Enhanced Aerosol Particle Growth Sustained by High Continental Chlorine Emission in India

Sachin S. Gunthe[1*], Pengfei Liu[2,3*], Upasana Panda[1,4], Subha S. Raj[1], Amit Sharma[1$], Eoghan Darbyshire[5&], Ernesto Reyes-Villegas[5], James Allan[5,6], Ying Chen[7,8], Xuan Wang[9], Shaojie Song[3], Mira L. Pöhlker[10], Liuhua Shi[11], Yu Wang[5], Snehitha M. Kommula[1], Tianjia Liu[12], R. Ravikrishna[13], Gordon McFiggans[5], Loretta J. Mickley[3], Scot T. Martin[3,12], Ulrich Pöschl[10], Meinrat O. Andreae[10,14,15], and Hugh Coe[5]

[1]EWRE Division, Dept. of Civil Engineering, Indian Institute of Technology Madras, Chennai, India
[2]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA
[3]John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA
[4]Academy of Scientific and Innovative Research (AcSIR), Department of Environment and Sustainability, CSIR – Institute of Minerals and Materials Technology, Bhubaneswar, India
[5]Department of Earth and Environmental Sciences, School of Natural Sciences, University of Manchester, Manchester, UK
[6]National Centre for Atmospheric Science, University of Manchester, Manchester, UK
[7]Lancaster Environment Centre, Lancaster University, Lancaster, UK
[8]Data Science Institute, Lancaster University, Lancaster, UK
[9]School of Energy and Environment, City University of Hong Kong, Hong Kong SAR, China
[10]Multiphase Chemistry and Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
[11]Gangarosa Department of Environmental Health, Rollins School of Public Health, Emory University, Atlanta, Georgia, USA
[12]Dept of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA
[13]Dept of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India.
[14]Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA, USA
[15]Department of Geology and Geophysics, King Saud University, Riyadh, Saudi Arabia

[$]Now at Department of Civil and Infrastructure Engineering, Indian Institute of Technology Jodhpur, Karwar, Jodhpur, India
[&]Now at The Conflict and Environment Observatory, Hebden Bridge, West Yorkshire, UK

Many cities in India experience severe deterioration of air quality in winter. Particulate matter is a key atmospheric pollutant that impacts millions of people. In particular, high levels of particulate matter reduce visibility, which has severely damaged the economy and endangered human lives. But the underlying chemical mechanisms and physical processes responsible for initiating haze and fog formation remain poorly understood. Here we present the measurement results of chemical composition of particulate matter in Delhi and Chennai. We find persistently high chloride in Delhi and episodically high chloride in Chennai. These measurements, combined with thermodynamic modeling, suggest that in the presence of excess ammonia in Delhi, high local emission of hydrochloric acid partitions into aerosol water. The highly water-absorbing and soluble chloride in the aqueous phase substantially enhances aerosol water uptake through co-condensation, which sustains particle growth leading to haze and fog formation. We, therefore, suggest that the high local concentration of gas-phase hydrochloric acid, possibly emitted from plastic-contained waste burning and industry causes some 50% of the reduced visibility. Our work implies that identifying and regulating gaseous hydrochloric acid emissions could be critical to improve visibility and human health in India.

The 2018 World Air Quality Report mentioned New Delhi the “world air pollution capital.” In 2017–2018, particulate matter (PM) concentrations exceeded 200 μg m^{-3} and 600 μg m^{-3} for PM with diameter less than 1.0 μm and 2.5 μm, respectively (i.e., PM_1 and $PM_{2.5}$)[1, 2]. The severe pollution, also evidenced by high aerosol optical depth (AOD) over the Indo-Gangetic Plain (IGP) (Fig. 1), is associated with increased respiratory and cardiovascular diseases, poor visibility, and economic damages[3]. For example, persistent poor visibility over the New Delhi airport due to fog and haze has incurred significant financial losses to airline industries[4] and led to increasing vehicular deaths[3]. According to one estimate, in 2017 over Delhi alone, ~12,000 excess deaths can be attributed to exceedingly high $PM_{2.5}$ concentrations[5].

Numerous observational studies focusing on surface PM concentrations have been conducted over India during the last decade[2, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. Although much progress has been made in measuring the seasonal variability of PM and its chemical composition, understanding of the underlying mechanisms responsible for the reduced visibility and deterioration of air quality over Delhi and the IGP remains limited. For example, it is unclear why the PM in Delhi has a higher potential to form haze and fog than other polluted Asian cities[18] although a large fraction of Delhi PM is primary organic matter[2, 19], which is less hygroscopic[20].

Here we present new chemical composition measurements of non-refractory PM smaller than 1 μm (NR-PM_1) from Delhi and a relatively cleaner Chennai (Fig. 1). Measurements are combined with thermodynamic modeling (Methods) to elucidate sources of the observed high chloride concentrations and the implications for PM concentrations and visibility. We report that high non-refractory particulate chloride in Delhi likely results from gas-particle partitioning of HCl gas into aerosol water under typical winter haze conditions of high relative humidity (RH), low temperatures, and excess ammonia. The HCl is apparently emitted from continental anthropogenic sources, including industrial and combustion processes. In the process of co-condensation, the particulate chloride can take up more water, enhancing haze and fog formation. Our field observations and model calculations show that 50% visibility reduction in Delhi during the winter can be attributed to chloride co-condensation mechanism. In Chennai, high chloride concentrations in NR-PM_1 have been observed during the Bhogi festival, when bonfires are prevalent. The high levels of particulate chloride could participate in nighttime multiphase-chemistry producing reactive chlorine species, further affecting ozone and secondary organic aerosol production. These results highlight the uniqueness of atmospheric chemical processes in India, and suggest the importance of regulating chlorine anthropogenic sources.

Variations in PM_1 chemical composition over Delhi and Chennai

The chemical compositions of NR-PM_1 have been observed at diverse locations across India in the present study and literature[2, 10, 12, 14, 17] (Fig. 1; Extended Data Figs. 1 and 2). Consistent with other global regions, organic aerosol (OA) comprised a major fraction of NR-PM_1. The chloride fraction, however, at least episodically, remained an order of magnitude higher than the global average[21] over the Indo-Gangetic Plain (IGP) and metro cities. Especially, chloride comprises ~10% of NR-PM_1 mass in Delhi, which is comparable to other major inorganic components such as sulfate and nitrate. Several other studies using traditional sample-based techniques also reported a high chloride mass fraction in Delhi[9, 19, 22]. These high chloride fractions in NR-PM_1 observed over inland India are unexpected, as dominant source of tropospheric chloride in NR-PM_1 was thought to be acid displacement mobilizing HCl from sea salt particles[23].

Fig. 2 shows the time series of the NR-PM_1 chemical composition measured in Delhi and Chennai. Total NR-PM_1 reveals pronounced daily variations, with higher concentrations at night. At both sites, OA constitutes the largest mass fraction of total NR-PM_1 (69% and 48% for Delhi and Chennai, respectively). Factor analysis suggests that primary organic aerosol (POA), i.e., the sum of hydrocarbon-like OA (HOA), biomass burning OA (BBOA), and cooking OA (COA) comprises 60% and 48% of the mass fraction of total OA for Delhi and Chennai, respectively (Methods; Extended Data Fig. 3), indicating a high contribution from open and domestic burning sources. Intermittent high chloride concentration occurs over Delhi, consistent with previous studies[2, 19, 22, 24, 25]. In Delhi, chloride constitutes the second-largest mass fraction of total NR-PM_1 (10.3%), higher than sulfate (6.8%) or nitrate (6.4%) (Extended Data Fig. 2). During the ten days of polluted episodes with high chloride and high OA in this study (~42% of total days in the campaign, light purple shading areas in Fig. 2a; P1), the daily mean mass fraction of chloride reaches 15.6% of NR-PM_1, higher than episodic values recorded elsewhere in India (Fig. 1; Extended Data Fig. 1). In comparison, the daily mean chloride mass fraction remains

3.7% during episodes of low chloride and high OA (7 days, 25% of total campaign; light green shadings in Fig. 2a; P2), comparable to the typical conditions in other polluted cities in India and China[26]. In Delhi, the NR-PM_1 chloride mass fraction is positively associated with the total NR-PM_1 concentration, indicating enhanced contribution of chloride during highly polluted conditions (Extended Data Fig. 4). The highest chloride fraction averaged over the entire campaign occurs from 04:00–09:00 (local time, Fig. 2c; Extended Data Fig. 5), amounting 24% of NR-PM_1 for Delhi. High levels of chloride also occur in this time frame during P1. A plausible explanation is that these morning hours have the lowest temperatures and highest RH in a day, which favors the partitioning of gas-phase HCl to PM (Fig. 2c).

We hypothesize that the observed chloride in Delhi originates from a complex array of combustion sources and industrial processes. Among the identified OA factors, the biomass burning organic aerosol fraction (i.e., BBOA-to-OA ratio) correlates best with the chloride to OA (Cl-to-OA) ratio (r=0.47, N=1977). (normalize by OA to eliminate the apparent correlation related to the diurnal variation of ventilation that simultaneously affect BBOA and Cl concentrations). During P2 days, the Cl-to-OA ratio linearly increases with the BBOA-to-OA ratio (Fig. 2e and the inset), indicating that chloride/HCl might be co-emitted with BBOA from biomass burning and biofuel combustion. During morning hours, when Cl is partitioning into the particle phase, the chloride to organic carbon (Cl-to-OC) and chloride to black carbon (Cl-to-BC) ratios are similar to the emission ratios of HCl-to-OC and HCl-to-BC, reported for biomass burning and biofuel combustion (Extended Data Fig. 6). During P1, the overall positive correlation of Cl-to-OA ratio with BBOA-to-OA ratio suggests that combustion still be a persistent source of chloride. The Cl-to-OA and Cl-to-BC values, however, are comparable to the emission ratios reported for open burning of mixed garbage[27, 28, 29, 30], higher than that for burning of biomass and biofuel (Extended Data Fig. 6). An exponential increase during P1 in Cl-to-OA observed with respect to BBOA-to-OA ratio indicates additional primary HCl sources. Results from the Lagrangian model STILT suggest additional emissions may come from industries located north-northwest of the observational site (Methods; Extended Data Fig. 7). A large number of illegal, informal, and unorganized metal processing units, as well as e-waste recycling and handling units, plastic processing units, and medical waste management facilities are widespread in that area (Extended Data Fig. 7), and the use of acids by these industries[31, 32, 33, 34, 35, 36] may contribute to the direct HCl gas emissions.

Contrary in Chennai, even though it is located on the coast, chloride on average constituted just 2.7% of total NR-PM_1. However, on 14-January-2019, the Bhogi festival took place in Chennai causing chloride concentrations reaching 40 $\mu g\ m^{-3}$ during the night, corresponding to 11% of total NR-PM_1 (Fig.2b and 2d; Extended Data Fig. 3). During Bhogi, large-scale burning of wood logs, solid waste, and wooden furniture takes place, following an old and important tradition (ref.[37]; Methods). The solid waste burned contains a significant amount of plastics, such as polyvinyl chloride (PVC), and burning of such waste releases HCl gas[38], which can then partition into the aqueous particle phase[39]. We find a strong linear relationship between the BBOA-to-OA ratio and the Cl-to-OA ratio (Fig. 2f), indicating increased chloride concentration from combustion of mixed wood and solid waste in Chennai. Other than during the Bhogi festival, the campaign-averaged chloride level in Chennai was lower than the observed average in Delhi, most likely due to lower HCl emissions and less favorable meteorological conditions– i.e., higher temperatures and lower RH compared to Delhi (Extended Data Fig. 2). Similarly, enhanced chloride concentrations were also observed in Ahmedabad during the Diwali festival, and in Kanpur during a high biomass burning event[10, 12, 14] (Fig. 1).

Thermodynamic modeling

The observed chloride in NR-PM_1 is generally in the form of ammonium-chloride[23, 40], produced by the reaction with NH_3 in the atmosphere from the direct HCl emissions[41, 42]. Figure 3a shows that sulfate and nitrate, the predominant inorganic species of fine PM in most regions, account for only 50% of the inorganic anions in Delhi PM. Chloride, as the single largest inorganic anion in Delhi PM, neutralized 50% of ammonium, on par with sulfate and nitrate combined. The refractory forms of chloride, such as sodium chloride from sea salt and potassium chloride from biomass burning, are not included here because these species do not vaporize at 600 °C, which is a requirement of the instrumentation used here (i.e., the mass spectrometer vaporizer). From a global budget perspective, acid displacement and heterogeneous reactions on sea salt particles is a major source of HCl[43]. In the IGP, however, it is highly unlikely that marine-originated chlorine sources can contribute significantly to HCl and non-refractory chloride.

To further explain the unique thermodynamic nature of the chloride-rich Delhi PM, we analyzed the observed aerosol composition, RH, and temperature with a thermodynamic model (ISORROPIA-II,[44] Methods). For a sensitivity analysis of chemical conditions, the predicted equilibrium fraction of Cl in the particle phase (i.e., $Cl^-/(Cl^- + HCl)$) across different concentrations of total sulfuric acid and ammonia is shown in Fig. 3b. Three distinct regimes of aqueous fraction of chloride were identified, suggesting high fraction of Cl in the particle phase is strongly dependent on the presence of excess ammonia in the atmosphere. Previous studies have reported high gas-phase ammonia concentrations over Delhi (~30 $\mu g\ m^{-3}$; shown by the green box in Fig. 3b[45]), indicating an ammonia excess regime explaining high chloride concentrations in our observations. In the chemical regime of Delhi, decreasing the sulfate concentration would marginally reduce particle-phase chloride, mainly because of the decrease in sulfate-associated liquid water. Ammonia appears to be a controlling factor for chloride partitioning. To decrease the particle phase Cl fraction, however, an aggressive ammonia emission reductions would be required (more than 50% reduction in total ammonium), a difficult task as in India it is largely emitted from agricultural sources, including livestock and fertilizer use. Reducing the anthropogenic sources of HCl appears to be the only feasible approach to effectively control the particle phase chloride concentration.

Both the PM chloride concentration and chloride fraction in NR-PM_1 show strong temperature and RH dependence (Extended Fig. 8). To explain these behaviors, we performed thermodynamic calculations for a wide range of temperature and RH values (Fig. 3c). For the observed range of temperature (10–18°C) and RH (70–85%) during morning hours (04:00–09:00 LT) over Delhi, the predicted fraction of Cl in the particle phase ranged from 80% to 99%. By comparison, during afternoon hours (14:00–18:00 LT), this fraction was consistently less than 30%. The contrast in the partitioning behavior for different hours of the day was driven by changes in both PM-associated liquid water and ambient temperature. These results are consistent with the observations showing that the chloride content of NR-PM_1 was high during morning hours and decreased substantially in the afternoon (Extended Data Fig. 5). Besides the thermodynamically driven partitioning, other factors, such as shallow boundary layer during early morning hours, which cannot explain the increase of chloride mass fraction, can further enhance the concentrations of chloride and other PM species, causing severe visibility reduction at this time of day.

The measurements indicate a strong correlation between chloride and liquid water content of PM over a wide range of RH and PM mass concentrations (Fig. 3d). This positive correlation is in line with the model prediction indicating co-condensation of chloride occurs along with water uptake (Extended Fig. 9; red dashed line in Fig. 3d). Co-condensation has been reported previously for organic vapors[46] and nitric acid[47], using parameterizations and modeling approaches primarily concluding that water-soluble, and semi-volatile species, such as organic vapors and nitric acid, can significantly enhance the water uptake and cloud activation tendency of atmospheric PM. The gas-particle partitioning of HCl and NH_4Cl experiences a similar co-condensation process as organic vapors and nitric acid, but causes a greater increase in hygroscopicity of particles. Ambient in-situ observations indeed confirm that PM in Delhi exhibits higher water uptake capability compared to other polluted megacity Beijing[18], consistent with this study. This high hygroscopicity is unexpected based on conventional understanding due to high organic mass fraction (60-70%) of the NR-PM_1 in Delhi, higher than the typical value of 40-50% in polluted Beijing[48]. A higher organic fraction, which is less hygroscopic than inorganic salts, is typically associated with lower hygroscopicity[20].

Here we show that chloride co-condensation can explain the observed high hygroscopicity of Delhi PM. Following the method described by ref[18], we derived the aerosol light-extinction enhancement factor f(RH) in Delhi based on ambient measurements of visibility and $PM_{2.5}$ (Methods). The visibility provides a direct measure of light extinction under ambient conditions. The f(RH) represents the ratio of the mass extinction coefficient at elevated RH to that at dry conditions (RH <35%). This approach is found to be most suitable to investigate co-condensation effect as it does not perturb the concentrations of soluble gases such as HCl, HNO_3, and NH_3, which otherwise may get evaporated during the measurements owing to conditioning of air samples.

Role of high chloride in visibility reduction

The visibility-derived *f*(RH) values were compared with the thermodynamic results (Fig. 4a). Two modeling cases were formulated to illustrate the effect of chloride co-condensation (Methods). In the modeled case considering chloride co-condensation, a total chloride concentration of 25 $\mu g\ m^{-3}$ (gas phase+particle phase, HCl equivalent) was used (blue curve in Fig. 4a). The model yields a change in particle composition, which causes a light-extinction enhancement that is consistent with the measurements (Extended Data Fig. 9). The reference case (red curve) considers a chloride-free environment–i.e., the total chloride concentration was set to zero. For both cases, the RH values were varied from <35% to >90%, and the equilibrium partitioning of water and semi-volatile species between gas and particle phases was calculated. The model results agree well with the observed *f*(RH) when chloride was included in the model, whereas in the case without chloride, the modeled *f*(RH) is biased low compared to measurements. For RH from 90–95%, which consistently occurs over Delhi during winter haze episodes, high value of 5 of *f*(RH) indicates a strong water uptake by PM. For RH values beyond 95%, *f*(RH) values are expected to be much higher than the value of 5 as reported here comparable to the hygroscopicity of pure ammonium sulfate[49]. At a similar RH level, the modeled *f*(RH) without accounting chloride has a smaller value of 2.5. Thus, presence of HCl can strongly enhance water uptake through co-condensation into the PM contributing ~50% of the visibility degradation during the haze/fog events.

We also show that the co-condensation mechanism can also lower the barrier of cloud activation[47], thus promoting fog/cloud formation. The cloud condensation nuclei (CCN) activation of typically sized particles was calculated by combining the thermodynamic model with the Kelvin effect to calculate the Köhler curves (Methods). Figure 4b shows the effect of higher HCl concentration in the atmosphere on the equilibrium supersaturation ratios. Particles with 100 nm dry diameter have full CCN activation at a critical supersaturation of 0.13%, factor of two lower when the atmosphere is considered without chloride (i.e., 0.28%). This indicates a strong cloud activation capability of PM over Delhi at times when chloride is abundant. The enhanced particle growth encompassing a wide range of water vapor concentration (from sub-to super-saturated range) corresponds with the period from late evening to early morning an intense fog formation period over Delhi.

In summary, these analyses examines the complex chemical and physical processes and underlying mechanisms related reduced visibility in Delhi, which have large negative consequences on the economy and societal well-being. We find that water uptake and fog formation are significantly increased by co-condensation processes involving semi-volatile species, especially chloride (Fig. 4c). In the presence of abundant ammonia and at high RH, the gas-phase HCl co-condenses with water into the PM to form NH_4Cl, significantly enhancing particle light scattering. The widespread burning of diverse, significant and unaccounted waste including plastic, and processing of e-waste combined with primary emissions from various industrial sources[32, 34, 50] throughout Delhi, likely represent a large but not yet well-quantified HCl source.

In addition to the deterioration of visibility, the chlorine-rich atmosphere in India represents other environmental implications. For example, burning of chlorine-containing plastics, as present in e-waste, can emit a large amount of dioxins and other persistent organic pollutants (POPs[50]) that are highly toxic and can accumulate in the food chain (Fig. 4c). Gaseous and particulate chloride can also affect atmospheric chemistry in other ways[23]. In a polluted environment containing these species, the aqueous-phase reaction of chloride with N_2O_5 at nighttime extends the NO_x lifetime producing nitryl chloride ($ClNO_2$), which in turn photolyzes during daytime enhancing ozone and PM production via Cl atom pathways[51, 52, 53, 54]. The oxidation pathways over India thus may be significantly different from other continental regions due to high HCl concentrations. Additional measurements are required to explore the scale, sources, and significance of HCl emissions. While the role of HCl emissions reported here is important in controlling water uptake and visibility reduction, we emphasize the need for continued efforts by policy makers in reducing the key precursors and major primary sources of particulate pollution, including ammonia emissions from agriculture, burning of crop residue, biofuel combustion, emissions from coal fired power plants, small scale processing industries, and automobiles. We emphasize the urgency of systematic and long-term measurements of PM composition (refractory and non-refractory) and hygroscopicity as well as of gas-phase HCl, ozone, and POPs to better understand their role in regional climate, atmospheric chemistry, visibility degradation, and human health in India. These findings may help frame overall better policies to synergistically tackle the concurrent environmental issues in India, including air pollution, solid-waste management comprising e-waste, and food safety. Strong regulation on open waste dumping and burning and on industrial chlorine emissions appears to be necessary.

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Correspondence to: Sachin S. Gunthe (s.gunthe@iitm.ac.in) and Pengfei Liu (pengfei.liu@eas.gatech.edu)

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List of Figures

Figure 1. Non-refractory chemical components in sub micrometer particulate matter (NR-PM$_1$), measured by Aerosol Mass Spectrometer (AMS) and Aerosol Chemical Speciation Monitor (ACSM) over India. ACSM data is derived from this work (with red text) and AMS from literature (with black text). Markers on the map shows the measurement locations. Details of the measurement campaigns are summarized in Extended Data Fig. 1. The South Asia map is coded by orange color for the annual mean (Feb. 2018 – Jan. 2019) of aerosol optical depth (AOD) derived from MODIS. Pie charts represent different chemical species in NR-PM$_1$ for various locations over India connected by corresponding lines. Total mass concentrations of NR-PM$_1$ (in micrograms per cubic meter) are also marked for the respective pie charts. The pie charts represent the mass for the entire campaigns (connected by solid lines) and high chloride episode, if present (connected by dashed lines).

Figure 2. Time series of NR-PM$_1$, diel variations of chloride, and scatter plots of Cl-to-OA versus BBOA-to-OA ratios over Delhi and Chennai. (a-b) Time series of chemical components in NR-PM$_1$ measured during field campaigns in (a) Delhi and (b) Chennai. Purple shadings in (a) indicate the high-chloride-high-organics (P1) episode, and the green shadings show the low-chloride-high-organics (P2) periods. The insert in panel (b) shows the enhanced concentrations, particularly that of organics and chloride, during the Bhogi festival in Chennai on 14 Jan. (c-d) Diel variations of chloride concentration for (c) Delhi and (d) Chennai. The center line and the box edges represent the median and quartiles for the dataset, respectively. Whiskers mark the highest and the lowest values that are within 1.5 times the interquartile range of the box edges. Open squares represent the mean values. Dashed lines show the mean diel variations for the high chloride episodes. Diel variations of the temperature and relative humidity in Delhi are also shown (c; right axis and color bar). Purple shading indicates the values considered between 4 and 9 a. m. local time. (e-f) Relationship between chloride to organic aerosol (Cl-to-OA) and biomass burning organic aerosol to organic aerosol (BBOA-to-OA) ratio for (e) for Delhi and (f) Chennai. Insert in (e) shows the data from P2 days. Square markers and error bars represent mean and ±1 standard deviation.

Figure 3. Thermodynamic modeling of the gas-particle partitioning of chloride in Delhi. (a) Ion balance of NR-PM$_1$ in Delhi measured by the ACSM. The colored lines indicate anion-to-cation ratios for sulfate (red), sulfate + nitrate (blue), and sulfate + nitrate + chloride (purple) , and the black denotes 1:1 line. (b) Fraction of chloride in the particle phase as a function of total

ammonium (gas phase + particle phase) and total sulfate modeled by the thermodynamic model, assuming the aerosol adopts a metastable state. The simulations used a campaign-averaged RH of 57% and temperature of 17 °C for Delhi. Total nitrate was assumed to increase with increasing total sulfate, with a mass ratio of 1:1, consistent with the measurements in Delhi. A total chloride concentration of 25 μg m^{-3} was used in the simulations. Typical total ammonium and total sulfate values of Delhi, as inferred from the literature[32] and the field measurements of this study, are marked by the green box. The dashed line represents the condition in which the total ammonia is neutralized by sulfate ($\mathrm{n(NH_x) = 2\,n(SO_4^-)}$). The solid curve represents the condition in which the total ammonia is fully neutralized by sulfate, nitrate, and chloride, i.e., $\mathrm{n(NH_x) = 2\,n(SO_4^-) + n(NO_3^-) + n(Cl^-)}$. (c) Modeled aqueous fraction of chloride as a function of temperature and relative humidity. The points show the measured particle-phase chloride concentrations during the high-chloride episodes as a function of temperature and relative humidity. The boxes indicate conditions of morning and afternoon hours during the field campaign in Delhi. (d) Measured particle-phase chloride as a function of aerosol liquid water derived from model (Methods section). The red dashed line shows the increase of the modeled particle-phase chloride with an increasing RH from 15% to 90% (Extended Data Fig. 9), assuming total Cl is 25 μg m^{-3}. The PM liquid water associated with inorganics was calculated using the ISORROPIA II model in reverse mode based on the ACSM measured chemical composition. The aerosol liquid water associated with organics was calculated using a hygroscopicity parameter $\kappa = 0.1$[20, 49].

Figure 4. The impact of chloride co-condensation on PM hygroscopic growth and cloud/fog formation. (a) Extinction enhancement factors *f*(RH) calculated based on observed visibility and $PM_{2.5}$ measurements and modeled using ISORROPIA II. Blue circles represent the calculated *f*(RH) based on visibility and $PM_{2.5}$ (ref.[18]). Error bars represent the uncertainty estimated using bootstrapping. Blue and red curves represent the *f*(RH) modeled using ISORROPIA II with and without consideration of chloride, respectively (see Methods). (b) Köhler curves calculated with and without the co-condensation of chloride. Critical supersaturation values (SS_{crit}) are labeled in the figure. Shaded regions in (a) and (b) represents the uncertainty in model derived parameters calculated using Monte-Carlo simulations. (c) Schematic showing the HCl emission from trash burning and industrial sources, co-condensation of chloride, and the possible influences on haze and fog formation. Other potential environmental impacts, such as the influence on ozone chemistry and co-emission of persistent organic pollutants are also depicted.

Methods

1. Sampling Sites:

Delhi.

The aerosol sampling in Delhi was conducted at Indian Meteorological Department (IMD) campus (28.589008^0 N, 77.222575^0 E; 200 m asl) during February–March 2018 using advanced instrumentation under Atmospheric Pollution and Human Health Program under Process Analysis, Observations and Modeling–Integrated Solutions for Cleaner Air for Delhi (APHH – PROMOTE) campaign. All the instruments were placed in an air-conditioned container connected to a dedicated inlet with a sampling height of ~5 meters above the ground. The inlet was constructed of stainless steel with a cyclone separator and with proper protection, to avoid any blockage in the inlet. The air sampled can be considered as representative of the region in view of the average time and duration of the sampling. Briefly, the capital city of India, considered to be one of the most populated and polluted cities in the world, experiences very diverse climatic conditions. The winters, from December–February are mildly cold (with average diurnal temperatures 5–20°C) and humid (average diurnal relative humidity of 45–95%). During the winter season, owing to frequent inversions, the boundary layer depth is generally less than 100 m, especially during early morning hours before sunrise, when the temperature reaches its minimum. During the winter season, Delhi experiences very high aerosol mass burdens attributed to local emissions and regional transport[1].

The sampling site is surrounded by small and medium scale industries within a 25 km vicinity, dealing with metal processing, paper production, plastic and medicine manufacturing, e-waste handling and recycling, medical waste management, dumping sites management, etc., which cause emission of various toxic gases and pollutants into the atmosphere of Delhi[11, 19, 31, 32, 33, 34, 35, 50, 55]. According to an estimate, on average 606 tons per km^2 of municipal solid waste (MSW) are illegally dumped in Delhi, resulting 557 thousand tons of MSW lying on streets and open areas, including 38 thousand tons of plastic[34]. Delhi experiences open MSW burning of 216 thousand tons per year[56] that burnt at non-designated places and also ending up as fuel for brick kilns[42]. This waste mainly constitutes diverse trash, but a common and abundant component is a mixed plastic from food wrappers to e-waste handling. Large numbers of informal and unorganized e-waste handling and recycling, and metal processing units are prevalent across Delhi[34] (Extended Data Fig. 7). E-waste handling units aim to retrieve copper, silver, and gold from printed circuit boards, cables, scrap plastics, and batteries with processes that use acids and open burning. The metal processing industries use acids for pickling and polishing purposes. Interestingly, HCl is widely used in the steel processing industries for pickling to remove iron oxides and scale from the surface of steel. In metal industries, HCl is also widely used for aluminum etching, metal cleansing, and metal pre-fixing. These processes are known to emit the HCl directly in the atmosphere. It is also important to note that HCl and particulate Cl can be also emitted from agricultural crop residue burning, which is prevalent in northern India during October and November. However, our measurements were carried out during February, which is not the crop residue burning season in northern India.

Chennai. The measurements of aerosol composition, using an ACSM and an Aethalometer (AE33) were carried out in Chennai during 5-January-2019 to 5-February-2019, with an aim to complement the Delhi measurements and to cover the festival of Bhogi, so characteristic features associated with trash/waste burning could be investigated. Please note, as discussed below, the Bhogi festival is marked by large scale wood and domestic waste/trash burning in this region. Chennai, the fourth most populated city in India (>5 million) is a South-Eastern coastal urban city and unlike Delhi experiences a tropical hot and humid climate with higher temperatures during the measurement period. Daytime average temperatures ranged from 20–29°C and relative humidities from 50–90%. The sampling was carried out with a dedicated inlet with proper protection from insect and other blockages. The instruments were housed at Indian Institute of Technology Madras in a temperature-controlled laboratory (12.99N, 80.23E; 14 m asl). The campaign in Chennai was planned in such a way that the measurements covered the period of a local festival, called Bhogi, which is celebrated in the middle of January (mostly on the 14th), marking the beginning of the Tamil month of Thai, and is one of the biggest and most important festivals in the state of Tamilnadu. In this part of India, it is considered to be even more important and bigger than the festival of Deepawali and is celebrated across entire Tamilnadu including Chennai. Previous researchers have reported air quality deterioration with pollutants exceeding levels well above the standard limits during the Bhogi festival[37]. As a customary and old tradition during this festival, people thoroughly clean their houses and remove all unwanted and unusable goods. Another important ritual, which follows the cleaning, called Bhogi Mantalu, is to throw all unwanted and unusable household items in a fire fuelled by wood and cow-dung cakes as a religious belief. The burning generally starts on the evening of the festival and continues till early morning. During our measurement period, the festival was on 14 January, and as can be seen from Fig. 2b, the NR-PM$_1$ mass concentration reached a peak value of 320 µg m^{-3} (Extended Data Fig. 2) as a result of emissions due to burning. During the entire campaign, sulfate was found to be the second largest mass contributor to the NR-PM$_1$ after organics. During the Bhogi burning, however, particulate chloride was the second largest mass contributor.

2. Instrumentation:

An Aerodyne aerosol chemical speciation monitor (ACSM)[57] was deployed at the Indian Meteorological Department (IMD), New Delhi, from 1$^-$Feb to 3-March 2018 and at the Indian Institute of Technology Madras from 5-Jan to 5-Feb 2019 to measure the chemical composition of non-refractory submicron aerosol particles (with vaporization temperature <600^{0}C), including organics (Org), sulfate (SO$_4$), nitrate (NO$_3$), ammonium (NH$_4$) and chloride (Cl) at high time resolution (about 15 minutes) and high mass sensitivity. Maintenance and calibration of the instrument were performed before the start of each campaign and once during the campaign as per the normal protocols[58]. For the ambient measurements, briefly, ambient air was drawn through a stainless-steel tube and a $PM_{2.5}$ cyclone to remove the coarse mode particles. The air sample was then passed through a silica gel dryer to avoid water condensation in the sampling line before reaching the ACSM inlet, out of which 0.085 L/min (85 cm^{-3}) was isokinetically allowed to pass into the ACSM sampling valve. The particles were sampled into a vacuum chamber through an aerodynamic lens (approx. 2 torr). Then the PM was flash vaporized on a hot surface at around 600 ^{0}C and ionized, followed by subsequent detection using a quadrupole mass spectrometer. Theoretically, the concentrations of the chemical species are proportional to the measured ion signal.

The mass calibrations were performed using a TSI electrostatic classifier (SMPS; TSI 3082) as differential mobility analyzer (DMA) to select the desired particle sizes with ammonium nitrate and ammonium sulfate. The calibration resulted in a response factor (RF) 7.65×10^{-11} with relative ionization efficiency (RIE) for ammonium of 4.96 and sulfate of 1.08 at Chennai; the values for Delhi were 7.65×10^{-11}, 4.96, and 0.9, respectively. The 3σ uncertainties of ACSM for ammonium, chloride, sulfate, organics, nitrate are 0.284 $\mu g/m^3$, 0.011 $\mu g/m^3$, 0.024 $\mu g/m^3$, 0.148 $\mu g/m^3$, 0.012 $\mu g/m^3$ respectively for 30 min averages. A default RIE value of 1.3 was used for chloride. Given the unique composition of Delhi particulate matter, the phase state can be different from typical ambient measurements in other environments across the globe where composition-dependent CE was used[59]. Therefore, a collection efficiency of 0.5 was used throughout, assuming most of the particles to be semi solid inside the ACSM, in line with previous literature[59]. It is important to note that though assumption of non-size dependent CE may affect the absolute aerosol mass concentration, whereas the relative mass abundance and hence the hygroscopicity will not change with CE for internally mixed aerosols.

3. Thermodynamic Modeling

Thermodynamic equilibrium between an NH_4^+-H^+-SO_4^{2-}-NO_3^--Cl^--H_2O inorganic particulate matter and its gaseous precursors (NH_3, HNO_3, and HCl) is calculated using the ISORROPIA[44, 60, 61] model (version II; https://www.epfl.ch/labs/lapi/isorropia/). The ISORROPIA is a computational efficient and rigorous aerosol thermodynamics model that is widely used in the atmospheric aerosol community. The ISORROPIA solves thermodynamic equilibrium for either a closed system (i.e., forward mode, which takes input of total concentration of both gas- and particle-phases for each species), or an open system (reverse mode, which takes input of particle-phase concentration for each species). For both modes, the equilibrium state is calculated at given temperature and RH values. The output of ISORROPIA provides gaseous and particulate mass concentrations for each species, as well as the mass concentration of aerosol liquid water content. For all calculations presented here, we assumed the PM adopted a metastable thermodynamic state.

Here we employed the forward mode of ISORROPIA to calculate the gas-particle partitioning of chloride. For simulations with consideration of chloride, a fixed total concentration of gaseous and particulate chloride of 25 μg m^{-3} (mass concentration as the form of HCl) was used. Such a high concentration of chloride is necessary to reproduce the observed high PM chloride during morning hours in Delhi. We systematically tested the partitioning behaviors of chloride for a wide range values of various input parameters, including sulfate concentration, total ammonium, temperature, and RH (Fig. 3 b and c). We used the reverse mode of ISORROPIA to calculate the aerosol liquid water content associated with inorganic PM with input of measured aerosol inorganic composition, temperature, and RH in Delhi (Fig. 2d). The liquid water content in ISORROPIA is estimated with the Zdanovskii-Stokes-Robinson (ZSR) mixing rule[62], linking the water uptake of the multicomponent system to the hygroscopicity of each individual electrolyte. For the additional water uptake of organic PM, we assumed a constant hygroscopicity parameter κ=0.1[20, 63]. The ISORROPIA model does not consider the effect of surface tension, and the aerosol water activity (a_w) equals RH.

We calculated the aerosol hygroscopic growth and cloud condensation nuclei (CCN) activation for scenarios with and without chloride (Fig. 4 a and b). Thermodynamic equilibrium of inorganic PM and its precursor gases was calculated using ISORROPIA-II in the forward mode. For both scenarios, we randomly sampled sulfate and nitrate concentrations from measured values during the high chloride high organic period (P1) with replacement (i.e., bootstrapping, N = 1000), and the mean (±s.d.) values for the resampled population were 4.2±1.8 μg m^{-3} and 5.6±2.9 μg m^{-3} for sulfate and nitrate, respectively. The total ammonium (i.e., gaseous+particulate) was randomly sampled from a Gaussian distribution with a mean value of 30 μg m^{-3} and 5 μg m^{-3} s.d. The simulation with chloride included a total chloride concentration of 25±5 μg m^{-3}. In addition to the inorganic species, a non-volatile organic PM of 42.9±27.9 μg m^{-3}, bootstrapped from P1, was added in the multicomponent system, and a hygroscopicity κ value of 0.1 was used in the calculations of water uptake for organic PM. These values used in the simulations are consistent with the measurements during the high chloride period of Delhi, with uncertainty and variability taken into account (Extended Data Fig. 2). A campaign-averaged temperature of 17 °C in Delhi was used in the simulations. Thermodynamic equilibrium states were calculated for different RH values, and the RH-dependent PM composition for the simulation with chloride is shown in Extended Data Fig. 9. Based on the calculated water uptake for inorganic and organic PM components, we modelled the CCN activation for particles with an initial dry dimeter of 100 nm (Fig. 4b). We calculated the hygroscopicity κ value at a_w=0.99 (the upper limit of the ISORROPIA model) for the mixed inorganic-organic particle. Hygroscopic growth at higher a_w values were extrapolated using this constant κ value. This extrapolation is valid because >99% of chloride partitions to the particle phase at a_w=0.99, and further water uptake at higher a_w values does not significantly enhance the hygroscopicity. A surface tension value of pure water (0.072 N m^{-1}) was used in the calculations of CCN activation.

The inferred HCl gas phase concentration was further used to calculate the ratios of HCl:BC and HCl:OC, which was further used to compare with the same ratio derived from the literature for various types of emissions, including open biomass burning, open burning of mixed garbage, and burning of plastic waste[27, 28, 30, 38]. The detailed results in this regard obtained from current measurements and as obtained from the literature for various emission ratios from different type of combustions are shown in Extended data Fig. 6.

4. Light-Extinction Enhancement factor

Following the work of Wang and Chen[18], we derived the measured light-extinction enhancement factor (*f*(RH)) of aerosol hygroscopic growth from ambient observations. We selected the period of winter (December to mid-February) to spring (mid-February to March) with high concentrations of chloride reported[2], to investigate the effect of chloride co-condensation. Hourly observations during 2015-2019, including $PM_{2.5}$ from the U.S. Embassy in Delhi (https://www.airnow.gov/), along with visibility and meteorological parameters from the Indira Gandhi International Airport (DEL, only 7 km away from the U.S. Embassy, https://www.ncdc.noaa.gov/) were used in the analysis. The $PM_{2.5}$ and visibility observations were well calibrated and quality-controlled according to the protocols of the U.S. Environmental Protection Agency[64, 65], and the National Oceanic and Atmospheric Administration, National Climatic Data Center[66], respectively. The RH values were calculated from dew point temperature and temperature using the Magnus formula[67]. The periods with wind speed larger than 6.5 m/s or RH higher than 95% were excluded from analysis, to minimize the uncertainties induced by dust and the low accuracy of the RH sensor under high RH conditions[18]. We projected the data pairs of RH, $PM_{2.5}$, and visibility into eight RH-bins (with borders of 30%, 40%, 50%, 60%, 70%, 80%, 85%, 90% and 95%), with more than 400 pairs within each bin. The light extinction coefficient of aerosol particles was derived from visibility data using the Koschmieder's equation[68]. Then, the mass extinction efficiency for each RH-bin, *E*(RH) with units of m^2/g, was derived as the slope between light extinction coefficient and $PM_{2.5}$ concentration with least squares fit linear regression. By normalizing the *E*(RH) with *E*(30%-40%), we derived the *f*(RH) for each RH bin. The uncertainty of *f*(RH) was estimated using bootstrapping[69] by resampling 1 million times from the observations within each RH bin.

The modeled *f*(RH) was calculated for two scenarios with and without chloride (Fig. 4a). Thermodynamic equilibrium and water uptake were calculated following the methods described in Section 3. Hygroscopicity parameter κ_{chem} values for PM_1 were derived from the modeled chemical composition and water uptake. The chemical composition-derived κ_{chem} was then linked with *f*(RH) following a physical-based empirical approach[18, 49, 70, 71]. In this approach, the *f*(RH) was parameterized in the form of κ-Kohler theory[70]:

$$f(RH) = \frac{1 + \kappa_{opt}\frac{RH}{1-RH}}{1 + \kappa_{opt}\frac{RH_{ref}}{1-RH_{ref}}}$$

where κ_{opt} is the optical hygroscopicity. The optical-based κ_{opt} value for bulk $PM_{2.5}$ can be related to κ_{chem} defined for submicrometer particles using the equation below:

$$\kappa_{opt} = \kappa_{chem} \cdot R_{\kappa}$$

where the ratio R_{κ} is determined by the particle number size distribution and chemical composition. The values of R_{κ} ranged 0.58-0.77 based on the study for Beijing[71]. An average value of 0.69 was used in the present study following the work by Wang and Chen[18].

5. Factor analysis

Source apportionment of the OA mass spectra obtained from ACSM for both the sites has been performed using the unconstrained positive matrix factorization (PMF) algorithm implemented in Multilinear Engine (ME-2) developed by ref.[72] utilizing source finder tool (SoFi v4.8) in Igor pro[73]. Further, the PMF is a bilinear unmixing receptor model for factor analysis developed by ref.[72, 74] that simplifies the complex data sets to a linear combination of source types and their time dependent concentration. In PMF, the measured organic mass spectra represented in the form of a matrix $\mathbf{X_{m*n}}$ (organic mass spectra in m rows and ion fragments in n columns) is factorized into two sub matrices, the time series $\mathbf{G_{m*p}}$ and the factor profiles $\mathbf{F_{p*n}}$, where p is the number of factors/OA sources selected.

$$\mathbf{X=GF+E}$$

Here, $\mathbf{E_{m*n}}$ is the residual matrix containing the fraction of the matrix X that is unexplained by the model solution. The model then uses a least square algorithm to minimize the object function Q as given in the below equation:

$$Q=\sum_{i=1}^{m}\sum_{j=1}^{n}\left(e_{ij}\middle|\sigma_{ij}\right)^{2}$$

where e_{ij} represents the squared residuals and σ_{ij} are the respective measurement uncertainties. The extraction procedure of organic mass spectra, corresponding error matrices, time and m/z values as model input has been adopted from ref[57, 75]. The input data were created up to m/z 120 and analyzed while increasing the number of factors from two to eight. The optimum number of factors was obtained after careful evaluation of several parameters including residuals, time series, Q/Qexp values of various solutions gained by running the model from different initial conditions (SEED run). For Delhi, a five-factor solution profile was found to be the most suitable. The factors were assigned after comparing the mass spectra profiles with some known references from published literature[73] including 1-hydrocarbon-like OA (HOA), 2-biomass burning related OA (BBOA), 3-cooking OA (COA), 4-oxygenated primary OA (OPOA), and 5-oxygenated OA (OOA)

Similarly, for Chennai, the analysis with a higher number of factors (greater than four) resulted in splitting of identified sources. Thus, the results with four factors/ OA sources: HOA, BBOA, Semivolatile/Less-oxidized-oxygenated organic aerosols (SV-OOA/LO-OOA), Low volatile/More-oxidized-oxygenated organic aerosols (LV-OOA/MO-OOA), seemed to be environmentally and mathematically acceptable for the measured data.

6. STILT (Stochastic Time-Inverted Lagrangian Transport) model simulations

We used the Stochastic Time-Inverted Lagrangian Transport (STILT) model, version 2.0, to simulate the transport of an ensemble of 10,000 air particles to the receptor site, 72 hours back in time[76]. We performed a total of 1,830 simulations, one for each ACSM measurement instance for available meteorological data. While the meteorology from the Global Data Assimilation System (GDAS) we use to drive STILT is coarse, at 0.5°x0.5° spatial resolution, STILT can resample the influence footprint to a finer spatial resolution. STILT-v2.0 uses a Gaussian kernel density estimator with modified vertical dilution in the hyper near field (1-10 km from the receptor) to allocate the influence of air particles according to a user-specified footprint grid, which we define as a regional domain (72-82°E, 23-33°N) at 0.01°x0.01° spatial resolution. We use the STILT footprints to determine the average sensitivity of the receptor to nearby polluting sources for low Cl and high Cl modes.

Data availability

The non-refractory PM_1 species from literature shown in Fig. 1 are available in Extended Data Table 1. All other data displayed in figures, including concentrations of non-refractory PM_1 species measured by the ACSM in Delhi and Chennai in this study, and aerosol liquid water modeled by ISORROPIA II, are available in the figshare repository: https://doi.org/10.6084/m9.figshare.13277486

Code availability

The aerosol thermodynamic model ISORROPIA II is available from Dr. Athanasios Nenes at the website: https://www.epfl.ch/labs/lapi/software/isorropia/. Other codes used in this paper are available from the corresponding author Dr. Pengfei Liu (pengfei.liu@eas.gatech.edu) upon reasonable request.

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