalayan and IGP aerosol particles aged under UV light at a moderate RH of $50\% \pm 10\%$. This mass loss is attributed to the formation and volatilization of photoproducts within the QCM flow cell^{3,4,52}. Throughout the 24 hours of UV exposure, mass losses under 300 and 340 nm UV irradiation were significantly greater for the Leh samples than for those from Delhi, suggesting much greater photolytic mass loss in Himalayan aerosols. This difference likely stems from variations in chemical composition, with Leh aerosols

potentially containing more secondary organic aerosols (SOAs) that absorb UV radiation and generate smaller volatile compounds^{3,4}. Conversely, Delhi aerosols may be primarily composed of less volatile SOAs predominantly arising from vehicular emissions and biomass burning^{4,53,54}. Additionally, when comparing the mass-loss fractions from photolytic aging experiments under 300 nm UV light to those under 340 nm UV light for the same duration, the latter shows reduced mass loss. This can be attributed to the weaker light absorption and potentially lower quantum yield at the longer wavelength⁵². The mass fraction remaining curves plateau at the end of the experiment period, indicating the presence of photo-recalcitrant aerosols after the more photolabile compounds have been degraded. While the differences in photolytic mass loss across different aerosol types are complex and suggest factors like molecular structure and light absorption properties play a role, these results align with previous QCM and other technique measurements of photolytic mass loss in various aerosols^{3,4,52,55}.

Discussion

This study utilized an ultrasensitive QCM technique to analyze the properties of ambient aerosol particles collected from two significantly contrasting environments in India: the heavily polluted urban megacity of Delhi in the IGP and Leh, a pristine high-altitude site in the climate-sensitive Himalayan region. For the first time at this unique Himalayan site, we report data on the aerosol's mass-based growth factor, hygroscopicity parameter, and photolytic mass loss across a broad range of RH values, establishing a critical comparative baseline between these locations. The QCM approach notably increased the precision and accuracy of measurements of water uptake, particularly under low humidity conditions, as evidenced by the detailed representation of film mass changes (gf_m) observed below the deliquescence relative humidity. Our findings highlight a clear dependence of aerosol phase behavior on chemical composition and initial phase state: Delhi's aerosol particles exhibited very low hygroscopicity parameters (κ_m) and delayed or absent DRH, indicative of compositions primarily characterized by less soluble, high molecular weight organics, presumably including polycyclic aromatic hydrocarbons (PAHs) and other anthropogenic pollutants, which likely promote an amorphous or metastable phase state. Conversely, Leh's aerosols displayed somewhat higher κ_m values and a discernible DRH, indicative of a higher concentration of hygroscopic, more soluble secondary organic aerosols (SOAs), likely produced from biogenic emissions, together with inorganic constituents that may favor the formation of a more crystalline phase.

This chemical disparity underscores the complexity introduced by the solubility of various organic species, which substantially alters the hygroscopic behavior of aerosols. Furthermore, our QCM analysis revealed that photolytic mass loss was significantly greater for the aerosol particles from the Himalayas, attributable to their higher photolability, particularly in the case of SOAs, compared to the more stable, less volatile aerosol particles in IGP. This confirms that the chemical composition plays a pivotal role not only in dictating the hygroscopic complexity but also in determining the atmospheric fate of aerosols through their photolysis rates.

Similar contrasts in aerosol phase state have been reported across different environments worldwide, highlighting the strong influence of aerosol composition and ambient conditions on particle water uptake and phase behavior. In the Amazon tropical rainforest, submicrometer particles were found to be predominantly in the liquid state at RH above 80%, with near-surface particles inferred to remain liquid for most of the time under both wet and dry seasons⁵⁶. Similarly, ambient aerosol particles in the Southern Great Plains of Oklahoma exhibited RH-dependent phase changes, highlighting the importance of relative humidity in controlling the physical state of atmospheric aerosols⁵⁷. In the highly polluted atmosphere of Beijing, China, submicrometer aerosol particles transitioned from a semisolid to a liquid state when RH increased above approximately 60% and remained predominantly liquid during heavy haze episodes, highlighting the role of aerosol liquid water content and chemical composition in regulating particle phase state⁵⁸.

Our findings strongly emphasize the urgent need for additional high-sensitivity measurements, such as those provided by the QCM, to span a wider range of ambient locations and to include laboratory-generated aerosols. It is essential to accurately capture the dynamic impacts of rapid changes in RH and UV irradiation on aerosol properties, specifically linking these changes back to the precursors of both anthropogenic and biogenic emissions. A comprehensive understanding of these intricate interactions is vital for refining atmospheric models and reducing uncertainties concerning the impacts of climate change and air pollution.

Methods

Study Area and Sampling Sites

PM_{2.5} was collected from two locations in India during June-August 2024, corresponding to the Indian Summer Monsoon (ISM) season. The first location is the University of Ladakh, Taru, in Leh district (34.18°N, 77.41°E; 3,500 meters above mean sea level (amsl)), recognized for its cold desert environment. Situated at the western end of the Indian Himalayas, this high-altitude area features sparse vegetation and experiences harsh weather conditions, including low atmospheric pressure, intense solar radiation, and significant temperature fluctuations between day and night. Temperatures can soar to 35°C in summer and plunge to as low as – 28°C in winter. Due to its position in the rain shadow zone of the Himalayan region, Leh receives minimal influence from the southwest summer monsoon, with most precipitation falling as snow in winter^{59–62}. With little industrial activity and a low population density, this site provides a relatively pristine environment ideal for examining background aerosol characteristics with limited anthropogenic influence.

The second location is at the Indian Institute of Tropical Meteorology (IITM) in Delhi (28.63°N, 77.17°E; approximately 220 meters amsl). This site is situated on the northern edge of the Central Ridge reserve forest in a densely populated urban environment^{63,64}. Delhi, located in the semi-arid Indo-Gangetic Plain, is influenced by local emissions, mainly from vehicular traffic and the combustion of residential solid

fuels, as well as long-range transport of mineral dust. The city's climate includes extremely hot summers (with temperatures surpassing 45°C) and cold winters (dropping to around 3°C). The monsoon season occurs from late June to mid-September. The geographical and topographical characteristics of the Indo-Gangetic Plain, flanked by the Himalayas to the north and various plateau systems to the south, lead to the buildup and trapping of aerosols in the region⁶⁵. As shown in Figure S8, the two sampling locations experienced contrasting RH conditions, with mean RH values of 55.5% at the Himalayan site and 72.7% at the IGP site. This spatial variation in RH provides important meteorological context for understanding the contrasting water uptake and hygroscopic behavior of the sampled aerosols. The surrounding topographical features of the two sampling sites are shown in Figure S5⁶⁶.

Experimental Setup and Measurements

In Leh, PM_{2.5} was collected on PTFE (polytetrafluoroethylene) filters using an Airshed PM_{2.5} sampler during July and August 2024. In Delhi, sampling was carried out in June 2024 with an Envirotech APM 550M sampler. Both samplers were operated at a flow rate of 16.67 L/min. Following sample collection, the aerosol particle-loaded filter was gently pressed onto a clean QCM sensor (Novaetech, AT5-14-12-AU), resulting in the transfer of a thin residual film of aerosol particles onto the sensor surface upon detachment of the filter⁶⁷. The aerosol particle-coated QCM sensors were subsequently mounted in a temperature-controlled window module flow cell (Biolin Scientific, Q-Sense, QWM401) maintained at 22–23°C. The flow cell was continuously purged with zero air at a total flow rate of 30 cm³/min. RH within the cell was varied between dry conditions (< 5% RH) and humidified conditions (10–95% RH) by controlling the mixing ratios of dry and humidified air using two mass flow controllers. The RH and temperature of the air entering and exiting the flow cell were continuously monitored using a thermohygrometer (Testo Smart 650i). To investigate photolytic mass loss, the aerosol-coated QCM sensor was placed in the window module and exposed to UV radiation at wavelengths of 300 and 340 nm using UV LEDs (M300L4 and M340L4, respectively; Thorlabs) under controlled conditions of 50 ± 10% RH. The corresponding changes in aerosol mass were continuously monitored using the QCM (Figure S7). The selected wavelengths represent UV-B (300 nm) and UV-A (340 nm) radiation, respectively, and are relevant to solar radiation reaching the troposphere under typical atmospheric conditions. The QCM enabled continuous monitoring of the mass loss from the aerosol film during UV irradiation⁵². A quantitative comparison of the experimental radiation dose with ambient exposure could be performed in future studies using calibrated UV power meters to measure irradiance under both experimental and ambient conditions.

Using a highly sensitive QCM, hygroscopic properties were investigated, encompassing the hygroscopic growth factor, the hygroscopicity parameter, deliquescence relative humidity (DRH), and the mass fraction remaining after photolysis. The robustness and precision of this methodology were established by comparing the measurements of the hygroscopic growth factor and DRH for ammonium sulfate (Figure S3) and sucrose (Figure S6) with previous results^{1,7,68,69}. By employing κ-Köhler theory, which provides insights into aerosol water uptake characteristics, the hygroscopicity parameter (κ) was

evaluated over a wide range of relative humidity conditions^{7,12,47}. The frequency shift (Δf_R) measured at a given RH was normalized with respect to the frequency shift (Δf_S) of the dry aerosol sample deposited at RH < 5%, yielding the normalized frequency shift (Δf_N) (1):

$$\Delta f_N = \left(\frac{\Delta f_R}{\Delta f_S} \right) \times (-100) \%$$

1

The normalized frequency shift was used to account for differences in initial particle loading among samples. The derivative of Δf_N with respect to RH was subsequently calculated as $d(\Delta f_N)/d(RH)$. The RH at which $d(\Delta f_N)/d(RH) \geq 1$ was considered DRH of the aerosol particles^{1,7}. The hygroscopicity parameter (κ_m) was calculated from the mass-based hygroscopic growth factor (gf_m) using κ -Köhler theory (2):

$$\kappa_m = \left(\frac{1}{a_w} - 1 \right) (gf_m - 1)$$

2

where a_w is the water activity, approximated by the fractional RH under equilibrium conditions, and gf_m represents the mass-based hygroscopic growth factor at a given RH. The hygroscopicity parameter (κ_m) was therefore evaluated over the measured RH range to characterize the water uptake behavior of the aerosol particles.

Chemical Characterization of Aerosols

The chemical characterization of aerosol particles collected from Leh and Delhi was conducted using a variety of analytical techniques. During the same sampling period in Leh, an Airshed high-volume sampler was used to collect PM_{2.5} aerosol particles on quartz filter papers (Whatman; 8×10 inches) for chemical composition analysis. The high-volume sampler was operated at a flow rate of 1.36 m³/min. Water-soluble inorganic ions (WSIs) in the aerosol samples from both locations were measured using ion chromatography (IC; Metrohm Eco IC, with an 863 Compact Autosampler). A 9 cm² portion of the quartz filter containing the collected PM_{2.5} from the respective sampling period was immersed in 30 mL of deionized water in pre-cleaned borosilicate test tubes and allowed to soak for 12 h to maximize the extraction of water-soluble components. The extracts were then sonicated for 40 min at 22°C and subsequently filtered to remove suspended particulate matter⁷⁰. Anions, including F⁻, HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻, were separated using a Metrosep A Supp 5–250/4.0 column, while cations, including NH₄⁺, Mn²⁺, Ca²⁺, and K⁺, were analyzed using a Metrosep C 6–150/4.0 column.

For the samples from Leh, heavy and trace metals (Li, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Pd, Cd, Sn, Sb, Cs, Ba, La, Ce, Pt, Hg, Tl, and Pb) were quantified using inductively coupled plasma mass

spectrometry (ICP-MS; NexION 300X, Perkin Elmer). A 15 cm² portion of the filter (5×3 cm) was excised and subjected to acid digestion in HDPE–Teflon vessels using a mixture of 0.5 mL HF and 1.5 mL HNO₃. The samples were maintained at 90–120°C on a hot plate for 4 h to facilitate complete digestion. Following digestion, 2.5 mL of HClO₄ was added to the resulting clear solution, which was further subjected to open-vessel digestion at 220–240°C for 4 h until the acid mixture was completely evaporated⁷⁰.

Organic carbon (OC) and elemental carbon (EC) levels were determined using a DRI Model 2015 OC/EC Thermal/Optical Carbon Analyzer, following the IMPROVE-A protocol, where a 1 cm² punch area of each filter was used to analyze the carbon content. For the Delhi samples, data on heavy and trace metals, as well as OC and EC concentrations, were obtained from Bhowmik et al.^{52,57}, where similar analyses were performed during the same season, providing a comprehensive assessment of the chemical composition across both sites.

Declarations

Competing Interests

Sachin S. Gunthe is an Associate Editor of npj Clean Air, and he was not involved in the journal's review of, or decisions related to, this manuscript. The remaining authors declare no competing interests.

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Author Contribution

S.S.G. conceived the research idea and S.S., P.L. and S.S.G. conceptualized research experiments. S.S. designed the research experiment, and independently planned and executed the field measurement campaign for aerosol sampling in complex terrain of Ladakh at 3500 meters above mean sea level with support from A.S., T.A., and S.Sh. S.S. coordinated the aerosol sampling in Delhi with support from A.K.S., and D.K.B. The QCM experiments in the laboratory including validations were led by S.S. with support from C.J., and B.B. S.S. also led the chemical data analyses of the collected samples with support from R.S. The data analysis was led by S.S. with M.D. helping in satellite data analysis for AOD and meteorology over India. S.S., P.L., and S.S.G. carried out the scientific interpretation of the QCM experiment results with critical inputs from S.T.M., M.O.A., R.R., and G.P. S.S. wrote the manuscript under the mentorship of S.S.G. with valuable edits from S.T.M and M.O.A. All co-authors discussed the results and commented on the manuscript.

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Data availability

Data can be obtained from the corresponding author upon reasonable request.

Code availability

Code can be obtained from the corresponding author upon reasonable request.

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Figures

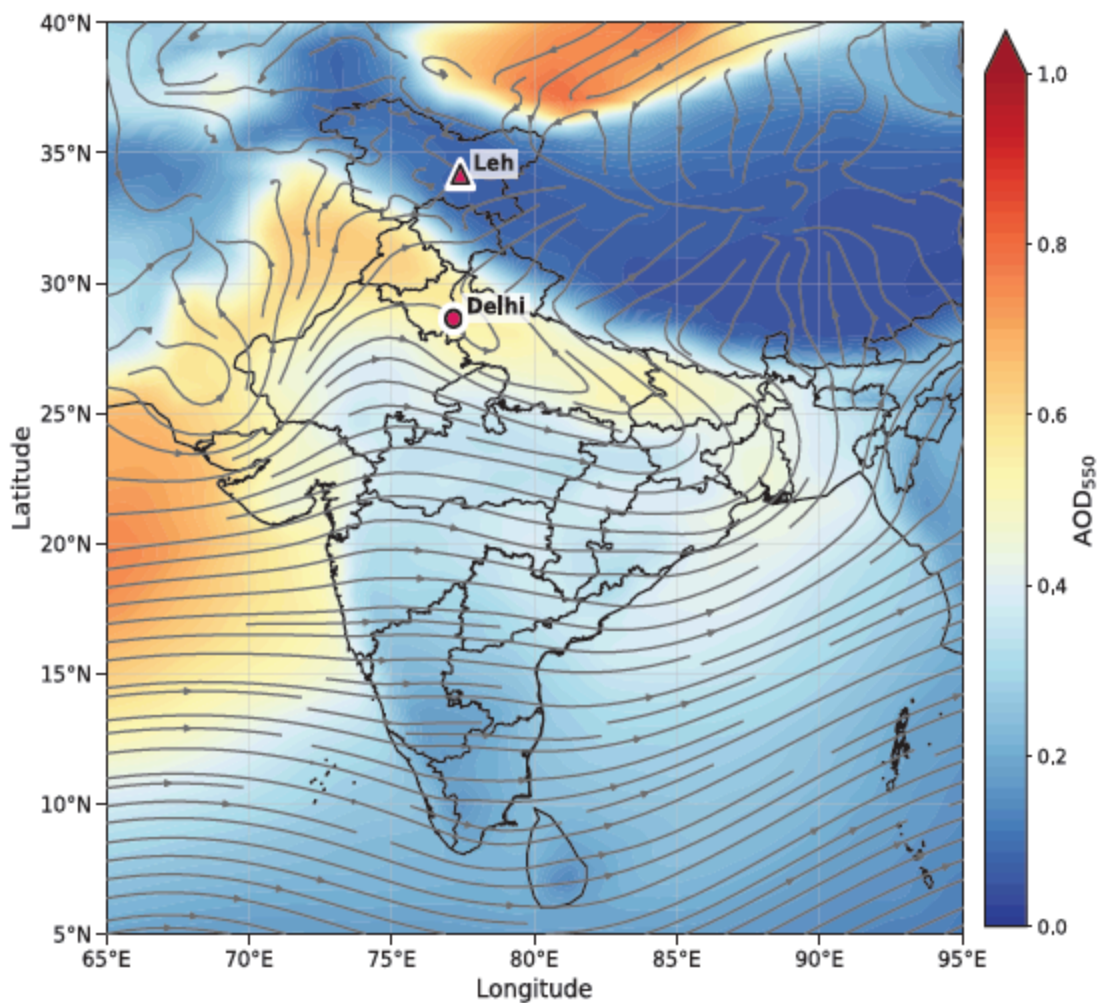


Figure 1

AOD distribution and wind patterns (June-August 2024). This figure presents the spatial distribution of mean Aerosol Optical Depth (AOD) across the Indian subcontinent, utilizing MERRA-2 reanalysis data. The map clearly demonstrates the contrast in aerosol loading between the two observation sites: Leh exhibits substantially cleaner air (lower AOD) than Delhi. The wind streamlines, derived from ERA5 reanalysis data, indicate the prevailing horizontal wind flow during the study period and are normalized to emphasize wind direction. Note that the Delhi sampling occurred in June 2024, while the Leh sampling took place in July-August 2024, ensuring both represent the same seasonal conditions.

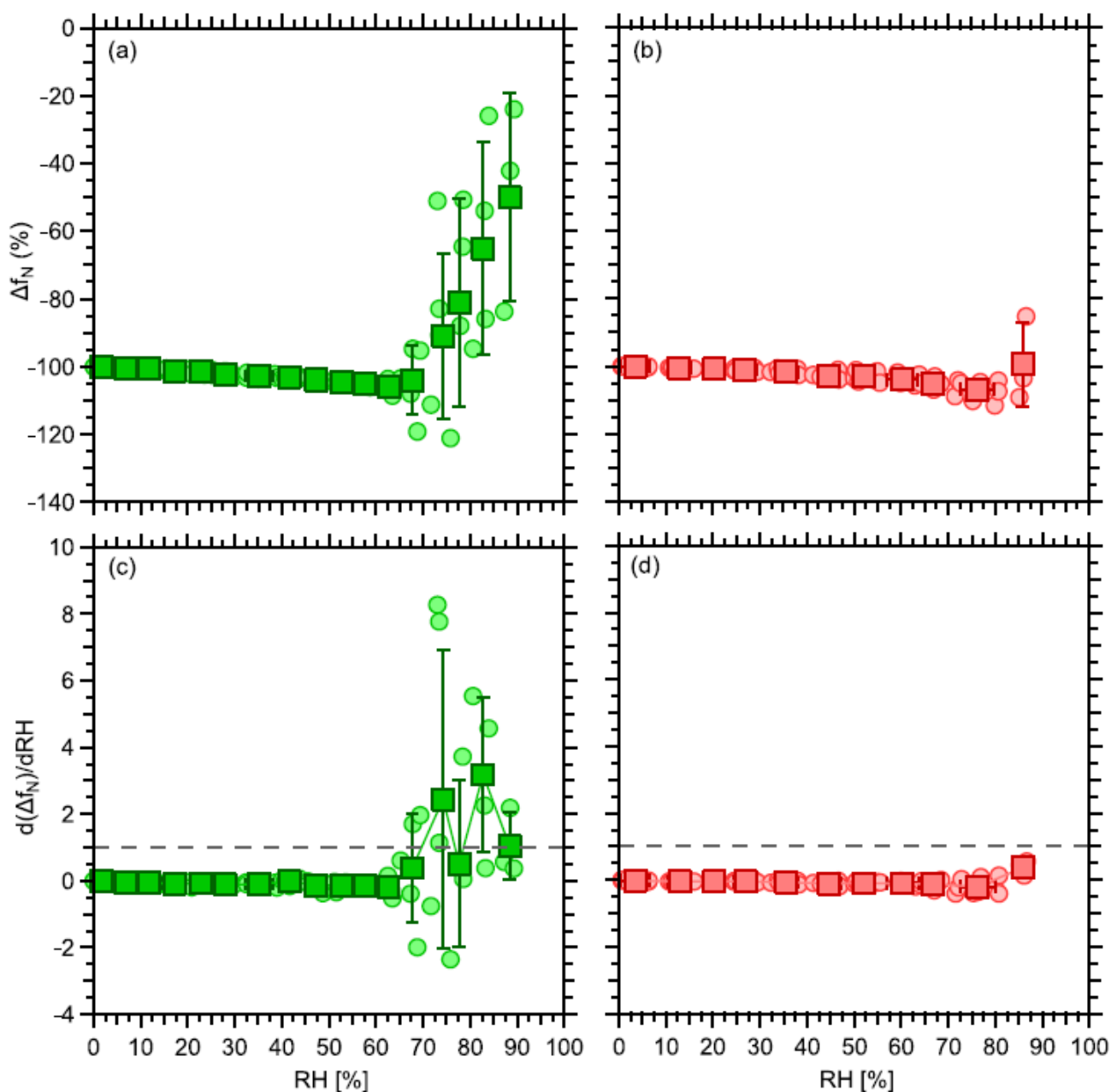


Figure 2

Humidity-driven phase change (deliquescence) in PM_{2.5} aerosols from Leh and Delhi. This figure details the hygroscopic behavior of ambient PM_{2.5} particles (Leh: green; Delhi: red). Panels (a) and (b) illustrate the change in normalized QCM oscillation frequency (Δf_N %) as a function of relative humidity (RH), demonstrating water uptake by the collected aerosol particles. The decrease in Δf_N (normalized to the dry state at RH < 5%) tracks the progressive absorption of water by the aerosols. Panels (c) and (d) show the first derivative, $d(\Delta f_N)/d(RH)$ vs. RH, which is used to precisely identify the Deliquescence Relative Humidity (DRH). The DRH occurs when the rate of water uptake, $d(\Delta f_N)/d(RH)$ reaches or surpasses 1

(indicated by the dashed line). Square markers indicate mean values, with error bars representing ± 1 standard deviation.

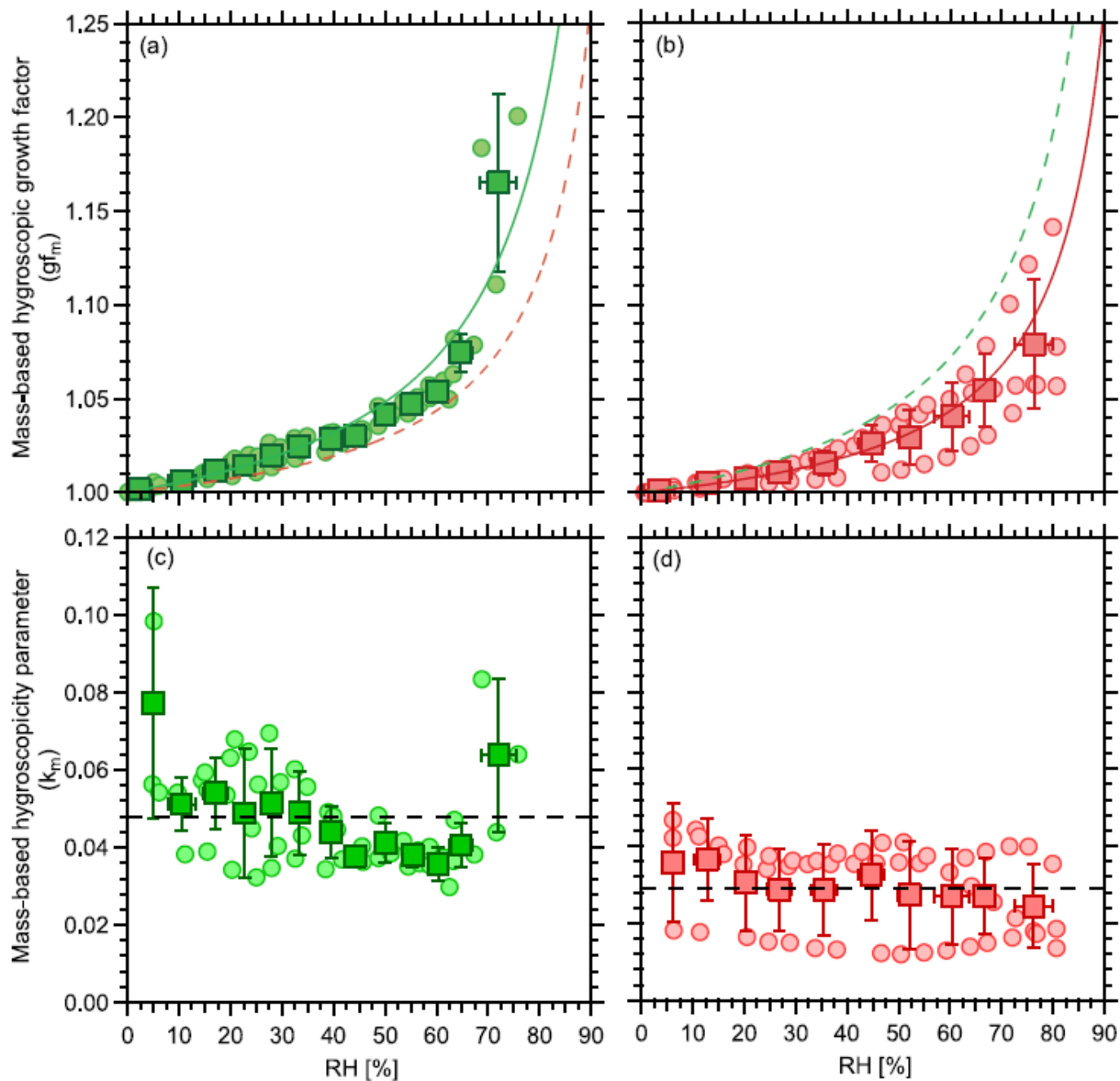


Figure 3

Hygroscopicity of ambient PM_{2.5} aerosol particles from Leh (green) and Delhi (red) during June-August (2024). Panels (a) and (b) represent the mass-based hygroscopic growth factor (gf_m) of PM_{2.5} derived from measurements using a quartz crystal microbalance (QCM) under varying subsaturated relative humidity (RH) conditions. Solid lines show κ -Köhler growth factor fits based on the mean mass-based hygroscopicity parameter (κ_m) for the respective locations. Dashed line in panel (a) represents κ -Köhler

fits using κ values from Delhi, while the dashed line in panel (b) shows κ -Köhler fits using κ values from Leh, enabling a cross-site comparison. Panels (c) and (d) present κ values calculated from g_{fit} using κ -Köhler theory across RH conditions. Dashed lines indicate the mean κ for each location. Square markers indicate mean values, with error bars representing ± 1 standard deviation.

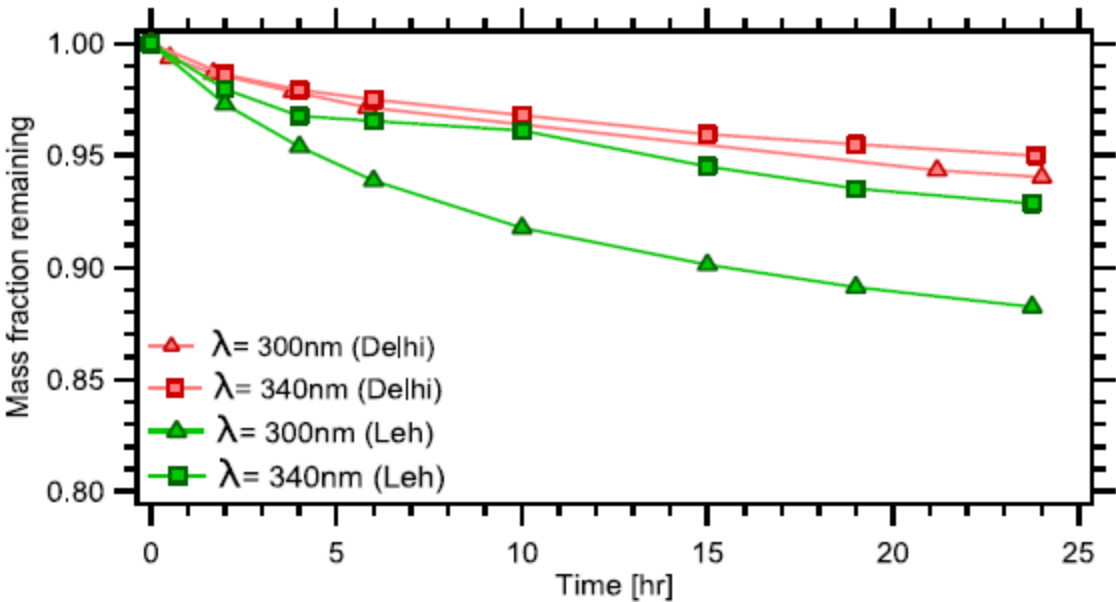


Figure 4

PM_{2.5} mass fraction remaining during UV photolysis (Leh vs. Delhi). The time-dependent degradation of PM_{2.5} aerosol mass, measured by a Quartz Crystal Microbalance (QCM), is compared for samples from Leh (green) and Delhi (red). The mass fraction remaining is tracked while the particles undergo photolysis due to UV irradiation at two different wavelengths: 300 nm (triangles) and 340 nm (squares). All measurements were performed at a consistent relative humidity of 50±10% RH.

Supplementary Files

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