Complex Interplay Between Organic and Secondary Inorganic Aerosols With Ambient Relative Humidity Implicates the Aerosol Liquid Water Content Over India During Wintertime

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Abstract  Aerosol Liquid Water Content (ALWC), a ubiquitous component of atmospheric aerosols, modulates atmospheric chemistry through aerosol surface reactions and reduces the atmospheric visibility. However, the complex dependency of ALWC on aerosol chemistry and relative humidity (RH) in the Indian region remains poorly characterized. Here, we combine available measurements of aerosol chemical composition with thermodynamic model, ISORROPIA2.1, to reveal a comprehensive picture of ALWC in fine mode aerosols during the winter season over the Indian continental region. The factors modulating ALWC are primarily dependent on the RH, such that the effect of aerosol dry mass and hygroscopicity are significant at high RH while the effect of hygroscopicity significantly reduces with decreasing RH. ALWC is observed to display a sharp non-linear rise, beyond a critical value of ambient RH dependent on the particle hygroscopicity. Further analysis by coupling Weather Research Forecasting-Chem simulation with ISORROPIA2.1 revealed significant spatial heterogeneity in ALWC over India, strongly associating with regions of high aerosol mass loading and RH. The Indo-Gangetic Plain is consequently observed to be a hotspot of higher ALWC, which explains the prevalent conditions of haze and smog during winter in this region. Our findings re-emphasize that high aerosol mass resulting from intense pollution is vital in modulating aerosol–climate interaction under favorable meteorological conditions. Observations suggest the need for localized pollution control strategies, directed at the reduction in aerosol emissions of specific chemical composition observed to contribute to the enhancement in PM through an increase in ALWC during wintertime in the region.

Plain Language Summary  Water vapor condenses on particulates in the air (known as atmospheric aerosols) due to the presence of chemical species with high water affinity. The condensed water, referred to as Aerosol Liquid Water Content (ALWC), is primarily responsible for weather conditions of low visibility like haze and smog, which have impacts on human health, and economy. This study has calculated ALWC using existing measurement data of the chemical composition of fine sized aerosols from literature, for contrasting and diverse environments in India. The study has focused on the winter season marked by spike in pollution levels and haze. Relative humidity, total particle concentration, and chemical composition were identified to play a significant role in influencing ALWC. The Indo-Gangetic Plain has been identified to be a hotspot of high ALWC due to high pollution levels and relative humidity, particularly during winter season. The study emphasizes on the extensive study of local aerosol chemistry for targeted reduction of the emission of specific chemical species, which would enable the improvement of air pollution and visibility reduction in the region.

1. Introduction

Aerosol Liquid Water Content (ALWC) is a significant component of atmospheric aerosols that affects their size, lifetime, and chemical properties. The presence of ALWC is primarily due to the absorption of water vapor by the chemical species that constitute the aerosols (Seinfeld & Pandis, 2016). Uptake of ALWC occurs drastically when these aerosols are subjected to ambient relative humidity (RH) greater than critical values known as deliquescence RH (DRH) for single component particles and mutual deliquescence RH (MDRH) for multicomponent particles
ions in the particle phase of aerosols at locations with high ambient RH thus facilitates the rapid growth of aerosols by water uptake, leading to enhanced surface area for heterogeneous reactions, higher aqueous phase reaction rates and uptake coefficients of trace acidic gases (Cheng et al., 2016; Faust et al., 2017; Hennigan et al., 2008; Kommula et al., 2021; Song et al., 2019; Y. Wang et al., 2020). Therefore, ALWC serves as a medium for chemical reactions in aerosols, especially at high RH. The consequent secondary formation of highly hygroscopic species through gas to particle partitioning processes leads to further water uptake, causing a positive feedback effect on the water uptake by aerosols (Cheng et al., 2016; Huang et al., 2014; G. Wang et al., 2016; Z. Wu et al., 2018). Enhanced ALWC uptake involving highly hygroscopic species like NO$_3^-$ has been observed to dilute aerosol acidity, thereby increasing the pH (Y. Cao et al., 2020). The higher pH generates favorable conditions for further partitioning of NO$_3^-$ ions in the particle phase of aerosols at locations with high NH$_3$ emissions (Guo et al., 2016). Due to its key role in the dilution of H$^+$ ions in the aerosols, ALWC has hence been identified to be a major factor determining the aerosol pH (Zheng et al., 2020). ALWC also modifies the optical properties of aerosols by increasing their extinction coefficient, consequently enhancing the Aerosol Optical Depth (AOD) (Dougle et al., 1996; Sequeira & Lai, 1998). Moreover, high ALWC leads to poor visibility in the form of haze and smog over highly polluted locations (Chen et al., 2012; Dall’Osto et al., 2009; Gunthe et al., 2021). These effects ultimately modify the planetary albedo and radiative forcing, thereby perturbing the Earth’s energy balance (Adams et al., 2001; Dougle et al., 1996; Liao & Seinfeld, 2005).

The water uptake by aerosols mainly depends on the particulate mass burden, aerosol number concentration, size distribution, composition of gas and aerosol phase, RH, and temperature (Bian et al., 2014; Kuang et al., 2018; Nguyen et al., 2016; Petters & Kreidenweis, 2007). The difference in the water activity between aerosol particles and their surroundings is the major driving force for the uptake of ALWC and hence, ambient RH, being a proxy for the activity of water vapor in the atmosphere under sub-saturated conditions, is an important parameter governing ALWC (Seinfeld & Pandis, 2016). Thus, higher the RH level in the atmosphere, greater is the driving force for water uptake by aerosols (Bian et al., 2014; P. F. Liu et al., 2011; Shen et al., 2019; Z. Wu et al., 2018). Aerosol hygroscopicity, a measure of the affinity of aerosol particles toward water, is primarily a function of chemical composition in the particulate phase. The composition of atmospheric aerosols is, however, complex, ranging from inorganic species of high hygroscopicity to insoluble soot and a myriad of slightly soluble organic compounds, leading to varying levels of particle hygroscopicity in diverse environments. At high RH and low temperature, secondary formation of aerosols and their growth through heterogeneous gas to particle reactions are favored, which are observed to considerably alter the particulate chemical composition (Cheng et al., 2016; Faust et al., 2017; Kommula et al., 2021; P. F. Liu et al., 2011; Y. Wang et al., 2020). Chemical composition also varies with the size of aerosols, further adding to the complexity of aerosol hygroscopicity (Boreddy et al., 2021; Deshmukh et al., 2016; S. Kumar et al., 2018).

Being an important component of ambient aerosols, the real time measurement of ALWC is of great significance, which, however, has not been feasible yet due to technical limitations (Kuang et al., 2018). Hence, ALWC is generally measured indirectly by experimental techniques, which usually involve the measurement of the difference in the volume of ambient aerosols at conditions of controlled lower and higher RH. The difference is then used to calculate the aerosol growth factor (GF) (Bian et al., 2014; Fajardo et al., 2016; Jin et al., 2020; Kuang et al., 2018). Another common method is the estimation of ALWC using thermodynamic models, based on the assumption of thermodynamic equilibrium within the particle phase and between the particle and surrounding gaseous phases. Numerous models based on thermodynamic equilibrium have been reported in literature including EQUIL, MARS, AIM, SCAPE, EQUISOLV and ISORROPIA (Bassett & Seinfeld, 1983; Jacobson et al., 1996; Kim et al., 1993; Nenes et al., 1998; P. Saxena et al., 1986; Wexler & Clegg, 2002; Wexler & Seinfeld, 1991), which mostly consider the aerosol chemistry pertaining to the inorganic species only. Nguyen et al. (2016) estimated ALWC using the model ISORROPIA2.1 with Aerosol Mass Spectrometer (AMS) based chemical composition measurements from various locations worldwide, providing a comprehensive overview of the prevalence of ALWC. Such studies have not, however, examined the diverse and contrasting environments
as in the Indian region. Model estimates of ALWC have shown appreciable correlation to measurement values in numerous closure studies (Bian et al., 2014; Fajardo et al., 2016; Jin et al., 2020; Kuang et al., 2018; Shen et al., 2019). Combining observations from experimental and modeling data, hygroscopicity of individual inorganic and organic compounds have also been parameterized in various studies (H. J. Liu et al., 2014; Petters & Kreidenweis, 2007).

The Indian region continues to experience severe air pollution, with many of its cities among the most polluted areas in the world (D. Ghosh & Parida, 2015). Modeling studies have identified an increasing trend in the aerosol loading across the Indian region with significant seasonal variability (Babu et al., 2013; Krishna Moorthy et al., 2013). Such high aerosol loading has been associated with severe health consequences such as respiratory-cardiovascular diseases and premature mortality (Balakrishnan et al., 2018; Conibear et al., 2018; David et al., 2019; Guttikunda & Goel, 2013; Lelieveld et al., 2015; Pandey et al., 2021). Moreover, poor visibility caused by the consequent haze and smog has had economic implications in the region by disturbing surface-air transport and day-to-day activities (Kulkarni et al., 2019). Although numerous studies have measured fine mode particulate matter and their chemical composition using online and offline techniques to address their air quality and public health impacts (Agarwal et al., 2020; Ajith et al., 2022; Deshmukh et al., 2016; Gani et al., 2019; Gunthe et al., 2021; Jain et al., 2021; Kommula et al., 2021; Kompalli et al., 2020; A. Kumar & Sarin, 2010; S. Kumar et al., 2018; Mukherjee et al., 2018; Rastogi et al., 2016; Rengarajan et al., 2011; Thamban et al., 2019), fewer studies, however, have focused on the estimation of ALWC in this region (Acharja et al., 2022; Boreddy et al., 2021; Kommula et al., 2021; Satsangi et al., 2021). The winter season, particularly over the continental part of India, is marked by high atmospheric stability due to weak winds and temperature inversion, leading to poor dispersion of polluted air masses (S. Raj et al., 2021; Rastogi et al., 2016; Satsangi et al., 2021; M. Saxena et al., 2017). Studies have observed pronounced diurnal variations of RH and temperature during winter, resulting in strong radiative thermal inversions and causing a shallow nocturnal planetary boundary layer (Arun et al., 2018; Murthy et al., 2020; S. Raj et al., 2021). The stagnation and accumulation of aerosol emissions complemented by such favorable meteorological conditions enhance secondary aerosol mass, further aggravating the aerosol loading (Rastogi et al., 2016; Satsangi et al., 2021). Secondary aerosol formation results from the oxidation reaction of acidic gases SO$_2$, NO$_x$ and HCl with NH$_3$ emissions, leading to the nucleation and growth of highly hygroscopic inorganic species and also by nucleation and condensation of organic aerosols from the atmospheric oxidation of volatile organic compounds (VOC) (Deshmukh et al., 2016; Satsangi et al., 2021; Singh & Kulshrestha, 2012). These atmospheric processes consequentially lead to widespread occurrences of haze and smog, especially in the Indo Gangetic Plain (IGP) region (Gunthe et al., 2021; Kumari et al., 2021; Ram & Sarin, 2011; Satsangi et al., 2021).

Thus, measurement of particulate matter and their chemical characterization needs to be complemented by an adequate understanding of the characteristics of ALWC at varying conditions of RH. In this work, a comprehensive analysis is performed to understand the dependence of the water uptake and hygroscopic characteristics of atmospheric aerosols on their concentration, chemical composition and ambient RH. ALWC is estimated from chemical composition obtained from field measurements of fine mode aerosols from 10 diverse locations in India using thermodynamic modeling, focusing on the winter season. The data under consideration is characterized by experimental and modeling data, hygroscopicity of individual inorganic and organic compounds have also been parameterized in various studies (H. J. Liu et al., 2014; Petters & Kreidenweis, 2007).

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2. Methodology

2.1. Calculation of ALWC From Chemical Composition Data

ALWC arises due to the absorption of water vapor by the various chemical species constituting the aerosol mass. Hence, the estimation of ALWC by thermodynamic models are generally based on the chemical composition of ambient aerosols. The Zdanovskii Stokes Robinson (ZSR) correlation (Stokes & Robinson, 1966) is a commonly used correlation, also utilized by ISORROPIA2.1, the model used in this study to estimate ALWC and is described as-

$$ W = \sum \frac{M_i}{m_0} (\alpha_{ui}) $$

(1)
where W is the mass concentration of the water taken up by the aerosol (kg m\(^{-3}\) air), \(M_i\) is the molar concentration of the \(i\)th electrolyte (mol m\(^{-3}\) air), and \(m_{oi}(a)\) is the molality of an aqueous binary solution of the \(i\)th electrolyte with the same activity \(a_i\) as in the multicomponent solution. The ZSR rule describes the water uptake of internally mixed particles as the sum of the water uptake by the constituent chemical compounds.

Though ambient aerosols are composed of various chemical compounds, the measurement of the chemical composition of aerosols is only feasible in terms of ionic concentrations. Deduction of the cation-anion associations that occur in ambient aerosols from the ionic concentration data is hence important in the calculation of ALWC. Ideally, an ionic balance procedure between cations and anions could be used to identify the cation-anion associations. Several such procedures exist in literature, but with various drawbacks. The ion pairing scheme by Gysel et al. (2007) is a commonly used method for ion balance but it is limited to only NH\(_4\)\(^+\), SO\(_4^{2-}\), and NO\(_3^-\) ions. Alastuey et al. (2005) and Mirante et al. (2014) have suggested a comprehensive ion balance methodology by incorporating all other major ionic species. However, considerable uncertainty is associated with the concentration of certain ionic species in the present data that the ion balance may not be sufficiently accurate to be generalized for the diverse environmental conditions under consideration. For example, Cl\(^-\) depletion at marine locations results in uncertainty regarding the sea salt origin of the measured Cl\(^-\) (Kaushik et al., 2021; Sarin et al., 2011). Thermodynamic models implicitly perform ion balance for various calculations including that of ALWC, but these involve the basic assumption that the aerosols are internally mixed (Fountoukis & Nenes, 2007a) while under ambient atmospheric conditions, aerosols may be externally mixed from different sources. Hence, these models may not be able to accurately predict the cation-anion associations among ions of diverse origins like sea salt spray, dust re-suspension or emissions from combustion of fuels. For instance, thermodynamic models have predicted CaSO\(_4\) in the aerosol, based on filter measurements of chemical composition at locations with high concentration of Ca\(^{2+}\) (Lin et al., 2013, 2014; Tao et al., 2014). Prediction of insoluble CaSO\(_4\) may be inconsistent with the fact that the filter measurements were water soluble, due to the nature of the filter technique used.

Therefore, ion balance predictions associated with aerosol chemistry models require caution, especially when the measured aerosols are expected to be externally mixed. Appropriate assumptions are made in the present study to ensure that the above uncertainties do not affect the ALWC calculated based on measurements from different locations using different techniques. The average chemical composition of ambient aerosols at different locations across India during wintertime was documented from various field campaign data reported in literature. Since the present study focuses only on the fine mode ambient aerosols, the chemical composition data of PM\(_{1.0}\) aerosols measured using spectrometric techniques as well as that of PM\(_{2.5}\) aerosols measured using filter based techniques were collected. The upcoming sections describe the nature of these different experimental data sets and the precautions taken to ensure basic compatibility among each other.

### 2.2. Analysis of Chemical Composition Data of PM\(_{1.0}\)

The spectrometric methods used to measure PM\(_{1.0}\) include the AMS and Aerosol Chemical Speciation Monitor (ACSM). The measured data consists of mass concentrations of inorganic ions - sulfate (SO\(_4^{2-}\)), nitrate (NO\(_3^-\)), ammonium (NH\(_4^+\)), chloride (Cl\(^-\)), and organic matter (OM). These instruments do not measure the concentration of refractory chemical species, which are mostly of sea salt or dust origin (Canagaratna et al., 2007; Nuaaman et al., 2015; Schlag et al., 2016; Zhang et al., 2017). This is because the measurements made by ACSM and AMS are sensitive to only non refractory salts like (NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)NO\(_3\), and NH\(_4\)Cl (among the inorganic salts), which are ionizable at 600°C, the temperature of the in-built vaporiser used in the instruments (Canagaratna et al., 2007; Nuaaman et al., 2015). Hence, the anionic species measured by ACSM/AMS are associated only with NH\(_4^+\) and hence, the cation-anion associations are easier to define in these measurements. The locations with ACSM/AMS based aerosol chemical composition data considered in this analysis include New Delhi (Gani et al., 2019), Kanpur (Thamban et al., 2019), Chennai (Kommula et al., 2021), Mahabaleshwar (Mukherjee et al., 2018), Bhubaneswar (Kompalli et al., 2020), and Thiruvananthapuram (Ajith et al., 2022). The collected chemical composition data for the winter months is averaged over the respective campaign periods as shown in Table S1 in Supporting Information S1 while the geographical and winter time meteorological information are displayed in Table S2 in Supporting Information S1.
2.3. Analysis of Chemical Composition Data of PM$_{2.5}$

The filter-based data set comprises of the mass concentration of organic carbon (OC) and inorganic ions—sulfate (SO$_2^-$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), chloride (Cl$^-$), sodium (Na$^+$), calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), and potassium (K$^+$). Since a large number of cationic and anionic concentrations are measured using filter-based measurements, there is significant uncertainty regarding the cation-anion associations, as discussed in the preceding section. Hence, only those locations have been chosen where the cationic composition is NH$_4^+$ dominant, so that it is conclusive that the measured anions are dominantly associated with NH$_4^+$. Based on this assumption, only SO$_2^-$, NO$_3^-$, NH$_4^+$ and Cl$^-$ concentrations were placed under consideration from the filter data set, which also ensured uniformity and basic compatibility with the ACSM/AMS based data set. Field studies have reported the dominance of these ionic species in fine mode aerosols during wintertime in the Indian region, compared to summer and monsoon (Agarwal et al., 2020; Rastogi et al., 2016; M. Sharma et al., 2007). Most of these species are mainly formed by secondary particle formation from their precursor gases, enabled by high ambient RH, low temperature and atmospheric stability during wintertime (Chutia et al., 2011; Ram et al., 2010; M. Saxena et al., 2017; Singh & Kulshrestha, 2012; Stockwell et al., 2000). Studies have reported NH$_4^+$ to be the most dominant cation to correlate with the anionic species during the winter season (Agarwal et al., 2020; Deshmukh et al., 2016; Rastogi et al., 2016; Rengarajan et al., 2011). Furthermore, the Indian region generally experiences winds from continental locations during wintertime (Agarwal et al., 2020; Deshmukh et al., 2016; A. Ghosh et al., 2021; Jain et al., 2021; P. Kumar & Yadav, 2016; S. Kumar et al., 2018; A. Kumar et al., 2020), enriched in precursor gases, which are the products of crop residue burning, biomass burning, and industrial emissions (Agarwal et al., 2020; Deshmukh et al., 2016; Rastogi et al., 2016). A pollutant enriched atmosphere, complemented by favorable meteorological conditions have been observed to result in high loading of secondary species in the region during winter (Ojha et al., 2020). These reasons explain the observed dominance of NH$_4^+$ in the chemical composition at the selected locations and enable us to exclude other cations from the analysis without significant loss of accuracy of the prediction of ALWC. It is expected that the uncertainty produced in the calculated ALWC by disregarding other measured cations would be insignificant compared to the uncertainties caused by inclusion of these species, which may result in erroneous prediction of cation-anion associations. Coastal locations with filter data were also excluded, where effects like chloride depletion are expected to be prominent. For continental locations, which are being considered in this study, winds from the coasts are dominant only during the monsoon season (P. Kumar & Yadav, 2016; A. Kumar et al., 2020), thus implying minimal influence of sea salt aerosols in these regions during winter. For a quantitative representation of the assumptions, the dominance of NH$_4^+$ was expressed in terms of the fraction of NH$_4^+$ among cations on equivalent molar basis, which essentially represents the contribution of NH$_4^+$ relative to all cations in neutralizing the anions. Only those locations with fraction greater than 0.7 were chosen for the analysis, as shown in Table S1 in Supporting Information S1. The molar ratio NH$_4^+/\text{SO}_2^-$ ≥ 1.5 has also been used to infer complete neutralization of SO$_2^-$ by NH$_4^+$ as described in various studies (Agarwal et al., 2020; Pathak et al., 2009; Satsangi et al., 2021) and has been calculated and tabulated in Table S3 in Supporting Information S1 for the data under consideration.

The locations where filter-based data are available include Patiala (Rastogi et al., 2016), Ahmedabad (Rengarajan et al., 2011), Bhopal (S. Kumar & Raman, 2016; Samiksha et al., 2021) and Amritsar (S. Kumar et al., 2018). The compiled average aerosol chemical composition at these locations have been summarized in Table S1 in Supporting Information S1 and the geographical, winter time meteorological information in Table S2 in Supporting Information S1. Few locations with data on only inorganic ion concentrations and no OC concentration, such as Mount Abu (A. Kumar & Sarin, 2010), Sikandarpur (Agarwal et al., 2020) and Patna (A. Kumar et al., 2020) are also included for additional analysis based on the concentration of potassium (K$^+$). It is evident from Tables S1 and S2 in Supporting Information S1, that all these locations not only represent diverse environmental conditions but also those which are meteorologically distinct even during the same season. Since the ACSM/AMS and filter based data correspond to different aerosol size ranges (PM$_{1.0}$ and PM$_{2.5}$, respectively), the data sets have been separately analyzed without any inter-comparison.

The lack of organics concentration in the filter-based data needed to be accounted for, since organics have a significant influence on the overall hygroscopicity of ambient aerosols and hence, OM was estimated from filter-based OC measurements. Organic matter could be significantly composed of water soluble species, which are generally labeled as water soluble organic carbon (WSOC), formed from oxidation of VOCs or aging of primary organic aerosol emissions (Faust et al., 2017). WSOC ratio has been reported to be high in the IGP region
in India (Ram et al., 2010). In fact, earlier studies have estimated significantly high hygroscopicity for OM, which meant that they could have an enhancing effect on the overall water uptake characteristics of ambient aerosols (Cruz & Pandis, 2000; Engelhart et al., 2011; Fajardo et al., 2016; Jin et al., 2020). Studies have also shown that water contributed by OM could be significant as an enabler for secondary aerosol formation reactions (Jin et al., 2020). Thus, in this study, OM was estimated for the filter based locations using the OC data by multiplying a mass conversion factor to the OC mass concentration as suggested in literature (Patel & Rastogi, 2018; Rastogi et al., 2016).

\[
\text{Organic Matter} = \text{Mass factor} \times \text{Organic Carbon}
\]  

(2)

Mass conversion factor is the ratio of an estimated molecular weight of OM to the molecular weight of carbon and is determined based on the type of location. A mass conversion factor of 1.6 and 1.9 is recommended in literature for urban and aged aerosols respectively (Turpin & Lim, 2001).

2.4. Thermodynamic Modeling of ALWC

The ALWC prediction for all locations was determined using the thermodynamic model ISORROPIA2.1 based on the average aerosol chemical composition, RH, and temperature. The model considers only inorganic species (SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}, NH\textsubscript{4}, Cl, Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and K\textsuperscript{+}) in its calculations and does not account for the presence of any OM (Fountoukis & Nenes, 2007a) in the aerosols. ISORROPIA2.1 exhibits rapid and robust convergence, with excellent performance with regard to computational speed, which makes it extremely suitable for incorporation into large-scale atmospheric transport and air quality models (Fountoukis & Nenes, 2007a). Closure studies show that ALWC predictions made by ISORROPIA have agreed with GF based measurements for RH > 60% (Bian et al., 2014; Jin et al., 2020; Tan et al., 2017). Reported discrepancies were assumed to occur due to various reasons including the difficulty to model highly non ideal behavior of concentrated aqueous phase of the aerosol at low RH (Wexler & Clegg, 2002) and lower number of species under consideration in the model, which could lead to errors in the estimated MDRH points (Bian et al., 2014).

Since the measured data consists of only particle phase concentrations and no gaseous phase concentrations, the analysis was performed in the reverse mode of ISORROPIA. The reverse mode assumes the total particle phase concentration as the basis for the model to predict the equilibrium gaseous phase concentrations based on gas-particle partitioning and distribution of chemical species in the solid and liquid phases within the particle. Calculations were performed in the metastable mode of ISORROPIA2.1. Experimental and field observations on the phase state of ambient atmospheric aerosols have indicated the dominance of the metastable state, wherein the aerosols are expected to coexist in liquid state below their mutual deliquescence point (Rood et al., 1989; Tang & Fung, 1997; Tang et al., 1995). Aerosols have been observed to display hysteresis with respect to their phase state, in which water uptake occurs at DRH/MDRH and the transition back to a dry state occurs at a significantly lower critical RH known as the efflorescence RH (Rood et al., 1987). Thus, observations of metastable state may be explained by the strong diurnal cycling of RH in the atmosphere (Shrestha et al., 2013).

As discussed in the preceding section, ISORROPIA utilizes the ZSR correlation (Equation 1) to estimate ALWC. The model does not consider the aerosol curvature effects described by the Kelvin effect to be significant in its calculations (Nenes et al., 1998). The ambient vapor pressure of water is also considered to be unaffected by water uptake by the aerosols and hence, the water activity in any phase, under the assumptions of phase equilibrium between all three phases, is assumed to be the RH of ambient air, expressed on a scale ranging from 0.0 to 1.0.

\[
\alpha_w = RH
\]  

(3)

The nature of organic species is generally complex that they may contribute positively or negatively to the aerosol hygroscopicity based on it’s chemical composition (Cruz & Pandis, 2000; P. Saxena et al., 1995). Despite this uncertainty, the contribution of organics to the ALWC was estimated by applying the \(\kappa\)-Kohler theory (Petters & Kreidenweis, 2007) with the ZSR mixing rule,

\[
V_{w,\text{arg}} = V_{d,\text{arg}} \kappa_{\text{arg}} \frac{\alpha_w}{1 - \alpha_w}
\]  

(4)
where $V_{w,\text{org}}$ is the ALWC corresponding to the organics, $V_{d,\text{org}}$ is the volume of the organics and $\kappa_{\text{org}}$ is the hygroscopicity parameter corresponding to the organics and $a_w$ is the water activity, which is assumed to be equal to the RH. $V_{d,\text{org}}$ is calculated by dividing the organic mass concentration by an assumed organic density of 1.4 g/cm$^3$ (Jin et al., 2020; Turpin & Lim, 2001). As discussed earlier, OM may have significant hygroscopicity as in the case of WSOC, for which $\kappa$ was observed to be as high as 0.3 in several studies (Lambe et al., 2011; Massoli et al., 2010). Since WSOC has not been quantified for all locations under consideration in the respective measurement data, a nominal value of $\kappa_{\text{org}}$ was assumed as recommended from literature, based on the type of location. $\kappa_{\text{org}}$ was assumed to be 0.08 and 0.13 for urban and rural locations, respectively (Nguyen et al., 2016). The $V_{w,\text{org}}$ thus calculated was added to the ALWC predicted by ISORROPIA for the inorganics to obtain the total volume of ALWC, $V_w$. Thus, in the present study, the hygroscopicity of the organic aerosols is distinguished on the basis of environment dependent properties of organic aerosols (e.g., urban vs. rural). Further differentiation is not feasible from the existing compilation of chemical composition data available in the literature. However, the measurement of WSOC using filter techniques may aid in the better estimation of the water uptake characteristics of organic aerosols. Recent studies have assumed kappa for WSOC to be as high as 0.3 for the calculation of ALWC (Boreddy et al., 2021), significantly modifying the organic aerosol hygroscopicity. We propose that future measurements of OM using filter techniques need to include that of WSOC, so as to improve the modeling of the water uptake ability of the various organic aerosols.

### 2.5. Estimation of Inorganic Chemical Compounds

The ALWC predicted by the ZSR correlation (Equation 1) in ISORROPIA2.1 is based on the assumption that the total water content is the sum of contribution of various individual chemical compounds formed by the ionic species present in the aerosol, which has been validated by previous studies (Petters et al., 2009; Z. J. Wu et al., 2013). It is interesting to note that the correlation neglects any interactions occurring between these chemical compounds within the bulk of the aerosol particle (Moore & Raymond, 2008).

In order to analyze the inorganic compounds contributing to the predicted ALWC, the ion balance performed by ISORROPIA2.1 was determined by running the model in dry mode (Almeida et al., 2019; Tao et al., 2021). ISORROPIA2.1 predicts the salt species based on the relative concentration of NH$_4^+$, Na$^+$ and crustal ion concentrations, parameterized as sulfate, sodium and crustal ratios (Fountoukis & Nenes, 2007a). The mass concentration of salt species obtained from the model were used to calculate their individual contribution to ALWC using the ZSR correlation. The water uptake of a particular salt is the ratio of its molar concentration and binary molality as shown in Equation 1. The binary molalities of individual salts were determined using parametric data for the correlation between binary molality and activity obtained from literature (Fountoukis & Nenes, 2007a; Pilinis & Seinfeld, 1987). The water uptake per unit mass of individual salt species were also calculated for a range of RH.

### 2.6. Estimation of Hygroscopicity Parameter $\kappa$

The hygroscopicity parameter $\kappa$ is a single parameter representation for the particle hygroscopicity, which is defined through its effect on the water activity of the solution within the particle (Petters & Kreidenweis, 2007).

$$
\kappa = \frac{V_w}{V_d} \frac{1 - a_w}{a_w}
$$

Equation 5, may be redefined for multicomponent mixtures using the $\kappa$ mixing rule-

$$
\kappa_{\text{total}} = \sum_i k_i e_i
$$
where $\kappa$ and $\epsilon$ are the hygroscopicity parameter and volume fraction of the individual component $i$ in the mixture. This mixing rule may be represented in terms of organic and inorganic fractions as:

$$\kappa_{\text{total}} = \kappa_{\text{org}} \cdot (1 - f_{\text{org}}) + \kappa_{\text{inorg}} \cdot f_{\text{org}}$$

Equation 7 parameterizes the hygroscopicity of inorganic and organic species ($\kappa_{\text{org}}$ and $\kappa_{\text{inorg}}$ respectively) separately and relates them to $\kappa_{\text{total}}$, $f_{\text{org}}$, and $f_{\text{inorg}}$ represent volumetric fraction of organic and inorganic matter respectively. Considering that chemical compositions are generally expressed in terms of mass, it is more convenient to express the mixing rule in terms of mass fractions. Such a mixing rule had been earlier suggested by Gunthe et al. (2009), where the assumption of mass fraction was made as a first order approximation. The relative error caused by the assumption of mass fraction was examined by comparing $\kappa_{\text{total}}$ with $\kappa_{\text{mix}}$ calculated using the mass fraction based mixing rule. Figure S1 in Supporting Information shows that $\kappa_{\text{total}}$ and $\kappa_{\text{mix}}$ follow the 1:1 line with a correlation of fit of $R^2 = 0.85$ (considering data points for only the available 10 locations). Hence, the assumption of mass fraction is not expected to cause significant error in the estimation of $\kappa_{\text{total}}$.

The reverse mode calculation in ISORROPIA 2.1 is based on the assumption of a fixed chemical composition of the aerosol phase, irrespective of the RH. However, in the ambient, partitioning of chemical species between the gaseous and aerosol phases is enhanced with increase in RH, leading to aerosol growth and secondary aerosol formation (Gunthe et al., 2021; M. Saxena et al., 2017). Gas to particle partitioning would alter the chemical composition of the aerosol phase depending on the RH, and this indicates a strong dependence of particle phase chemical composition on RH. Gas to particle partitioning is modeled in the forward mode of ISORROPIA2.1, where the total species concentration consisting of both gaseous and aerosol phase is provided as input to the model and the species are partitioned between both the phases based on the RH and temperature. This calculation is not feasible in the present study due to lack of gas phase measurements and hence, the reverse mode is used. The reverse mode of ISORROPIA2.1 is not sensitive to the temperature due to different reasons. Equation 1 shows that the ZSR rule used to calculate ALWC is not sensitive to temperature. Since gas to particle partitioning processes, which are temperature dependent, are not accounted in the reverse mode, the effect of temperature does not reflect on the particle phase composition derived in ISORROPIA2.1. Hence, the effect of temperature is not directly analyzed in this study. However, its effect is expected to reflect in the measured chemical composition data compiled in this study and will be discussed in the subsequent sections. Since the particle phase chemical composition is assumed to be constant across all RH in reverse mode, $\kappa$, which is a function of chemical composition, could be calculated as a characteristic parameter for a given location. $\kappa$ is thus estimated using Equation 5, by a fit between the $V_{\text{mix}} / V_{\text{org}}$ ratio and $\alpha$, for a range of RH. The $\kappa$ associated with the inorganics was also fitted separately, using only the inorganic dry mass and corresponding ALWC predicted by the model.

### 2.7. Estimation of ALWC Combining WRF-Chem Simulation With ISORROPIA2.1

Weather Research Forecasting (WRF) model coupled with Chemistry (WRF-Chem) was used to simulate the chemical composition of $\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, and organics over the Indian region. Important details about the version, domain, resolution, boundary conditions, meteorological and chemical fields, and emission inventory used for the WRF-Chem simulations are discussed elsewhere (Chutia et al., 2019). Briefly, the WRF-Chem simulations were carried out using the 3.9.1.1. version of the model with high spatial resolution of 12 × 12 km for January 2011, using updated anthropogenic emission inventory, Emissions Database for Global Atmospheric Research- Hemispheric Transport of Air Pollution. The model output has been rigorously validated against the comprehensive gas phase observational data set of VOC over the Indian region for the month of January 2011. Model results over parts of India, particularly over the hot spots of anthropogenic emission, appeared to have reproduced the observational data with good qualitative and quantitative agreement (Chutia et al., 2019). We used the WRF-Chem simulated $\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, organic mass concentrations, and RH over the Indian region (Figure S6 in Supporting Information S1) to couple with ISORROPIA2.1 and derive the ALWC over the Indian region, with the same resolution as that of the WRF-Chem output.
3. Results and Discussion

3.1. Overview of ALWC Over the Indian Region

Figure 1 shows the spatial distribution of the annual mean of AOD for the year 2017 using data from Moderate Resolution Imaging Spectroradiometer, as a nominal representation of the spatial distribution of aerosol loading over the Indian region. The Indo-Gangetic Plain (IGP), spread from the state of Punjab in the west to West Bengal in the east, is a hot spot of aerosol emissions, as evident from the figure. The AOD levels in the region are consistently greater than 0.5, with even higher intensity hotspots at some locations marked by AOD >0.8. The high aerosol loading in the IGP is attributed to fossil fuel combustion from thermal power plants and vehicles, dust transport, agricultural residue burning, solid biomass burning for domestic cooking and heating, and persistent waste burning (Jat & Gurjar, 2021; Ojha et al., 2020). Modeling studies have further reported the widespread enhancement of fine particulate matter across the IGP, especially during wintertime (Ojha et al., 2020). The measured average chemical composition of aerosols consisting of various inorganic and organic species is marked in Figure 1 as pie charts for the corresponding locations on the map, using the data summarized in Table S1 in Supporting Information S1. The aerosol chemical composition at the locations was determined as the average over the respective measurement periods during winter, where the composition of PM_{1.0} was measured using online real-time AMS/ACSM (locations marked in violet text) and that of PM_{2.5} were derived from filter based measurements (locations marked in black text). The pie charts evidently show heterogeneity in the total aerosol mass burden and chemical composition across the locations under consideration, which represent distinct environmental conditions as discussed earlier. The total dry aerosol mass of PM_{1.0} and PM_{2.5} determined as the sum of the mass concentrations of all measured species, is also marked corresponding to the locations, to nominally represent the location based aerosol mass loading. For PM_{1.0}, the total dry aerosol mass ranged from the lowest value of 12.4 μg m^{-3} at Mahabaleshwar, a pristine high-latitude location in the Western Ghat mountain range, to the highest value of 406.4 μg m^{-3} at Kanpur, a hot spot of anthropogenic emissions in the IGP. The same for PM_{2.5} ranged from 43.5 μg m^{-3} at Ahmedabad, a city with the influence of winds from the Thar desert as well as the Arabian Sea, to the highest value of 135.8 μg m^{-3} at Patiala, located in the western IGP. The PM_{1.0} concentration in the coastal locations (Bhubaneshwar, Chennai, Thiruvananthapuram) is generally observed to be an order of magnitude lower than that at the continental locations, which may be due to the dispersion of the polluted air masses by air masses with higher wind speeds and of marine origin (Kommula et al., 2021).

The observed chemical heterogeneity needs to be discussed in terms of the variation of the ionic species across diverse environmental conditions. Since the data has been compiled from different experimental campaigns in different years, we have exercised restraint in the quantitative interpretation of the data. The discussion in this study only attempts to observe the trends in the chemical composition across the locations. The percentage of SO_{4}^{2-} in the dry mass ranges from 8.21% in New Delhi to 33.41% in Chennai in PM_{1.0}, and from 8.46% in Amritsar to 26.35% in Bhopal in PM_{2.5}. SO_{4}^{2-} is generally formed through different mechanisms of oxidation from the precursor SO_{2} gas (Agarwal et al., 2020; Deshmukh et al., 2016; A. Kumar & Sarin, 2010; Rengarajan et al., 2011), which is predominantly emitted by the combustion of coal used in thermal power plants (S. Kumar et al., 2018; Rastogi et al., 2016). Higher temperatures enhance the availability of OH radicals required for the photochemical oxidation of SO_{2} to SO_{4}^{2-} (Chatterjee et al., 2010; Gani et al., 2019; Mallik et al., 2019). The fraction of SO_{4}^{2-} is observed to increase with a decrease in latitude and coincidentally, it is in line with the solar irradiance and ambient temperature that follows the same trend. Thus, higher temperature and photochemical activity at lower latitudes are speculated to promote the formation of SO_{4}^{2-} through the photochemical oxidation (Chatterjee et al., 2010; Gani et al., 2019), combined with high regional emissions of SO_{2} (Mallik et al., 2019), resulting in the higher SO_{4}^{2-} at lower latitudes. The percentage of NO_{3}^{-} in the dry mass ranges from 3.14% in Thiruvananthapuram to 17.52% in Kanpur in PM_{1.0}, and from 2.76% in Ahmedabad to 16.45% in Patiala in PM_{2.5}. NO_{3}^{-} is formed through gas to particle conversion of precursor NO_{2} gases (Deshmukh et al., 2016; Rengarajan et al., 2011), prominently emitted by fossil fuel combustion in automobiles (Agarwal et al., 2020; Deshmukh et al., 2016; Rengarajan et al., 2011). The percentage of Cl^{-} in the dry mass ranges from 0.45% in Thiruvananthapuram to 11.8% in New Delhi in PM_{1.0}, and from 0.18% in Ahmedabad to 2.87% in Patiala in PM_{2.5}. Continental Cl^{-} is dominantly due to anthropogenic emissions from biomass burning, open waste burning (mainly of plastics like PVC), and brick kilns, either as primary emission as particulates or secondary emission in the form of HCl vapor (F. Cao et al., 2016; Engling et al., 2009; Gunthe et al., 2021; P. Kumar & Yadav, 2016; S. Kumar et al., 2015). Though Cl^{-} is naturally released as sea salt formed by wave crashing in the oceans, sea salt...
Figure 1. Average chemical composition of fine aerosols at locations over India during wintertime, based on Aerosol Chemical Speciation Monitor/Aerosol Mass Spectrometer (marked by violet text) or filter-based (marked by black text) measurements. The pie charts represent the average mass fraction of the concentration of different chemical species in the aerosols, measured at various locations indicated by the solid lines and square markers on the map. The basemap depicts the annual mean (year 2017) of Aerosol Optical Depth derived using Level 2 data from Moderate Resolution Imaging Spectroradiometer.
Cl\(^{-}\) is not expected in the PM\(_{1.0}\) data under consideration since the quantified Cl\(^{-}\) is of continental nature. Nor is it expected in the PM\(_{1.0}\) data under consideration in which the quantified Cl\(^{-}\) is of non refractory nature. The percentage of NH\(_{4}^{+}\) in the dry mass ranges from 6.42% in Thiruvananthapuram to 11.9% in Chennai in PM\(_{1.0}\), and from 7.36% in Ahmedabad to 12.19% in Patiala in PM\(_{2.5}\). NH\(_{4}^{+}\) is mainly formed through gas to particle conversion of NH\(_{3}\) gas through its reaction with acidic precursors like H\(_2\)SO\(_4\), HNO\(_3\) and HCl to form NH\(_{4}^{+}\) salts of SO\(_2^{-}\), NO\(_3^{-}\) and Cl\(^{-}\) (Deshmukh et al., 2016; Finlayson-Pitts & Pitts, 2000; S. K. Sharma et al., 2020; Singh & Kulshreshtha, 2012). Thus, NH\(_{3}\) is an important precursor for SO\(_2^{-}\), NO\(_3^{-}\) and Cl\(^{-}\) formation in PM\(_{1.0}\) and hence acts as an important driver for the formation of secondary inorganic aerosols in the fine mode (M. Sharma et al., 2007). NH\(_{3}\) is mainly emitted from decomposition of animal waste, fertilizer use (in the form of NH\(_{3}\) or urea), conversion of NO\(_x\) to elemental nitrogen in catalytic converters installed in vehicles and biomass burning (Aneja et al., 2012; A. Kumar & Sarin, 2010; M. Sharma et al., 2007; Singh & Kulshreshtha, 2012; Yadav & Kumar, 2014). The trends in the variation of NO\(_3^{-}\), Cl\(^{-}\) and NH\(_{4}^{+}\) among the locations are very similar and shows highest values at higher latitudes, coinciding with a decreasing trend of temperature with latitude. This may be explained by the favorable partitioning of NO\(_3^{-}\) and Cl\(^{-}\) from gas to particulate phase at lower temperatures, which consequently also drives the partitioning of NH\(_{4}^{+}\) (Adams et al., 1999; Deshmukh et al., 2016; Gunthe et al., 2021). Organic matter is observed to contribute a significant fraction of the total aerosol mass burden over all locations, ranging from 47.64% in Chennai to 69.73% in Thiruvananthapuram in PM\(_{1.0}\), and from 50.17% in Patiala to 67.37% in Ahmedabad in PM\(_{2.5}\) (estimated from OC measurements). It may be observed that the high fraction of OM at Thiruvananthapuram and Ahmedabad may be resulting in their lower mass fractions of NO\(_3^{-}\), Cl\(^{-}\) and NH\(_{4}^{+}\) in comparison to other locations at the lower latitudes. Organic matter is emitted from biomass and fossil fuel burning prominently. Biomass burning accounts for 70% of the total carbonaceous aerosol emissions in India, as noted in emission inventory models (Gustafsson et al., 2009). Further, photochemical oxidation reactions and condensation of organic vapors may lead to formation of WSOC (Faust et al., 2017). Organic matter contributes more than 50% of the total aerosol mass burden at almost all locations under consideration in general. Thus, it is expected to play an important role in determining the water uptake characteristics at various locations, subject to the assumption of limited hygroscopicity of organics (\(\kappa = 0.08\) or 0.13) (Nguyen et al., 2016).

Figure S2 in Supporting Information S1 shows the minimum, average, and maximum RH at 22 Indian locations, calculated as the three year average of RH during the winter months using air quality data from the monitoring stations of the Central Pollution Control Board and various State Pollution Control Boards. The dots represent the average RH while the whiskers represent the maximum and minimum RH for the corresponding locations. Using the average wintertime RH at the locations under consideration, wintertime ALWC at these locations was calculated using ISORROPIA2.1 based on the compiled aerosol chemical composition data. Due to the absence of monitoring stations at Mahabaleshwar and Bhubaneshwar, the average wintertime RH data was obtained from the respective campaign data for these locations in literature (Kompalli et al., 2020; Mukherjee et al., 2018). An overview of the distribution of ALWC across the locations at the respective average RH is given in Figure 2. The wet mass composition of aerosols, which includes the calculated ALWC, is represented as pie charts and they are labeled corresponding to the locations marked on the map. The fraction of ALWC in the aerosol wet mass is highlighted (colored light blue) on the pie charts and its corresponding mass concentration (in \(\mu\text{g m}^{-3}\) air) is also marked. The reported ALWC comprises of contributions by both organic and inorganic components of aerosols. The hygroscopicity parameter \(\kappa\) determined through fit, is displayed for every location (value enclosed within brackets) and the values have been summarized in Table S4 in Supporting Information S1. It is evident that ALWC is an important contributor to the total aerosol mass burden at all locations, irrespective of varying chemical composition, absolute PM mass and \(\kappa\) as evident from Figure 2. Thus, the ubiquity of ALWC in aerosols over the Indian region is established. The contribution of ALWC in the total aerosol dry mass is observed to range between 10% and 60% at the average wintertime RH across locations. \(\kappa\) varies from 0.17 in Thiruvananthapuram to 0.28 at New Delhi and Kanpur in PM\(_{1.0}\) data set and 0.18 at Ahmedabad to 0.28 at Patiala in PM\(_{2.5}\) data set. The highest ALWC in PM 1.0 has been reported at Kanpur (250.1 \(\mu\text{g m}^{-3}\) air) and the lowest at Mahabaleshwar (1.6 \(\mu\text{g m}^{-3}\) air). The highest ALWC in PM 2.5 has been reported at Patiala (199.5 \(\mu\text{g m}^{-3}\) air) and the lowest at Ahmedabad (7.7 \(\mu\text{g m}^{-3}\) air). These observations correlate well with the earlier observations regarding the trend in total dry aerosol mass from Figure 1. Kanpur and Patiala are cities in the polluted IGP with a high average RH of 75.5% and 88.9% respectively. Mahabaleshwar is a relatively pristine location with a low RH of 33.7%, while Ahmedabad has an average RH of 51.37%. The aerosol composition of Kanpur and Patiala has significant quantities of all inorganic species, while at Mahabaleshwar and Ahmedabad, sulfate dominates the inorganic
species. Thus, a strong interplay between different factors like aerosol mass loading, chemical composition, and RH is expected and therefore, a careful examination of the effect of individual factors on the ALWC uptake is undertaken in the subsequent sections.

3.2. Factors Affecting ALWC Over the Indian Region

The variation of ALWC requires to be analyzed with respect to the three governing factors- RH, absolute dry mass concentration, and chemical composition. From Figure S2 in Supporting Information S1, it can be observed that the minimum and maximum RH, representing drier and wetter aerosol conditions for the various locations in the Indian region lie at 35% and 95% RH, respectively. The average RH during wintertime is observed to be around 70% across most locations. To investigate the sensitivity of ALWC to RH, ALWC at chosen RH values of (a) 35%, (b) 70% and (c) 95% RH, representing the drier, average and wetter conditions has been calculated at all locations. The fraction of total ALWC (which includes contribution by both organic and inorganic matter, colored blue), is compared across diverse environmental conditions as shown in Figure 3 for three different ambient RH levels separately. The percentage of ALWC is lowest at Thiruvananthapuram (8%, 24%, 68% corresponding to 35%, 70%, 95% RH) and highest at Chennai (13% corresponding to 35% RH), New Delhi (33%, 78% corresponding to 70%, 95% RH) in the PM$_{1.0}$ data set. For the PM$_{2.5}$ data set, the percentage of ALWC is lowest at Bhopal (8% corresponding to 35% RH), Ahmedabad (26%, 69% corresponding to 70%, 95% RH) and highest

Figure 2. The fraction of Aerosol Liquid Water Content (ALWC) in the wet aerosol mass (colored blue), modeled at the respective average wintertime relative humidity at various locations over India is shown as pie charts. The mass fraction of all chemical species are also marked in various colors, as described in the legend. Solid lines and square markers denote the locations where measurements were done using either Aerosol Chemical Speciation Monitor/Aerosol Mass Spectrometer (violet text) or filter based methods (black text). The absolute mass of calculated ALWC (μg m$^{-3}$) and the hygroscopicity parameter kappa (in parenthesis) fitted for respective locations are marked beneath the respective pie charts.
The average percentage of ALWC is 11% for PM$_{1.0}$, 9% for PM$_{2.5}$ at 35% RH, 30% for PM$_{1.0}$, 28% for PM$_{2.5}$ at 70% RH and 74% for PM$_{1.0}$, 73% for PM$_{2.5}$ at 95% RH. The average percentage of ALWC is thus comparable for both, PM$_{1.0}$ and PM$_{2.5}$. The change in the ALWC percentage may be noted to be more pronounced from 70% to 95% RH compared with 35%–70% RH. At 35% RH, the percentage of the total aerosol mass burden occupied by ALWC is minimal. Up to the average ambient RH level of 70% RH, the percentage of ALWC has increased steadily with RH, while a sharp increase occurs at 95% RH. At this RH, the ALWC appears to dominate the total aerosol mass burden significantly that at least 70% of the total mass is occupied by ALWC. Therefore, high RH drives ALWC to dominate the total mass, irrespective of the aerosol chemical composition. This observation is consistent with previous studies, which have also observed that under high RH conditions, ALWC is the highest contributor to the overall aerosol mass burden (Bian et al., 2014; Jin et al., 2020; Nguyen et al., 2016; Shen et al., 2019).

Though considerable uniformity has been observed in the fraction of ALWC in the total aerosol mass at a particular RH, the absolute ALWC is strongly influenced by mass concentration and chemical composition. Figure 4 compares the water uptake characteristics between 35%, 70% and 95% RH further at different locations. Figure 4a compares the calculated absolute ALWC at the three RH for every location. The total ALWC is highest at Kanpur (45.44, 191.05 and 1447.50 μg m$^{-3}$ air at 35%, 70% and 95% RH respectively) and lowest at Mahabaleswar (1.68, 5.65 and 37.84 μg m$^{-3}$ air at 35%, 70% and 95% RH respectively) among the PM$_{1.0}$ data set. Among the PM$_{2.5}$ data set, it is highest at Patiala (16.43, 63.73 and 470.81 μg m$^{-3}$ air at 35%, 70% and 95% RH respectively) and the lowest ALWC at Bhopal (4.28 μg m$^{-3}$ air at 35%) and Ahmedabad (14.97, 97.28 μg m$^{-3}$ air at 70% and 95% RH respectively). Hence, the trend in the absolute ALWC is also observed to follow the same trend as that

**Figure 3.** Comparison of the mass fraction of Aerosol Liquid Water Content and chemical species in aerosols at relative humidity (RH) (a) 35%, (b) 70%, and (c) 95%, (representing minimum, average and maximum RH during wintertime) between various locations over India indicated by the number on x-axis. Aerosol Chemical Speciation Monitor/Aerosol Mass Spectrometer based locations are indicated by violet text and filter based locations are indicated by black text.
of the dry aerosol mass, as discussed from Figure 1. Hence, the absolute value of ALWC is strongly dependent on the aerosol dry mass concentration. The ALWC contributed by inorganics is highest at Kanpur (38.76, 162.09 and 1211.68 μg m\(^{-3}\) air at 35%, 70% and 95% RH respectively) and lowest at Mahabaleshwar (1.33, 4.13 and 25.45 μg m\(^{-3}\) air at 35%, 70% and 95% RH respectively) among PM\(_{1.0}\) data set. Among the PM\(_{2.5}\) data set, it is highest at Patiala (14.33, 54.64 and 396.85 μg m\(^{-3}\) air at 35%, 70% and 95% RH respectively) and lowest at Bhopal (3.25 μg m\(^{-3}\) air at 35%) and Ahmedabad (11.07 and 5.49 μg m\(^{-3}\) air at 70% and 95% RH respectively). It is hence evident that the magnitude of ALWC contributed by the inorganic matter is always greater than that contributed by OM despite the greater magnitude of the mass of OM with respect to inorganic matter, and this is speculated to be due to the assumed lower value of organic hygroscopicity.

These results also show a strong non-linear rise in the ALWC, in either case of organic or inorganic contribution. ALWC is observed to rise relatively slower from 35% to 70% RH, and a sharp rise thereafter is observed from 70% to 95% RH, which resulted in a jump by an order of magnitude in absolute ALWC. Thus, the water uptake by aerosols is strongly dependent on ambient RH, recording a slower rise at a lower RH range, which shifts to a steeper rise at a higher RH range. This observation is consistent with the non-linear trend in the variation of water
uptake per unit mass of individual inorganic species and OM with RH across the 35%–95% RH range, as shown in Figure S3a in Supporting Information S1. The data for the water uptake per unit mass of individual inorganic salt species was obtained from ISORROPIA2.1 while that of OM was calculated separately using Equation 5 of the $\kappa$-Kohler theory, assuming an average value of $\kappa_{org} = 0.1$. Thus, this observed non linearity in the variation of the total ALWC for a location with RH, may be well represented by Equation 5. The plot between the ratio of the volume of water $V_a$ and the volume of dry mass $V_d$ with $a_d$ (or RH) is observed to give a near perfect fit with a single parameter $\kappa$, with correlation of fit, $R^2 > 0.99$ in all cases. The results of the fit are summarized in Table S4 in Supporting Information S1. $\kappa$ characterizes the particle hygroscopicity, in Equation 5, which relates water uptake, dry aerosol mass and RH. $\kappa$ has been determined for the total chemical composition (organic + inorganic matter), as well as just the inorganic matter separately to obtain $\kappa_{total}$ and $\kappa_{inorg}$ respectively. The assumed $\kappa_{org}$ has also been tabulated for all locations considering limited hygroscopicity ($\kappa_{org} = 0.08$ or 0.13 for urban and rural locations respectively) as discussed in the methodology.

Figure S4 in Supporting Information S1 shows the variation of water uptake per unit dry mass with RH for $\kappa$ ranging from 0.1 to 0.6 in increments of 0.05, using Equation 4 of the $\kappa$-Kohler theory, where the water activity (corresponding to RH) was varied from 0.35 to 0.95. The non linear trend described earlier is clearly evident from the figure, but the steepness of rise is observed to depend on the $\kappa$. It can be observed that at lower RH, the ratio of ALWC to the aerosol dry mass ($M_d/M_j$) is comparable for all $\kappa$, while at higher RH, $M_d/M_j$ exhibited pronounced variation for different $\kappa$. Hence, high $\kappa$ may not enhance ALWC significantly at low RH as observed in previous studies (Tan et al., 2017). At lower RH range, the absolute dry mass would primarily determine the absolute ALWC. The critical value of RH as discussed in Jin et al. (2020), beyond which non linear rise occurs is observed to be dependent on $\kappa$. Equation 4 may also be expressed as-

$$ALWC = M_d \cdot \kappa \cdot f(RH)$$

Equation 8 shows that at a particular RH level, ALWC would depend on the dry mass concentration and particle hygroscopicity. In this study, we observe that the range of predicted $\kappa$ is confined to a relatively narrow range of 0.17–0.28, which would significantly affect ALWC only at higher RH as observed from Figure S4 in Supporting Information S1. Hence, it may be assumed that absolute dry mass concentration plays a dominant role in determining ALWC compared to the particle hygroscopicity, which is more significant at higher RH. In the ambient atmosphere, high ALWC at higher RH conditions serves as a reactor for gas to particle reactions, leading to favorable conditions of secondary aerosol formation and growth, provided there is sufficiently high concentration of gaseous precursors available in the atmosphere (Cheng et al., 2016; Huang et al., 2014; G. Wang et al., 2016; Z. Wu et al., 2018). This leads to enhanced mass of the aerosol phase with enhanced hygroscopicity due to uptake of secondary inorganic species, which further enhances ALWC. This indicates that in the ambient atmosphere, non linearity in the variation of ALWC with respect to RH would be even steeper, with a strong dependence of the particle hygroscopicity on RH. Due to lack of gaseous measurement data, we are restricted to the reverse mode of ISORROPIA2.1 for ALWC calculations, assuming fixed composition of the particle phase with respect to RH. Hence $\kappa$, a parameter for particle phase chemical composition, does not consequently vary with RH in this study, enabling us to parameterize a single value of $\kappa$ for a particular location irrespective of RH. Though this assumption doesn’t represent the ambient conditions, it should be noted that the data used for the analysis consists of chemical concentration data averaged over a considerable period of time, which would experience varying RH. Hence, the $\kappa$ estimated from averaged chemical composition data could be considered as a true representation of average aerosol hygroscopicity for a given location. The calculations, especially at higher RH may provide a reasonable lower bound estimate for ALWC. $\kappa$ predicted by this method also acts as a simple parameter for a particular location, facilitating the prediction of the water uptake characteristics of aerosols at that location using traditional measurements of aerosol chemical composition, which could be also used to model aerosol hygroscopicity in aerosol chemistry, transport and climate models with simple formulation.

While ALWC has been observed to be highly dependent on RH, it is also interesting to observe how different chemical species contribute to ALWC at different RH. Figure 4b shows the fractional contribution of OM and inorganic salt species to the ALWC across the three RH under consideration. ISORROPIA2.1 was used to predict the combinations of ionic species that make up the salts. In the $\text{NH}_4\text{SO}_4^+ - \text{NO}_2^- - \text{Cl}^-$ system, ISORROPIA2.1 predicts three regimes of salt species based on the ratio of the molar concentrations of $\text{NH}_4^+$ and $\text{SO}_4^{2-}$, quantified as the sulfate ratio ($R_{\text{SO}_4}$). The regimes are briefly described in Table S5 in Supporting Information S1 as sulfate super rich, sulfate rich and ammonium rich. From Figure 4b, the data set under analysis appears to fall under
only the sulfate rich and ammonium rich regimes. New Delhi, Kanpur, Mahabaleshwar, Bhubaneshwar among
the PM$_{1.0}$ data set and Patiala, Amritsar among the PM$_{2.5}$ data set fall under the ammonium rich regime. In
this regime, ISORROPIA2.1 neutralizes NH$_4^+$ with the anions in the order- SO$_4^{2-}$, NO$_3^-$ and Cl$^-$. Aerosols at
these locations are observed to be rich in NH$_4^+$, that they could neutralize SO$_4^{2-}$ completely as (NH$_4$)$_2$SO$_4$,
and then the excess NH$_4^+$ could neutralize NO$_3^-$ and Cl$^-$ wherever present. The model has predicted NH$_4$NO$_3$ at all locations
in this regime, implying the presence of excess and enough NH$_4^+$ for NO$_3^-$ neutralization. However, only at New
Delhi and Kanpur in the PM$_{1.0}$ has the model predicted NH$_4$Cl formation. Chennai and Thiruvananthapuram
among PM$_{1.0}$ data set, and Ahmedabad and Bhopal among the PM$_{2.5}$ data set fall under the sulfate rich regime,
where NH$_4^+$ is insufficient to neutralize SO$_4^{2-}$- that (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and the double salt of sulfate and bisul-
phate (NH$_4$)$_3$H(SO$_4$)$_2$ are expected to be formed. However, in the present analysis, NH$_4$HSO$_4$ out of the three
SO$_4^{2-}$ salts of NH$_4^+$, has not been predicted at any of the locations. Among the inorganic salt species, (NH$_4$)$_2$SO$_4$
remains the most prevalent contributor to ALWC across all locations in the Indian region. Across all locations in
the Indian region and over the entire range of RH, the contribution of OM to ALWC is much lower as compared
to inorganic matter. The limited hygroscopicity exhibited by OM is the reason for the low contribution to ALWC
despite organics being the species with the highest mass fraction in the dry chemical composition. Data on
WSOC concentration, which is unavailable in the present data set, may be used for a better estimation of the water
uptake assuming higher hygroscopicity for secondary organics in future studies.

It is interesting to note that the fractional contribution of each species is also observed to vary with RH. The
variation in the fractional contribution by OM and NH$_4$Cl with RH for the locations falling under the ammonium
rich regime locations does not show a stable trend. However, the fractional contribution of (NH$_4$)$_2$SO$_4$ clearly
decreases with RH while that of NH$_4$NO$_3$ increases. This may be explained from Figure S3b in Supporting
Information S1 where the water uptake by unit mass of individual species has been represented on a logarithmic scale
for better visualization. It is evident that (NH$_4$)$_2$SO$_4$ has higher water uptake than NH$_4$NO$_3$ at lower RH, which
reverses after around 80% RH. A similar comparison between salt species of the sulfate rich regime (NH$_4$)$_2$SO$_4$,
NH$_4$HSO$_4$ and (NH$_4$)$_3$H(SO$_4$)$_2$ in Figure S3b in Supporting Information S1 shows that the water uptake by (NH$_4$)
$_2$SO$_4$ > NH$_4$HSO$_4$ > (NH$_4$)$_3$H(SO$_4$)$_2$ at 35% RH and it changes to NH$_4$HSO$_4$ > (NH$_4$)$_2$HSO$_4$ ≈ (NH$_4$)$_3$SO$_4$
beyond 80% RH. These observations indicate the RH dependence of water uptake by individual NH$_4^+$ salts.

Since the present discussion focuses on ALWC corresponding to secondary inorganic species whose precursors
are mainly from anthropogenic emissions, it is also necessary to observe the effect of K$^+$ ions potentially released
by biomass burning activities on the ALWC. K$^+$ has been reported to be one of the dominantly emitted species
during biomass burning (F. Cao et al., 2016; Engling et al., 2009). Figure S5 in Supporting Information S1 compares
the ALWC from inorganic species and the individual contribution by various inorganic species, in scenarios where (a) K$^+$ ions were not considered in the analysis and (b) K$^+$ ions were incorporated. The analysis
is performed at the higher RH of 95%, considering the earlier observation that the aerosol chemical composition,
which defines hygroscopicity, plays a significant role in water uptake particularly at higher RH values. Inorganic
chemical composition data from three other locations- Mount Abu, Sikandarpur, and Patna, which satisfied the
criteria of ammonium rich locations were also included in the comparison (the data for these three locations was
not included in the main analysis due to lack of OC measurements). Figure S5a in Supporting Information S1
compares the absolute inorganic ALWC in both the scenarios. The results indicate minimal enhancement of
ALWC with the addition of K$^+$ at all locations. Figure S5b in Supporting Information S1 compares the contri-
bution of inorganic salt species in both the scenarios. The only K$^+$ salt predicted is K$_2$SO$_4$ and it has a minimal
contribution to the ALWC at all locations. However, the prediction of K$_2$SO$_4$ appears unrealistic, since the major
K$^+$ salt released from biomass burning is reported to be KCl (F. Cao et al., 2016). KCl may undergo reactions with
atmospheric H$_2$SO$_4$ and HNO$_3$ to form K$_2$SO$_4$ and KNO$_3$, respectively, the process being generally considered as
the aging of KCl, which evolves from biomass burning emissions (Li et al., 2003). Moreover, ISORROPIA2.1
considers K$^+$ to be of crustal origin and also assumes internal mixing of all species (Fountoukis & Nenes, 2007a).
These observations suggest that K$^+$ of biomass burning may not be accurately modeled by the internally mixed
assumption of ISORROPIA2.1. Since, the chemical composition data indicates low concentration of K$^+$ in the
aerosols and the results show insignificant effect on the ALWC prediction, K$^+$ may be excluded from the anal-
ysis. Figure S3a in Supporting Information S1 shows the water uptake characteristics of the salts of K$^+$. KCl
is observed to have significantly higher hygroscopicity whereas K$_2$SO$_4$ and KNO$_3$, exhibit the lowest hygroscopicity
among all the inorganic salts. Since KCl is observed to have significant hygroscopicity, ALWC may be influenced
3.3. Analysis of Hygroscopicity

Figure 5 gives a comprehensive analysis of the hygroscopicity of aerosols under diverse environmental conditions considered in this study and the relative contribution of organic and inorganic matter. Figure 5a shows the line plot of the variation of the $\kappa_{\text{inorg}}$ (marked pink) and $\kappa_{\text{total}}$ (marked violet) across all the locations. As discussed earlier and also as evident from Figure 2, the highest $\kappa_{\text{total}}$ was observed to be 0.28 at New Delhi and Kanpur and the lowest to be 0.17 at Thiruvananthapuram among PM$_{1.0}$ based locations, while the highest $\kappa_{\text{total}}$ for PM$_{2.5}$ based locations was observed to be 0.28 at Patiala and the lowest to be 0.18 at Ahmedabad. The highest $\kappa_{\text{inorg}}$ was observed to be 0.59 at New Delhi and the lowest to be 0.33 at Bhubaneshwar among PM$_{1.0}$ based locations. For PM$_{2.5}$ based locations, the highest $\kappa_{\text{inorg}}$ was observed to be 0.58 at Bhopal and the lowest to be 0.36 at Amritsar.

As expected, $\kappa_{\text{total}}$ is lower than the inorganic kappa at all locations due to the effect of the OM, which was assumed to have limited solubility in this study. The extent of lowering seemed to vary non uniformly and hence the contribution of OM to $\kappa_{\text{total}}$ needs to be elucidated. The mixing rule in Equation 7 was thus modified to the following form, representing the lowering of $\kappa_{\text{inorg}}$ to $\kappa_{\text{total}}$ as:

$$\kappa_{\text{inorg}} - \kappa_{\text{total}} = f_{\text{org}} \cdot (\kappa_{\text{inorg}} - \kappa_{\text{org}})$$

Thus, the lowering of $\kappa_{\text{inorg}}$ to $\kappa_{\text{total}}$ due to the effect of OM, is a function of the fraction of OM, $f_{\text{org}}$, and the difference between $\kappa_{\text{inorg}}$ and $\kappa_{\text{org}}$. The organic fraction ranges between 50% and 70% of the total aerosol mass and the relative difference between $\kappa_{\text{inorg}}$ and $\kappa_{\text{org}}$ changes considerably across locations too and hence, a combination of both factors determine the final $\kappa_{\text{total}}$. Figure 5b represents the dry chemical composition of the aerosols, where
the inorganic matter is represented in terms of the salt species. Observing $k_{\text{org}}$ from Figure 5a and the chemical composition in Figure 5b simultaneously, aerosols in the ammonium rich regime are observed to have a slightly higher hygroscopicity compared to those in the sulfate rich regime. From Figure S3b in Supporting Information S1, NH$_4$Cl appears to be the most hygroscopic salt among salts of NH$_4^+$ across the range of RH. As observed before, NH$_4$NO$_3$ takes up more water compared to salts of NH$_4^+$ and SO$_2^{-4}$ at higher RH, while at lower RH, the trend is reversed. Thus, NH$_4$Cl and NH$_4$NO$_3$ are responsible for the enhanced $k_{\text{org}}$ in the ammonium rich regime relative to the sulfate rich regime. Earlier studies have reported higher $k$ for NH$_4$Cl and NH$_4$NO$_3$ (Jin et al., 2020; H. J. Liu et al., 2014; Petters & Kreidenweis, 2007), thus corroborating our observation. Nevertheless, salts of NH$_4^+$ and SO$_2^{-4}$ remain the most prevalent species in aerosols across the Indian region over the entire range of environmental conditions investigated here.

3.4. Spatial Variation in ALWC

Figure 6 discusses the ALWC over the Indian region calculated by ISORROPIA2.1 using the concentration of chemical species- NH$_4^+$, SO$_2^{-4}$, NO$_3^{-}$ and OM from WRF-Chem simulations. The spatial variation of the mass concentration of these chemical species over the Indian region is shown in Figure S6 in Supporting Information S1. Since presence of Cl$^-$ has been observed to significantly enhance the ALWC, the lack of Cl$^-$ concentration data from WRF-Chem may have implications on the predicted ALWC and its spatial representation. Particulate chloride is a significant driver of ALWC, specifically in the Indo-Gangetic Plain (Gunthe et al., 2021), where high aerosol mass burden is observed. Thus, the lack of representation of chloride data is expected to underestimate the ALWC calculated using WRF-Chem simulated chemical composition over this region. As compared to other parts of India, since the Indo-Gangetic Plain is distinctly a region of disproportionately high aerosol mass loading, the bias in the estimation of ALWC due to lack of Cl$^-$ in WRF-Chem simulations is not expected to qualitatively alter our results. Nevertheless, we emphasize the use of chemical transport model with detailed chlorine chemistry for further detailed analysis and scientific understanding. Figure 6a shows the distribution of ALWC over the Indian region based on the spatial variation of RH estimated for January 2011 using WRF-Chem simulations, as shown in Figure 6b. West and east IGP appear to be a hotspot of ALWC, across a significant area. Scattered peaks of ALWC appear along the southern and eastern coastal areas, as well as the North eastern part of India. Parts of West, Central and South West India, however, display low ALWC concentration. To understand the effect of any uncertainties in the WRF-Chem data set on the ALWC predictions, a sensitivity analysis was performed by calculating the ALWC based on a 20% increase or decrease in the WRF-Chem predicted chemical concentrations. The results shown in Figure S7 in Supporting Information S1, show no noticeable change in the spatial variation of ALWC across the region. For case (a), the ALWC ranges from 0 to 70 μg/m$^3$ air while for case (b), the ALWC ranges from 0 to 100 μg/m$^3$ air, compared to the previously calculated range of 0–90 μg/m$^3$ air. Hence, the analysis of a 20% change in species concentrations on the ALWC is observed to cause no noticeable change in the spatial variation of ALWC and hence, we expect no major scientific implications on the qualitative findings reported here. Following the previous discussion on ALWC, the spatial variation of ALWC need to be elucidated with reference to the key factors governing it, namely, aerosol loading and RH. Figure 6b shows high RH in the IGP, eastern and southern coastal areas, Jammu and Kashmir and over North East India. Figure 6c shows the spatial variation of the total aerosol loading, calculated as the sum of the mass concentration of all species displayed in Figure S6 in Supporting Information S1. The aerosol dry mass peaks in West and East IGP compared to the rest of the Indian region. This observation coincides with the spatial trend of absolute ALWC, and hence, it may be inferred that absolute aerosol dry mass is the primary driver of high ALWC, supported by conditions of high RH. The spatial variation of chemical species in Figure S6 in Supporting Information S1 suggests that west and East IGP are hotspots of NH$_4^+$ and NO$_3^{-}$. As discussed earlier, NH$_4^+$ is a driver for secondary particle formation from precursor acidic gases like SO$_2$, NO$_3$ and HCl. Thus, high NH$_4^+$ emissions in the IGP possibly lead to aggravated secondary particle formation under high RH (Figure 6b) conditions, which are particularly persistent during the winter season. The impact of secondary particle formation manifests as high PM loading (Figure 6c), which further results in the high ALWC observed in these regions (Figure 6a). Figure 6d shows the variation of ambient temperature over the Indian region, obtained using WRF-Chem simulations, which, however, does not reflect on the ALWC calculations directly. However, the plot clearly shows a decrease in temperature with an increase in latitude over the region, which coincides with decreasing SO$_2^{-4}$ and increasing NO$_3^{-}$ concentrations with latitude. As discussed earlier, higher temperature and photochemical activity may...
promote the formation of $\text{SO}_2^-\text{O}_4^-$ through photochemical oxidation of $\text{SO}_2$ (Chatterjee et al., 2010; Gani et al., 2019; Mallik et al., 2019), while lower temperatures and higher RH promotes the gas to particle partitioning of $\text{NO}_3^-$ and $\text{Cl}^-$ (Adams et al., 1999; Deshmukh et al., 2016; Gunthe et al., 2021). This may suggest a strong dependence of aerosol chemical composition on temperature, which in turn, reflects on the ALWC.

Analysis similar to the preceding sections were additionally performed for the WRF-Chem data. The spatial variation of ALWC with RH was examined at RH of 35%, 70% and 95%. The results, as shown in Figure S8 in Supporting Information S1 on a logarithmic color scale ranging between 0.1 and 700 $\mu$g m$^{-3}$ air, indicates that the spatial distribution of ALWC is similar across the three RH, with high ALWC in the IGP, south India and parts of the Western coast and low ALWC at Jammu and Kashmir and parts of North East India at the upper heights of the Himalayas. Analysis of the spatial distribution of prospective salt species formed from the WRF-chem based ionic species concentration has been performed using the dry mode of ISORROPIA2.1 (as discussed earlier) and the results are shown in Figure S9 in Supporting Information S1. Figure S6a in Supporting Information S1 shows the WRF-Chem estimated $\text{SO}_2^-\text{O}_4^-$ to be at higher concentrations over the Central-Eastern India, South India, and coastal Indian region, consistent with previous studies (Mallik et al., 2019). Thus, in the salt species based
analysis too, (NH₄)₂SO₄ is observed to be the dominant salt species over these regions (Figure S9b in Supporting Information S1), and are speculated to be responsible for the scattered peaks of ALWC observed in the region. On the other hand, the IGP is observed to be a hotspot of NH₂NO₃ (Figure S9a in Supporting Information S1), correlating well with high concentration of NH₄⁺ and NO₃⁻ as estimated by WRF-Chem in the region (Figure S6 in Supporting Information S1). NH₂NO₃ is stable only at low temperature and high RH (Adams et al., 1999; Deshmukh et al., 2016) and may be expected to be a dominant salt species in the aerosols as predicted over the IGP region.

The IGP experiences severe haze and smog during winter, which may hence be attributed to high PM loading over this region, with conditions further aggravated by high RH, which lead to enhancement of secondary aerosol formation and high ALWC. The IGP region may benefit from the reduction of NH₄⁺ and NO₃⁻ over SO₄²⁻, due to observed higher hygroscopicity and abundance of NH₂NO₃ over other salts. The effectiveness of the choice of the species, NH₄⁺ or NO₃⁻ would also depend on numerous factors, which include the presence of excess NH₂ or high Cl⁻. At locations with excess NH₂, secondary aerosol formation and subsequent ALWC may be more responsive to the reduction of NO₃⁻ emissions rather than NH₂ (Acharja et al., 2022). Reduction of NH₂ also poses a very difficult challenge, since the greatest emissions of gaseous NH₂ is from livestock and the usage of fertilizers in the agriculture industry (Gunthe et al., 2021). At locations in the IGP like New Delhi, with high Cl⁻ in the aerosols, reduction of HCl emissions also, would have a larger impact on the reduction of ALWC (Gunthe et al., 2021). Thus, the study re-emphasizes the importance of improvized pollution control strategies targeting emissions of specific chemical species in a highly localized manner for the improvement of ambient air quality in the Indian region.

4. Conclusions

A comprehensive analysis was performed to elucidate the role of aerosol mass concentration, composition and ambient RH on the water uptake characteristics of fine mode aerosols (comprising SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺ and OM) over the Indian region during wintertime. ALWC was derived for PM₁.₀ at six locations and PM₂.₅ at four locations using the thermodynamic model ISORROPIA2.1 at 35%, 70% and 95% RH, representing the minimum, average, and maximum RH during wintertime in the region. The presented analyses is strongly in line with previous literature indicating the ubiquitous nature of ALWC such that it constitutes a significant fraction of the total aerosol mass burden at the average ambient RH. It was observed that ALWC emerges as the most dominant component of atmospheric aerosols at very high RH, where its mass could be 2–3 times that of the dry aerosol mass. The absolute value of ALWC is strongly dependent on the absolute dry mass concentration, implying that high ALWC is primarily due to heavy pollution load, further enhanced by high ambient RH. Strong non-linear dependence of ALWC on RH is observed, which increases slowly at lower RH, and evolves to a sharp rise beyond the critical RH, as discussed in Jin et al. (2020). The critical RH was observed to depend on the particle hygroscopicity modeled as κ. The non-linear rise may be further enhanced at locations where secondary aerosol formation under high RH conditions may result in enhanced particle hygroscopicity due to formation of hygroscopic secondary inorganic species. However, at low RH, ALWC was observed to be dependent on the absolute dry mass and not the particle hygroscopicity.

The key inorganic salt species predicted at the locations include (NH₄)₂SO₄ and (NH₄)₂H(SO₄)₂ at sulfate rich locations and (NH₄)₄SO₄, NH₄NO₃ and NH₄Cl at ammonium rich locations. NH₂NO₃ and NH₂Cl are formed at those locations with excess NH₄⁺ after neutralizing SO₄²⁻, and are observed to increase the κ of aerosols substantially, compared to the salts of NH₄⁺ and SO₄²⁻. Organic matter, exhibiting lower hygroscopicity, was observed to have a low contribution to the ALWC as compared to inorganics. High mass fraction of OM reduced the overall κtotal significantly at some locations. The spatial distribution of ALWC was calculated using the chemical composition of SO₄²⁻, NO₃⁻, NH₄⁺, OM and RH derived from WRF-Chem simulations. High PM loading, complemented by high RH was observed to drastically enhance the ALWC in the Indo-Gangetic Plain (IGP) region, which seems to explain the occurrence of haze and smog over the region. The distribution of ALWC across the Indian region at fixed RH revealed similar trends in variation at all three RH levels. Further, analysis of the occurrence of various salt species revealed that NH₂NO₃ is the primary cause of high ALWC over the IGP, while (NH₂)₂SO₄ dominated the peninsular region. Though the extreme aerosol loading and ALWC in the region is dependent on NO₃⁻ and NH₄⁺, the study calls for a localized examination of aerosol chemistry for the design of pollution abatement policies. The methods and assumptions used in this study may be utilized for a general analysis of the
hygroscopic characteristics of aerosols for the given environmental conditions, using simple measurements of respective chemical composition. We further argue that the analysis of ALWC under contrasting environments and covering distinct seasons is necessary alongside long-term measurements of the aerosol chemical composition to better understand regional aerosol atmospheric chemistry and to mitigate extreme pollution and climatic events occurring due to enhanced ALWC.

Data Availability Statement
The data used in the manuscript has been deposited in an open research depository, accessible at https://doi.org/10.6084/m9.figshare.19703182.v4 (Gopinath et al., 2022). The aerosol chemical composition data (named “Input_data.dat” in the depository) used for Aerosol Liquid Water Content (ALWC) calculations in this manuscript were obtained from various literature, and are also summarised in Table S1 in Supporting Information S1 (references enclosed therein). Meteorological data (named “RH_data.dat” in the depository) used in the study was obtained from the air quality monitoring data of Central Pollution Control Board and various state Pollution Control Boards, accessible at https://cpcb.nic.in/real-time-air-quality-data/. The modeling of ALWC was performed using the thermodynamic model ISORROPIA version 2.1 (Fountoukis & Nenes, 2007a, 2007b), accessible at https://www.epf1.ch/labs/lapi/software/isorrophia/. The ALWC calculated by the model has been deposited in the repository (named “ALWC_results.dat”). Further calculations were performed on MATLAB version R2020b (Mathworks Inc., 2020), licensed under IIT Madras and accessible at https://in.mathworks.com/products/matlab.html. The codes used for the calculations are available from SSG upon reasonable request. Figures were prepared using Igor Pro version 6.37 (WaveMetrics Inc., 2014), licensed by SSG and accessible at https://www.wavemetrics.com/downloads/current.

Acknowledgments
S. S. Gunthe acknowledges partial funding from the Ministry of Earth Sciences (sanction number MoES/16/04/2017-APHH (PROMOTE)), the Government of India, and the Department of Science and Technology (sanction number DST/CPP/Coll/141/2018C), the Government of India. This work was partially supported by the UK National Environment Research Council with grant reference numbers NE/P016480/1 and NE/P016472/1. N. Ojha acknowledges the Vikram computing resources at the PRL, Ahmedabad. A. K. Gopinath acknowledges MHRD, Government of India for his M. Tech. fellowship. S. S. Raj was the recipient of a scholarship from the Indo-German Centre for Sustainability through the German Academic Exchange Service under the initiative “A New Passage to India” funded through the Federal Ministry for Education and Research in 2019 and 2020. The authors are thankful to the three anonymous reviewers for their valuable suggestions and inputs during the review process.

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