

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

3
4 Sachin S. Gunthe^{1*}, Pengfei Liu^{2,3*}, Upasana Panda^{1,4}, Subha S. Raj¹, Amit Sharma^{1§}, Eoghan
5 Darbyshire^{5&}, Ernesto Reyes-Villegas⁵, James Allan^{5,6}, Ying Chen^{7,8}, Xuan Wang⁹, Shaojie
6 Song³, Mira L. Pöhlker¹⁰, Liuhua Shi¹¹, Yu Wang⁵, Snehitha M. Kommula¹, Tianjia Liu¹², R.
7 Ravikrishna¹³, Gordon McFiggans⁵, Loretta J. Mickley³, Scot T. Martin^{3,12}, Ulrich Pöschl¹⁰,
8 Meinrat O. Andreae^{10,14,15}, and Hugh Coe⁵

9
10 ¹EWRE Division, Dept. of Civil Engineering, Indian Institute of Technology Madras, Chennai,
11 India

12 ²School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA

13 ³John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge,
14 Massachusetts, USA

15 ⁴Academy of Scientific and Innovative Research (AcSIR), Department of Environment and
16 Sustainability, CSIR – Institute of Minerals and Materials Technology, Bhubaneswar, India

17 ⁵Department of Earth and Environmental Sciences, School of Natural Sciences, University of
18 Manchester, Manchester, UK

19 ⁶National Centre for Atmospheric Science, University of Manchester, Manchester, UK

20 ⁷Lancaster Environment Centre, Lancaster University, Lancaster, UK

21 ⁸Data Science Institute, Lancaster University, Lancaster, UK

22 ⁹School of Energy and Environment, City University of Hong Kong, Hong Kong SAR, China

23 ¹⁰Multiphase Chemistry and Biogeochemistry Department, Max Planck Institute for Chemistry,
24 Mainz, Germany

25 ¹¹Gangarosa Department of Environmental Health, Rollins School of Public Health, Emory
26 University, Atlanta, Georgia, USA

27 ¹²Dept of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

28 ¹³Dept of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India.

29 ¹⁴Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA, USA

30 ¹⁵Department of Geology and Geophysics, King Saud University, Riyadh, Saudi Arabia

31
32 [§]Now at Department of Civil and Infrastructure Engineering, Indian Institute of Technology
33 Jodhpur, Karwar, Jodhpur, India

34 [&]Now at The Conflict and Environment Observatory, Hebden Bridge, West Yorkshire, UK

35

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

52
53 The 2018 World Air Quality Report mentioned New Delhi the “world air pollution capital.”
54 In 2017–2018, particulate matter (PM) concentrations exceeded $200 \mu\text{g m}^{-3}$ and $600 \mu\text{g m}^{-3}$ for
55 PM with diameter less than $1.0 \mu\text{m}$ and $2.5 \mu\text{m}$, respectively (i.e., PM_{10} and $\text{PM}_{2.5}$)^{1, 2}. The severe
56 pollution, also evidenced by high aerosol optical depth (AOD) over the Indo-Gangetic Plain
57 (IGP) (Fig. 1), is associated with increased respiratory and cardiovascular diseases, poor
58 visibility, and economic damages³. For example, persistent poor visibility over the New Delhi
59 airport due to fog and haze has incurred significant financial losses to airline industries⁴ and led
60 to increasing vehicular deaths³. According to one estimate, in 2017 over Delhi alone, $\sim 12,000$
61 excess deaths can be attributed to exceedingly high $\text{PM}_{2.5}$ concentrations⁵.

62 Numerous observational studies focusing on surface PM concentrations have been
63 conducted over India during the last decade^{2, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17}. Although much progress
64 has been made in measuring the seasonal variability of PM and its chemical composition,
65 understanding of the underlying mechanisms responsible for the reduced visibility and
66 deterioration of air quality over Delhi and the IGP remains limited. For example, it is unclear
67 why the PM in Delhi has a higher potential to form haze and fog than other polluted Asian
68 cities¹⁸ although a large fraction of Delhi PM is primary organic matter^{2, 19}, which is less
69 hygroscopic²⁰.

70 Here we present new chemical composition measurements of non-refractory PM smaller
71 than $1 \mu\text{m}$ (NR-PM_{10}) from Delhi and a relatively cleaner Chennai (Fig. 1). Measurements are
72 combined with thermodynamic modeling (Methods) to elucidate sources of the observed high
73 chloride concentrations and the implications for PM concentrations and visibility. We report that

74 high non-refractory particulate chloride in Delhi likely results from gas-particle partitioning of
75 HCl gas into aerosol water under typical winter haze conditions of high relative humidity (RH),
76 low temperatures, and excess ammonia. The HCl is apparently emitted from continental
77 anthropogenic sources, including industrial and combustion processes. In the process of
78 co-condensation, the particulate chloride can take up more water, enhancing haze and fog
79 formation. Our field observations and model calculations show that 50% visibility reduction in
80 Delhi during the winter can be attributed to chloride co-condensation mechanism. In Chennai,
81 high chloride concentrations in NR-PM₁ have been observed during the Bhogi festival, when
82 bonfires are prevalent. The high levels of particulate chloride could participate in nighttime
83 multiphase-chemistry producing reactive chlorine species, further affecting ozone and secondary
84 organic aerosol production. These results highlight the uniqueness of atmospheric chemical
85 processes in India, and suggest the importance of regulating chlorine anthropogenic sources.

86 **Variations in PM₁ chemical composition over Delhi and Chennai**

87 The chemical compositions of NR-PM₁ have been observed at diverse locations across India
88 in the present study and literature^{2, 10, 12, 14, 17} (Fig. 1; Extended Data Figs. 1 and 2). Consistent
89 with other global regions, organic aerosol (OA) comprised a major fraction of NR-PM₁. The
90 chloride fraction, however, at least episodically, remained an order of magnitude higher than the
91 global average²¹ over the Indo-Gangetic Plain (IGP) and metro cities. Especially, chloride
92 comprises ~10% of NR-PM₁ mass in Delhi, which is comparable to other major inorganic
93 components such as sulfate and nitrate. Several other studies using traditional sample-based
94 techniques also reported a high chloride mass fraction in Delhi^{9, 19, 22}. These high chloride
95 fractions in NR-PM₁ observed over inland India are unexpected, as dominant source of
96 tropospheric chloride in NR-PM₁ was thought to be acid displacement mobilizing HCl from sea
97 salt particles²³.

98 Fig. 2 shows the time series of the NR-PM₁ chemical composition measured in Delhi and
99 Chennai. Total NR-PM₁ reveals pronounced daily variations, with higher concentrations at night.
100 At both sites, OA constitutes the largest mass fraction of total NR-PM₁ (69% and 48% for Delhi
101 and Chennai, respectively). Factor analysis suggests that primary organic aerosol (POA), i.e., the
102 sum of hydrocarbon-like OA (HOA), biomass burning OA (BBOA), and cooking OA (COA)
103 comprises 60% and 48% of the mass fraction of total OA for Delhi and Chennai, respectively
104 (Methods; Extended Data Fig. 3), indicating a high contribution from open and domestic burning
105 sources. Intermittent high chloride concentration occurs over Delhi, consistent with previous
106 studies^{2, 19, 22, 24, 25}. In Delhi, chloride constitutes the second-largest mass fraction of total
107 NR-PM₁ (10.3%), higher than sulfate (6.8%) or nitrate (6.4%) (Extended Data Fig. 2). During
108 the ten days of polluted episodes with high chloride and high OA in this study (~42% of total
109 days in the campaign, light purple shading areas in Fig. 2a; P1), the daily mean mass fraction of
110 chloride reaches 15.6% of NR-PM₁, higher than episodic values recorded elsewhere in India
111 (Fig. 1; Extended Data Fig. 1). In comparison, the daily mean chloride mass fraction remains

112 3.7% during episodes of low chloride and high OA (7 days, 25% of total campaign; light green
113 shadings in Fig. 2a; P2), comparable to the typical conditions in other polluted cities in India and
114 China²⁶. In Delhi, the NR-PM₁ chloride mass fraction is positively associated with the total
115 NR-PM₁ concentration, indicating enhanced contribution of chloride during highly polluted
116 conditions (Extended Data Fig. 4). The highest chloride fraction averaged over the entire
117 campaign occurs from 04:00–09:00 (local time, Fig. 2c; Extended Data Fig. 5), amounting 24%
118 of NR-PM₁ for Delhi. High levels of chloride also occur in this time frame during P1. A
119 plausible explanation is that these morning hours have the lowest temperatures and highest RH in
120 a day, which favors the partitioning of gas-phase HCl to PM (Fig. 2c).

121 We hypothesize that the observed chloride in Delhi originates from a complex array of
122 combustion sources and industrial processes. Among the identified OA factors, the biomass
123 burning organic aerosol fraction (i.e., BBOA-to-OA ratio) correlates best with the chloride to OA
124 (Cl-to-OA) ratio ($r=0.47$, $N=1977$). (normalize by OA to eliminate the apparent correlation
125 related to the diurnal variation of ventilation that simultaneously affect BBOA and Cl
126 concentrations). During P2 days, the Cl-to-OA ratio linearly increases with the BBOA-to-OA
127 ratio (Fig. 2e and the inset), indicating that chloride/HCl might be co-emitted with BBOA from
128 biomass burning and biofuel combustion. During morning hours, when Cl is partitioning into the
129 particle phase, the chloride to organic carbon (Cl-to-OC) and chloride to black carbon (Cl-to-BC)
130 ratios are similar to the emission ratios of HCl-to-OC and HCl-to-BC, reported for biomass
131 burning and biofuel combustion (Extended Data Fig. 6). During P1, the overall positive
132 correlation of Cl-to-OA ratio with BBOA-to-OA ratio suggests that combustion still be a
133 persistent source of chloride. The Cl-to-OA and Cl-to-BC values, however, are comparable to the
134 emission ratios reported for open burning of mixed garbage^{27, 28, 29, 30}, higher than that for
135 burning of biomass and biofuel (Extended Data Fig. 6). An exponential increase during P1 in
136 Cl-to-OA observed with respect to BBOA-to-OA ratio indicates additional primary HCl sources.
137 Results from the Lagrangian model STILT suggest additional emissions may come from
138 industries located north-northwest of the observational site (Methods; Extended Data Fig. 7). A
139 large number of illegal, informal, and unorganized metal processing units, as well as e-waste
140 recycling and handling units, plastic processing units, and medical waste management facilities
141 are widespread in that area (Extended Data Fig. 7), and the use of acids by these industries^{31, 32,}
142 ^{33, 34, 35, 36} may contribute to the direct HCl gas emissions.

143 Contrary in Chennai, even though it is located on the coast, chloride on average constituted
144 just 2.7% of total NR-PM₁. However, on 14-January-2019, the Bhogi festival took place in
145 Chennai causing chloride concentrations reaching 40 $\mu\text{g m}^{-3}$ during the night, corresponding to
146 11% of total NR-PM₁ (Fig.2b and 2d; Extended Data Fig. 3). During Bhogi, large-scale burning
147 of wood logs, solid waste, and wooden furniture takes place, following an old and important
148 tradition (ref.³⁷; Methods). The solid waste burned contains a significant amount of plastics, such
149 as polyvinyl chloride (PVC), and burning of such waste releases HCl gas³⁸, which can then

150 partition into the aqueous particle phase³⁹. We find a strong linear relationship between the
151 BBOA-to-OA ratio and the Cl-to-OA ratio (Fig. 2f), indicating increased chloride concentration
152 from combustion of mixed wood and solid waste in Chennai. Other than during the Bhogi
153 festival, the campaign-averaged chloride level in Chennai was lower than the observed average
154 in Delhi, most likely due to lower HCl emissions and less favorable meteorological conditions—
155 i.e., higher temperatures and lower RH compared to Delhi (Extended Data Fig. 2). Similarly,
156 enhanced chloride concentrations were also observed in Ahmedabad during the Diwali festival,
157 and in Kanpur during a high biomass burning event^{10, 12, 14} (Fig. 1).

158

159 **Thermodynamic modeling**

160 The observed chloride in NR-PM₁ is generally in the form of ammonium-chloride^{23, 40},
161 produced by the reaction with NH₃ in the atmosphere from the direct HCl emissions^{41, 42}. Figure
162 3a shows that sulfate and nitrate, the predominant inorganic species of fine PM in most regions,
163 account for only 50% of the inorganic anions in Delhi PM. Chloride, as the single largest
164 inorganic anion in Delhi PM, neutralized 50% of ammonium, on par with sulfate and nitrate
165 combined. The refractory forms of chloride, such as sodium chloride from sea salt and potassium
166 chloride from biomass burning, are not included here because these species do not vaporize at
167 600 °C, which is a requirement of the instrumentation used here (i.e., the mass spectrometer
168 vaporizer). From a global budget perspective, acid displacement and heterogeneous reactions on
169 sea salt particles is a major source of HCl⁴³. In the IGP, however, it is highly unlikely that
170 marine-originated chlorine sources can contribute significantly to HCl and non-refractory
171 chloride.

172 To further explain the unique thermodynamic nature of the chloride-rich Delhi PM, we
173 analyzed the observed aerosol composition, RH, and temperature with a thermodynamic model
174 (ISORROPIA-II,⁴⁴ Methods). For a sensitivity analysis of chemical conditions, the predicted
175 equilibrium fraction of Cl in the particle phase (i.e., Cl/(Cl + HCl)) across different
176 concentrations of total sulfuric acid and ammonia is shown in Fig. 3b. Three distinct regimes of
177 aqueous fraction of chloride were identified, suggesting high fraction of Cl in the particle phase
178 is strongly dependent on the presence of excess ammonia in the atmosphere. Previous studies
179 have reported high gas-phase ammonia concentrations over Delhi (~30 µg m⁻³; shown by the
180 green box in Fig. 3b⁴⁵), indicating an ammonia excess regime explaining high chloride
181 concentrations in our observations. In the chemical regime of Delhi, decreasing the sulfate
182 concentration would marginally reduce particle-phase chloride, mainly because of the decrease
183 in sulfate-associated liquid water. Ammonia appears to be a controlling factor for chloride
184 partitioning. To decrease the particle phase Cl fraction, however, an aggressive ammonia
185 emission reductions would be required (more than 50% reduction in total ammonium), a difficult
186 task as in India it is largely emitted from agricultural sources, including livestock and fertilizer

187 use. Reducing the anthropogenic sources of HCl appears to be the only feasible approach to
188 effectively control the particle phase chloride concentration.

189 Both the PM chloride concentration and chloride fraction in NR-PM₁ show strong
190 temperature and RH dependence (Extended Fig. 8). To explain these behaviors, we performed
191 thermodynamic calculations for a wide range of temperature and RH values (Fig. 3c). For the
192 observed range of temperature (10–18°C) and RH (70–85%) during morning hours (04:00–09:00
193 LT) over Delhi, the predicted fraction of Cl in the particle phase ranged from 80% to 99%. By
194 comparison, during afternoon hours (14:00–18:00 LT), this fraction was consistently less than
195 30%. The contrast in the partitioning behavior for different hours of the day was driven by
196 changes in both PM-associated liquid water and ambient temperature. These results are
197 consistent with the observations showing that the chloride content of NR-PM₁ was high during
198 morning hours and decreased substantially in the afternoon (Extended Data Fig. 5). Besides the
199 thermodynamically driven partitioning, other factors, such as shallow boundary layer during
200 early morning hours, which cannot explain the increase of chloride mass fraction, can further
201 enhance the concentrations of chloride and other PM species, causing severe visibility reduction
202 at this time of day.

203 The measurements indicate a strong correlation between chloride and liquid water content
204 of PM over a wide range of RH and PM mass concentrations (Fig. 3d). This positive correlation
205 is in line with the model prediction indicating co-condensation of chloride occurs along with
206 water uptake (Extended Fig. 9; red dashed line in Fig. 3d). Co-condensation has been reported
207 previously for organic vapors⁴⁶ and nitric acid⁴⁷, using parameterizations and modeling
208 approaches primarily concluding that water-soluble, and semi-volatile species, such as organic
209 vapors and nitric acid, can significantly enhance the water uptake and cloud activation tendency
210 of atmospheric PM. The gas-particle partitioning of HCl and NH₄Cl experiences a similar
211 co-condensation process as organic vapors and nitric acid, but causes a greater increase in
212 hygroscopicity of particles. Ambient in-situ observations indeed confirm that PM in Delhi
213 exhibits higher water uptake capability compared to other polluted megacity Beijing¹⁸, consistent
214 with this study. This high hygroscopicity is unexpected based on conventional understanding due
215 to high organic mass fraction (60-70%) of the NR-PM₁ in Delhi, higher than the typical value of
216 40-50% in polluted Beijing⁴⁸. A higher organic fraction, which is less hygroscopic than inorganic
217 salts, is typically associated with lower hygroscopicity²⁰.

218 Here we show that chloride co-condensation can explain the observed high hygroscopicity of Delhi
219 PM. Following the method described by ref¹⁸, we derived the aerosol light-extinction enhancement
220 factor $f(\text{RH})$ in Delhi based on ambient measurements of visibility and PM_{2.5} (Methods). The
221 visibility provides a direct measure of light extinction under ambient conditions. The $f(\text{RH})$
222 represents the ratio of the mass extinction coefficient at elevated RH to that at dry conditions (RH
223 <35%). This approach is found to be most suitable to investigate co-condensation effect as it does not

224 perturb the concentrations of soluble gases such as HCl, HNO₃, and NH₃, which otherwise may get
225 evaporated during the measurements owing to conditioning of air samples.

226 **Role of high chloride in visibility reduction**

227 The visibility-derived $f(\text{RH})$ values were compared with the thermodynamic results (Fig.
228 4a). Two modeling cases were formulated to illustrate the effect of chloride co-condensation
229 (Methods). In the modeled case considering chloride co-condensation, a total chloride
230 concentration of 25 $\mu\text{g m}^{-3}$ (gas phase+particle phase, HCl equivalent) was used (blue curve in
231 Fig. 4a). The model yields a change in particle composition, which causes a light-extinction
232 enhancement that is consistent with the measurements (Extended Data Fig. 9). The reference
233 case (red curve) considers a chloride-free environment—i.e., the total chloride concentration was
234 set to zero. For both cases, the RH values were varied from <35% to >90%, and the equilibrium
235 partitioning of water and semi-volatile species between gas and particle phases was calculated.
236 The model results agree well with the observed $f(\text{RH})$ when chloride was included in the model,
237 whereas in the case without chloride, the modeled $f(\text{RH})$ is biased low compared to
238 measurements. For RH from 90–95%, which consistently occurs over Delhi during winter haze
239 episodes, high value of 5 of $f(\text{RH})$ indicates a strong water uptake by PM. For RH values beyond
240 95%, $f(\text{RH})$ values are expected to be much higher than the value of 5 as reported here
241 comparable to the hygroscopicity of pure ammonium sulfate⁴⁹. At a similar RH level, the
242 modeled $f(\text{RH})$ without accounting chloride has a smaller value of 2.5. Thus, presence of HCl
243 can strongly enhance water uptake through co-condensation into the PM contributing ~50% of
244 the visibility degradation during the haze/fog events.

245 We also show that the co-condensation mechanism can also lower the barrier of cloud
246 activation⁴⁷, thus promoting fog/cloud formation. The cloud condensation nuclei (CCN)
247 activation of typically sized particles was calculated by combining the thermodynamic model
248 with the Kelvin effect to calculate the Köhler curves (Methods). Figure 4b shows the effect of
249 higher HCl concentration in the atmosphere on the equilibrium supersaturation ratios. Particles
250 with 100 nm dry diameter have full CCN activation at a critical supersaturation of 0.13%, factor
251 of two lower when the atmosphere is considered without chloride (i.e., 0.28%). This indicates a
252 strong cloud activation capability of PM over Delhi at times when chloride is abundant. The
253 enhanced particle growth encompassing a wide range of water vapor concentration (from sub-to
254 super-saturated range) corresponds with the period from late evening to early morning an intense
255 fog formation period over Delhi.

256 In summary, these analyses examines the complex chemical and physical processes and
257 underlying mechanisms related reduced visibility in Delhi, which have large negative
258 consequences on the economy and societal well-being. We find that water uptake and fog
259 formation are significantly increased by co-condensation processes involving semi-volatile
260 species, especially chloride (Fig. 4c). In the presence of abundant ammonia and at high RH, the

261 gas-phase HCl co-condenses with water into the PM to form NH_4Cl , significantly enhancing
262 particle light scattering. The widespread burning of diverse, significant and unaccounted waste
263 including plastic, and processing of e-waste combined with primary emissions from various
264 industrial sources^{32, 34, 50} throughout Delhi, likely represent a large but not yet well-quantified
265 HCl source.

266 In addition to the deterioration of visibility, the chlorine-rich atmosphere in India represents
267 other environmental implications. For example, burning of chlorine-containing plastics, as
268 present in e-waste, can emit a large amount of dioxins and other persistent organic pollutants
269 (POPs⁵⁰) that are highly toxic and can accumulate in the food chain (Fig. 4c). Gaseous and
270 particulate chloride can also affect atmospheric chemistry in other ways²³. In a polluted
271 environment containing these species, the aqueous-phase reaction of chloride with N_2O_5 at
272 nighttime extends the NO_x lifetime producing nitryl chloride (ClNO_2), which in turn photolyzes
273 during daytime enhancing ozone and PM production via Cl atom pathways^{51, 52, 53, 54}. The
274 oxidation pathways over India thus may be significantly different from other continental regions
275 due to high HCl concentrations. Additional measurements are required to explore the scale,
276 sources, and significance of HCl emissions. While the role of HCl emissions reported here is
277 important in controlling water uptake and visibility reduction, we emphasize the need for
278 continued efforts by policy makers in reducing the key precursors and major primary sources of
279 particulate pollution, including ammonia emissions from agriculture, burning of crop residue,
280 biofuel combustion, emissions from coal fired power plants, small scale processing industries,
281 and automobiles. We emphasize the urgency of systematic and long-term measurements of PM
282 composition (refractory and non-refractory) and hygroscopicity as well as of gas-phase HCl,
283 ozone, and POPs to better understand their role in regional climate, atmospheric chemistry,
284 visibility degradation, and human health in India. These findings may help frame overall better
285 policies to synergistically tackle the concurrent environmental issues in India, including air
286 pollution, solid-waste management comprising e-waste, and food safety. Strong regulation on
287 open waste dumping and burning and on industrial chlorine emissions appears to be necessary.

288 **References:**

- 289 1. Beig G, Srinivas R, Parkhi NS, Carmichael GR, Singh S, Sahu SK, *et al.* Anatomy of the
290 winter 2017 air quality emergency in Delhi. *Science of the Total Environment* 2019, **681**:
291 305-311.
- 292 2. Gani S, Bhandari S, Seraj S, Wang DYS, Patel K, Soni P, *et al.* Submicron aerosol
293 composition in the world's most polluted megacity: the Delhi Aerosol Supersite study.
294 *Atmospheric Chemistry and Physics* 2019, **19**(10): 6843-6859.
- 295 3. Dey S. On the theoretical aspects of improved fog detection and prediction in India.
296 *Atmospheric Research* 2018, **202**: 77-80.
- 297 4. Kulkarni R, Jenamani RK, Pithani P, Konwar M, Nigam N, Ghude SD. Loss to Aviation
298 Economy Due to Winter Fog in New Delhi during the Winter of 2011–2016. *Atmosphere*
299 2019, **10**(4): 198.
- 300 5. Balakrishnan K, Dey S, Gupta T, Dhaliwal RS, Brauer M, Cohen AJ, *et al.* The impact of
301 air pollution on deaths, disease burden, and life expectancy across the states of India: the
302 Global Burden of Disease Study 2017. *The Lancet Planetary Health* 2019, **3**(1): e26-e39.
- 303 6. Balachandran S, Meena BR, Khillare PS. Particle size distribution and its elemental
304 composition in the ambient air of Delhi. *Environment International* 2000, **26**(1-2): 49-54.
- 305 7. Cheng Z, Luo L, Wang SX, Wang YG, Sharma S, Shimadera H, *et al.* Status and
306 characteristics of ambient PM_{2.5} pollution in global megacities. *Environment*
307 *International* 2016, **89-90**: 212-221.
- 308 8. Monkkonen P, Uma R, Srinivasan D, Koponen IK, Lehtinen KEJ, Hameri K, *et al.*
309 Relationship and variations of aerosol number and PM₁₀ mass concentrations in a highly
310 polluted urban environment - New Delhi, India. *Atmospheric Environment* 2004, **38**(3):
311 425-433.
- 312 9. Pant P, Shukla A, Kohl SD, Chow JC, Watson JG, Harrison RM. Characterization of
313 ambient PM_{2.5} at a pollution hotspot in New Delhi, India and inference of sources.
314 *Atmospheric Environment* 2015, **109**: 178-189.
- 315 10. Rastogi N, Singh A, Satish R. Characteristics of submicron particles coming from a big
316 firecrackers burning event: Implications to atmospheric pollution. *Atmospheric Pollution*
317 *Research* 2019, **10**(2): 629-634.
- 318 11. Saxena M, Sharma A, Sen A, Saxena P, Saraswati, Mandal TK, *et al.* Water soluble
319 inorganic species of PM₁₀ and PM_{2.5} at an urban site of Delhi, India: Seasonal
320 variability and sources. *Atmospheric Research* 2017, **184**: 112-125.
- 321 12. Singh A, Satish RV, Rastogi N. Characteristics and sources of fine organic aerosol over a
322 big semi-arid urban city of western India using HR-ToF-AMS. *Atmospheric Environment*
323 2019, **208**: 103-112.
- 324 13. Srivastava A, Gupta S, Jain VK. Source apportionment of total suspended particulate
325 matter in coarse and fine size ranges over Delhi. *Aerosol and Air Quality Research* 2008,
326 **8**(2): 188-200.

- 327 14. Thamban NM, Joshi B, Tripathi SN, Sueper D, Canagaratna MR, Moosakutty SP, *et al.*
328 Evolution of Aerosol Size and Composition in the Indo-Gangetic Plain: Size-Resolved
329 Analysis of High-Resolution Aerosol Mass Spectra. *ACS Earth and Space Chemistry*
330 2019, **3**(5): 823-832.
- 331 15. Tiwari S, Srivastava AK, Bisht DS, Bano T, Singh S, Behura S, *et al.* Black carbon and
332 chemical characteristics of PM₁₀ and PM_{2.5} at an urban site of North India. *Journal of*
333 *Atmospheric Chemistry* 2009, **62**(3): 193-209.
- 334 16. Yadav S, Rajamani V. Air quality and trace metal chemistry of different size fractions of
335 aerosols in N-NW India - implications for source diversity. *Atmospheric Environment*
336 2006, **40**(4): 698-712.
- 337 17. Mukherjee S, Singla V, Pandithurai G, Safai PD, Meena GS, Dani KK, *et al.* Seasonal
338 variability in chemical composition and source apportionment of sub-micron aerosol over
339 a high altitude site in Western Ghats, India. *Atmospheric Environment* 2018, **180**: 79-92.
- 340 18. Wang Y, Chen Y. Significant Climate Impact of Highly Hygroscopic Atmospheric
341 Aerosols in Delhi, India. *Geophysical Research Letters* 2019, **46**(10): 5535-5545.
- 342 19. Jaiprakash, Singhai A, Habib G, Raman RS, Gupta T. Chemical characterization of
343 PM_{1.0} aerosol in Delhi and source apportionment using positive matrix factorization.
344 *Environmental Science and Pollution Research* 2017, **24**(1): 445-462.
- 345 20. Gunthe SS, King SM, Rose D, Chen Q, Roldin P, Farmer DK, *et al.* Cloud condensation
346 nuclei in pristine tropical rainforest air of Amazonia: size-resolved measurements and
347 modeling of atmospheric aerosol composition and CCN activity. *Atmospheric Chemistry*
348 *and Physics* 2009, **9**(19): 7551-7575.
- 349 21. Zhang Q, Jimenez JL, Canagaratna MR, Allan JD, Coe H, Ulbrich I, *et al.* Ubiquity and
350 dominance of oxygenated species in organic aerosols in anthropogenically-influenced
351 Northern Hemisphere midlatitudes. *Geophysical Research Letters* 2007, **34**(13).
- 352 22. Kumar B, Chakraborty A, Tripathi SN, Bhattu D. Highly time resolved chemical
353 characterization of submicron organic aerosols at a polluted urban location.
354 *Environmental Science: Processes & Impacts* 2016, **18**(10): 1285-1296.
- 355 23. Wang X, Jacob DJ, Eastham SD, Sulprizio MP, Zhu L, Chen QJ, *et al.* The role of
356 chlorine in global tropospheric chemistry. *Atmospheric Chemistry and Physics* 2019,
357 **19**(6): 3981-4003.
- 358 24. Kapoor RK, Murty BVR. Sulphate Aerosol at Delhi in Relation to the Associated
359 Chloride Component. *Journal of Applied Meteorology (1962-1982)* 1966, **5**(4): 493-499.
- 360 25. Perrino C, Tiwari S, Catrambone M, Torre SD, Rantica E, Canepari S. Chemical
361 characterization of atmospheric PM in Delhi, India, during different periods of the year
362 including Diwali festival. *Atmospheric Pollution Research* 2011, **2**(4): 418-427.
- 363 26. Song S, Nenes A, Gao M, Zhang Y, Liu P, Shao J, *et al.* Thermodynamic Modeling
364 Suggests Declines in Water Uptake and Acidity of Inorganic Aerosols in Beijing Winter

- 365 Haze Events during 2014/2015–2018/2019. *Environmental Science & Technology Letters*
366 2019, **6**(12): 752-760.
- 367 27. Akagi SK, Yokelson RJ, Wiedinmyer C, Alvarado MJ, Reid JS, Karl T, *et al.* Emission
368 factors for open and domestic biomass burning for use in atmospheric models.
369 *Atmospheric Chemistry and Physics* 2011, **11**(9): 4039-4072.
- 370 28. Christian TJ, Yokelson RJ, Cardenas B, Molina LT, Engling G, Hsu SC. Trace gas and
371 particle emissions from domestic and industrial biofuel use and garbage burning in
372 central Mexico. *Atmospheric Chemistry and Physics* 2010, **10**(2): 565-584.
- 373 29. Lemieux PM, Lutes CC, Abbott JA, Aldous KM. Emissions of Polychlorinated
374 Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from the Open Burning of
375 Household Waste in Barrels. *Environmental Science & Technology* 2000, **34**(3):
376 377-384.
- 377 30. Andreae MO. Emission of trace gases and aerosols from biomass burning - an updated
378 assessment. *Atmospheric Chemistry and Physics* 2019, **19**(13): 8523-8546.
- 379 31. Chakraborty P, Sampath S, Mukhopadhyay M, Selvaraj S, Bharat GK, Nizzetto L.
380 Baseline investigation on plasticizers, bisphenol A, polycyclic aromatic hydrocarbons
381 and heavy metals in the surface soil of the informal electronic waste recycling workshops
382 and nearby open dumpsites in Indian metropolitan cities. *Environmental Pollution* 2019,
383 **248**: 1036-1045.
- 384 32. Chakraborty P, Selvaraj S, Nakamura M, Prithiviraj B, Cincinelli A, Bang JJ. PCBs and
385 PCDD/Fs in soil from informal e-waste recycling sites and open dumpsites in India:
386 Levels, congener profiles and health risk assessment. *Science of the Total Environment*
387 2018, **621**: 930-938.
- 388 33. Chakraborty P, Zhang G, Cheng HR, Balasubramanian P, Li J, Jones KC. Passive air
389 sampling of polybrominated diphenyl ethers in New Delhi, Kolkata, Mumbai and
390 Chennai: Levels, homologous profiling and source apportionment. *Environmental*
391 *Pollution* 2017, **231**: 1181-1187.
- 392 34. Nagpure AS. Assessment of quantity and composition of illegal dumped municipal solid
393 waste (MSW) in Delhi. *Resources Conservation and Recycling* 2019, **141**: 54-60.
- 394 35. Pradhan JK, Kumar S. Informal e-waste recycling: environmental risk assessment of
395 heavy metal contamination in Mandoli industrial area, Delhi, India. *Environmental*
396 *Science and Pollution Research* 2014, **21**(13): 7913-7928.
- 397 36. Salam M, Varma A. Bacterial community structure in soils contaminated with electronic
398 waste pollutants from Delhi NCR, India. *Electronic Journal of Biotechnology* 2019, **41**:
399 72-80.
- 400 37. Suresh R, Janakiramayya MV, Sukumar ER. An account of fog over Chennai. *Mausam*
401 2007, **58**(4): 501-512.
- 402 38. Stockwell CE, Christian TJ, Goetz JD, Jayarathne T, Bhave PV, Praveen PS, *et al.* Nepal
403 Ambient Monitoring and Source Testing Experiment (NAMaSTE): emissions of trace

- 404 gases and light-absorbing carbon from wood and dung cooking fires, garbage and crop
405 residue burning, brick kilns, and other sources. *Atmospheric Chemistry and Physics* 2016,
406 **16(17)**: 11043-11081.
- 407 39. Fu X, Wang T, Wang SX, Zhang L, Cai SY, Xing J, *et al.* Anthropogenic Emissions of
408 Hydrogen Chloride and Fine Particulate Chloride in China. *Environmental Science &*
409 *Technology* 2018, **52(3)**: 1644-1654.
- 410 40. Saiz-Lopez A, von Glasow R. Reactive halogen chemistry in the troposphere. *Chemical*
411 *Society Reviews* 2012, **41(19)**: 6448-6472.
- 412 41. Andreae MO, Andreae TW, Annegarn H, Beer J, Cachier H, le Canut P, *et al.* Airborne
413 studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical
414 composition. *Journal of Geophysical Research-Atmospheres* 1998, **103(D24)**:
415 32119-32128.
- 416 42. Goetz JD, Giordano MR, Stockwell CE, Christian TJ, Maharjan R, Adhikari S, *et al.*
417 Speciated online PM1 from South Asian combustion sources - Part 1: Fuel-based
418 emission factors and size distributions. *Atmospheric Chemistry and Physics* 2018, **18(19)**:
419 14653-14679.
- 420 43. Finlayson-Pitts BJ. The tropospheric chemistry of sea salt: A molecular-level view of the
421 chemistry of NaCl and NaBr. *Chemical Reviews* 2003, **103(12)**: 4801-4822.
- 422 44. Fountoukis C, Nenes A. ISORROPIA II: a computationally efficient thermodynamic
423 equilibrium model for K⁺-Ca²⁺-Mg²⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O aerosols.
424 *Atmospheric Chemistry and Physics* 2007, **7(17)**: 4639-4659.
- 425 45. Singh S, Kulshrestha UC. Abundance and distribution of gaseous ammonia and
426 particulate ammonium at Delhi, India. *Biogeosciences* 2012, **9(12)**: 5023-5029.
- 427 46. Topping D, Connolly P, McFiggans G. Cloud droplet number enhanced by
428 co-condensation of organic vapours. *Nature Geoscience* 2013, **6(6)**: 443-446.
- 429 47. Kulmala M, Laaksonen A, Charlson RJ, Korhonen P. Clouds without supersaturation.
430 *Nature* 1997, **388(6640)**: 336-337.
- 431 48. Hu WW, Hu M, Hu W, Jimenez JL, Yuan B, Chen WT, *et al.* Chemical composition,
432 sources, and aging process of submicron aerosols in Beijing: Contrast between summer
433 and winter. *Journal of Geophysical Research-Atmospheres* 2016, **121(4)**: 1955-1977.
- 434 49. Petters MD, Kreidenweis SM. A single parameter representation of hygroscopic growth
435 and cloud condensation nucleus activity. *Atmospheric Chemistry and Physics* 2007, **7(8)**:
436 1961-1971.
- 437 50. Verma R, Vinoda KS, Papireddy M, Gowda ANS. Toxic Pollutants from Plastic Waste-
438 A Review. *Procedia Environmental Sciences* 2016, **35**: 701-708.
- 439 51. Behnke W, George C, Scheer V, Zetzsch C. Production and decay of ClNO₂, from the
440 reaction of gaseous N₂O₅ with NaCl solution: Bulk and aerosol experiments. *Journal of*
441 *Geophysical Research-Atmospheres* 1997, **102(D3)**: 3795-3804.

- 442 52. Cai XY, Griffin RJ. Secondary aerosol formation from the oxidation of biogenic
443 hydrocarbons by chlorine atoms. *Journal of Geophysical Research-Atmospheres* 2006,
444 **111**(D14).
- 445 53. Osthoff HD, Roberts JM, Ravishankara AR, Williams EJ, Lerner BM, Sommariva R, *et*
446 *al.* High levels of nitryl chloride in the polluted subtropical marine boundary layer.
447 *Nature Geoscience* 2008, **1**(5): 324-328.
- 448 54. Thornton JA, Kercher JP, Riedel TP, Wagner NL, Cozic J, Holloway JS, *et al.* A large
449 atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature*
450 2010, **464**(7286): 271-274.
- 451

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

454

455 **Acknowledgment:** S.S.G. acknowledges the partial funding from the Ministry of Earth Sciences
456 (MoES; sanction number: MoES/16/04/2017-APHH (PROMOTE)), Govt. of India and
457 Department of Science and Technology (DST; sanction number: DST/CCP/CoE/141/2018C),
458 Govt. of India. This work was partially supported by UK Natural Environment Research Council
459 with Grant. Reference Numbers: NE/P016480/1 and NE/P016472/1. P. L. acknowledges the
460 start-up funding support from Georgia Institute of Technology. All the authors are grateful to the
461 APHH-PROMOTE team for providing the logistic and experimental support during the
462 campaign. Help from Dr. Vijay Kumar Soni, Dr. Siddhartha Singh, and the staff at India
463 Meteorological Department, Delhi office is specially acknowledged for logistic support during
464 campaign and providing the meteorological data. S.S.G. thankfully acknowledges Alfatech
465 Services, New Delhi for their generous technical support during campaign. P.L. acknowledges
466 fruitful discussions with Nga Lee Ng and Lewis G. Huey. L.J.M. acknowledges helpful
467 discussions with Daniel Robie. U. Panda acknowledges CSIR for fellowship. S.S.G. was a
468 recipient of the Fulbright Fellowship. P.L. also holds an affiliate faculty position at Department
469 of Civil Engineering, IIT Madras.

470

471 **Author Contributions:** S.S.G. and P.L. designed the research. S.S.G., G.M., and H.C.
472 conceptualized and planned the field campaign. U. Panda, S.S.R., A.S., S. M. K. and E.D.
473 carried out the extensive field measurements and collected the ACSM data in Delhi and Chennai.
474 S.S.G., P.L., U. Panda, S.M.K., R.R., and M.L.P. conducted ACSM data analysis. S.S.G., P.L.,
475 X.W., J.A., E.R.V., and G.M. conducted the ACSM data interpretation. P.L., S.S., and S.S.G.
476 carried out the thermodynamic model simulations and conducted the data analysis and
477 interpretation. P.L., Y.C., Y.W., and S.S.G. conducted the calculation of light-extinction
478 enhancement factor and Köhler theory. T.L. performed the STILT simulation and performed the
479 data interpretation with help from P.L. and S.S.G. S.S.G. and P.L. led the manuscript writing

480 with specific inputs and edits from X.W., L.S., S.T.M., L.J.M., U. Pöschl, G.M., M.O.A., and
481 H.C. All co-authors discussed the results and commented on the manuscript.

482

483 The authors declare no conflict of interests.

484

485

List of Figures

486

487

488

489

490

491

492

493

494

495

496

497

498

Figure 1. Non-refractory chemical components in sub micrometer particulate matter (NR-PM₁), 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-PM₁ for various locations over India connected by corresponding lines. Total mass concentrations of NR-PM₁ (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).

499

500

501

502

503

504

505

506

507

508

509

510

511

512

513

514

515

516

517

Figure 2. Time series of NR-PM₁, 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-PM₁ 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) Delhi and (f) Chennai. Insert in (e) shows the data from P2 days. Square markers and error bars represent mean and ± 1 standard deviation.

518

519

520

521

522

Figure 3. Thermodynamic modeling of the gas-particle partitioning of chloride in Delhi. (a) Ion balance of NR-PM₁ 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

523 ammonium (gas phase + particle phase) and total sulfate modeled by the
524 thermodynamic model, assuming the aerosol adopts a metastable state. The
525 simulations used a campaign-averaged RH of 57% and temperature of 17 °C
526 for Delhi. Total nitrate was assumed to increase with increasing total sulfate,
527 with a mass ratio of 1:1, consistent with the measurements in Delhi. A total
528 chloride concentration of 25 $\mu\text{g m}^{-3}$ was used in the simulations. Typical total
529 ammonium and total sulfate values of Delhi, as inferred from the literature³²
530 and the field measurements of this study, are marked by the green box. The
531 dashed line represents the condition in which the total ammonia is neutralized
532 by sulfate ($n(\text{NH}_x) = 2 n(\text{SO}_4^-)$). The solid curve represents the condition in
533 which the total ammonia is fully neutralized by sulfate, nitrate, and chloride,
534 i.e., $n(\text{NH}_x) = 2 n(\text{SO}_4^-) + n(\text{NO}_3^-) + n(\text{Cl}^-)$. (c) Modeled aqueous fraction
535 of chloride as a function of temperature and relative humidity. The points
536 show the measured particle-phase chloride concentrations during the
537 high-chloride episodes as a function of temperature and relative humidity.
538 The boxes indicate conditions of morning and afternoon hours during the
539 field campaign in Delhi. (d) Measured particle-phase chloride as a function of
540 aerosol liquid water derived from model (Methods section). The red dashed
541 line shows the increase of the modeled particle-phase chloride with an
542 increasing RH from 15% to 90% (Extended Data Fig. 9), assuming total Cl is
543 25 $\mu\text{g m}^{-3}$. The PM liquid water associated with inorganics was calculated
544 using the ISORROPIA II model in reverse mode based on the ACSM
545 measured chemical composition. The aerosol liquid water associated with
546 organics was calculated using a hygroscopicity parameter $\kappa = 0.1$ ^{20, 49}.

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

562 **Methods**

563 **1. Sampling Sites:**

564 *Delhi.*

565 The aerosol sampling in Delhi was conducted at Indian Meteorological Department
566 (IMD) campus (28.589008⁰ N, 77.222575⁰ E; 200 m asl) during February–March 2018 using
567 advanced instrumentation under Atmospheric Pollution and Human Health Program under
568 Process Analysis, Observations and Modeling–Integrated Solutions for Cleaner Air for Delhi
569 (APHH – PROMOTE) campaign. All the instruments were placed in an air-conditioned
570 container connected to a dedicated inlet with a sampling height of ~5 meters above the ground.
571 The inlet was constructed of stainless steel with a cyclone separator and with proper protection,
572 to avoid any blockage in the inlet. The air sampled can be considered as representative of the
573 region in view of the average time and duration of the sampling. Briefly, the capital city of India,
574 considered to be one of the most populated and polluted cities in the world, experiences very
575 diverse climatic conditions. The winters, from December–February are mildly cold (with average
576 diurnal temperatures 5–20°C) and humid (average diurnal relative humidity of 45–95%). During
577 the winter season, owing to frequent inversions, the boundary layer depth is generally less than
578 100 m, especially during early morning hours before sunrise, when the temperature reaches its
579 minimum. During the winter season, Delhi experiences very high aerosol mass burdens
580 attributed to local emissions and regional transport¹.

581 The sampling site is surrounded by small and medium scale industries within a 25 km
582 vicinity, dealing with metal processing, paper production, plastic and medicine manufacturing,
583 e-waste handling and recycling, medical waste management, dumping sites management, etc.,
584 which cause emission of various toxic gases and pollutants into the atmosphere of Delhi^{11, 19, 31,}
585 ^{32, 33, 34, 35, 50, 55}. According to an estimate, on average 606 tons per km² of municipal solid waste
586 (MSW) are illegally dumped in Delhi, resulting 557 thousand tons of MSW lying on streets and
587 open areas, including 38 thousand tons of plastic³⁴. Delhi experiences open MSW burning of 216
588 thousand tons per year⁵⁶ that burnt at non-designated places and also ending up as fuel for brick
589 kilns⁴². This waste mainly constitutes diverse trash, but a common and abundant component is a
590 mixed plastic from food wrappers to e-waste handling. Large numbers of informal and
591 unorganized e-waste handling and recycling, and metal processing units are prevalent across
592 Delhi³⁴ (Extended Data Fig. 7). E-waste handling units aim to retrieve copper, silver, and gold
593 from printed circuit boards, cables, scrap plastics, and batteries with processes that use acids and
594 open burning. The metal processing industries use acids for pickling and polishing purposes.
595 Interestingly, HCl is widely used in the steel processing industries for pickling to remove iron
596 oxides and scale from the surface of steel. In metal industries, HCl is also widely used for
597 aluminum etching, metal cleansing, and metal pre-fixing. These processes are known to emit the
598 HCl directly in the atmosphere. It is also important to note that HCl and particulate Cl can be

599 also emitted from agricultural crop residue burning, which is prevalent in northern India during
600 October and November. However, our measurements were carried out during February, which is
601 not the crop residue burning season in northern India.

602 **Chennai.** The measurements of aerosol composition, using an ACSM and an Aethalometer
603 (AE33) were carried out in Chennai during 5-January-2019 to 5-February-2019, with an aim to
604 complement the Delhi measurements and to cover the festival of Bhogi, so characteristic features
605 associated with trash/waste burning could be investigated. Please note, as discussed below, the
606 Bhogi festival is marked by large scale wood and domestic waste/trash burning in this region.
607 Chennai, the fourth most populated city in India (>5 million) is a South-Eastern coastal urban
608 city and unlike Delhi experiences a tropical hot and humid climate with higher temperatures
609 during the measurement period. Daytime average temperatures ranged from 20–29°C and
610 relative humidities from 50–90%. The sampling was carried out with a dedicated inlet with
611 proper protection from insect and other blockages. The instruments were housed at Indian
612 Institute of Technology Madras in a temperature-controlled laboratory (12.99N, 80.23E; 14 m
613 asl). The campaign in Chennai was planned in such a way that the measurements covered the
614 period of a local festival, called Bhogi, which is celebrated in the middle of January (mostly on
615 the 14th), marking the beginning of the Tamil month of Thai, and is one of the biggest and most
616 important festivals in the state of Tamilnadu. In this part of India, it is considered to be even
617 more important and bigger than the festival of Deepawali and is celebrated across entire
618 Tamilnadu including Chennai. Previous researchers have reported air quality deterioration with
619 pollutants exceeding levels well above the standard limits during the Bhogi festival³⁷. As a
620 customary and old tradition during this festival, people thoroughly clean their houses and remove
621 all unwanted and unusable goods. Another important ritual, which follows the cleaning, called
622 Bhogi Mantalu, is to throw all unwanted and unusable household items in a fire fuelled by wood
623 and cow-dung cakes as a religious belief. The burning generally starts on the evening of the
624 festival and continues till early morning. During our measurement period, the festival was on 14
625 January, and as can be seen from Fig. 2b, the NR-PM₁ mass concentration reached a peak value
626 of 320 µg m⁻³ (Extended Data Fig. 2) as a result of emissions due to burning. During the entire
627 campaign, sulfate was found to be the second largest mass contributor to the NR-PM₁ after
628 organics. During the Bhogi burning, however, particulate chloride was the second largest mass
629 contributor.

630 **2. Instrumentation:**

631 An Aerodyne aerosol chemical speciation monitor (ACSM)⁵⁷ was deployed at the Indian
632 Meteorological Department (IMD), New Delhi, from 1-Feb to 3-March 2018 and at the Indian
633 Institute of Technology Madras from 5-Jan to 5-Feb 2019 to measure the chemical composition
634 of non-refractory submicron aerosol particles (with vaporization temperature <600°C), including
635 organics (Org), sulfate (SO₄), nitrate (NO₃), ammonium (NH₄) and chloride (Cl) at high time
636 resolution (about 15 minutes) and high mass sensitivity. Maintenance and calibration of the

637 instrument were performed before the start of each campaign and once during the campaign as
638 per the normal protocols⁵⁸. For the ambient measurements, briefly, ambient air was drawn
639 through a stainless-steel tube and a PM_{2.5} cyclone to remove the coarse mode particles. The air
640 sample was then passed through a silica gel dryer to avoid water condensation in the sampling
641 line before reaching the ACSM inlet, out of which 0.085 L/min (85 cm³) was isokinetically
642 allowed to pass into the ACSM sampling valve. The particles were sampled into a vacuum
643 chamber through an aerodynamic lens (approx. 2 torr). Then the PM was flash vaporized on a
644 hot surface at around 600 °C and ionized, followed by subsequent detection using a quadrupole
645 mass spectrometer. Theoretically, the concentrations of the chemical species are proportional to
646 the measured ion signal.

647 The mass calibrations were performed using a TSI electrostatic classifier (SMPS; TSI 3082) as
648 differential mobility analyzer (DMA) to select the desired particle sizes with ammonium nitrate
649 and ammonium sulfate. The calibration resulted in a response factor (RF) 7.65×10^{-11} with
650 relative ionization efficiency (RIE) for ammonium of 4.96 and sulfate of 1.08 at Chennai; the
651 values for Delhi were 7.65×10^{-11} , 4.96, and 0.9, respectively. The 3σ uncertainties of ACSM for
652 ammonium, chloride, sulfate, organics, nitrate are 0.284 $\mu\text{g}/\text{m}^3$, 0.011 $\mu\text{g}/\text{m}^3$, 0.024 $\mu\text{g}/\text{m}^3$, 0.148
653 $\mu\text{g}/\text{m}^3$, 0.012 $\mu\text{g}/\text{m}^3$ respectively for 30 min averages. A default RIE value of 1.3 was used for
654 chloride. Given the unique composition of Delhi particulate matter, the phase state can be
655 different from typical ambient measurements in other environments across the globe where
656 composition-dependent CE was used⁵⁹. Therefore, a collection efficiency of 0.5 was used
657 throughout, assuming most of the particles to be semi solid inside the ACSM, in line with previous
658 literature⁵⁹. It is important to note that though assumption of non-size dependent CE may affect
659 the absolute aerosol mass concentration, whereas the relative mass abundance and hence the
660 hygroscopicity will not change with CE for internally mixed aerosols.

661 **3. Thermodynamic Modeling**

662 Thermodynamic equilibrium between an $\text{NH}_4^+ \text{-H}^+ \text{-SO}_4^{2-} \text{-NO}_3^- \text{-Cl}^- \text{-H}_2\text{O}$ inorganic
663 particulate matter and its gaseous precursors (NH_3 , HNO_3 , and HCl) is calculated using the
664 ISORROPIA^{44, 60, 61} model (version II; <https://www.epfl.ch/labs/lapi/isorrophia/>). The
665 ISORROPIA is a computational efficient and rigorous aerosol thermodynamics model that is
666 widely used in the atmospheric aerosol community. The ISORROPIA solves thermodynamic
667 equilibrium for either a closed system (i.e., forward mode, which takes input of total
668 concentration of both gas- and particle-phases for each species), or an open system (reverse
669 mode, which takes input of particle-phase concentration for each species). For both modes, the
670 equilibrium state is calculated at given temperature and RH values. The output of ISORROPIA
671 provides gaseous and particulate mass concentrations for each species, as well as the mass
672 concentration of aerosol liquid water content. For all calculations presented here, we assumed the
673 PM adopted a metastable thermodynamic state.

674 Here we employed the forward mode of ISORROPIA to calculate the gas-particle
675 partitioning of chloride. For simulations with consideration of chloride, a fixed total
676 concentration of gaseous and particulate chloride of $25 \mu\text{g m}^{-3}$ (mass concentration as the form of
677 HCl) was used. Such a high concentration of chloride is necessary to reproduce the observed
678 high PM chloride during morning hours in Delhi. We systematically tested the partitioning
679 behaviors of chloride for a wide range values of various input parameters, including sulfate
680 concentration, total ammonium, temperature, and RH (Fig. 3 b and c). We used the reverse mode
681 of ISORROPIA to calculate the aerosol liquid water content associated with inorganic PM with
682 input of measured aerosol inorganic composition, temperature, and RH in Delhi (Fig. 2d). The
683 liquid water content in ISORROPIA is estimated with the Zdanovskii-Stokes-Robinson (ZSR)
684 mixing rule⁶², linking the water uptake of the multicomponent system to the hygroscopicity of
685 each individual electrolyte. For the additional water uptake of organic PM, we assumed a
686 constant hygroscopicity parameter $\kappa=0.1$ ^{20, 63}. The ISORROPIA model does not consider the
687 effect of surface tension, and the aerosol water activity (a_w) equals RH.

688 We calculated the aerosol hygroscopic growth and cloud condensation nuclei (CCN)
689 activation for scenarios with and without chloride (Fig. 4 a and b). Thermodynamic equilibrium
690 of inorganic PM and its precursor gases was calculated using ISORROPIA-II in the forward
691 mode. For both scenarios, we randomly sampled sulfate and nitrate concentrations from
692 measured values during the high chloride high organic period (P1) with replacement (i.e.,
693 bootstrapping, $N = 1000$), and the mean (\pm s.d.) values for the resampled population were 4.2 ± 1.8
694 $\mu\text{g m}^{-3}$ and $5.6 \pm 2.9 \mu\text{g m}^{-3}$ for sulfate and nitrate, respectively. The total ammonium (i.e.,
695 gaseous+particulate) was randomly sampled from a Gaussian distribution with a mean value of
696 $30 \mu\text{g m}^{-3}$ and $5 \mu\text{g m}^{-3}$ s.d. The simulation with chloride included a total chloride concentration
697 of $25 \pm 5 \mu\text{g m}^{-3}$. In addition to the inorganic species, a non-volatile organic PM of $42.9 \pm 27.9 \mu\text{g}$
698 m^{-3} , bootstrapped from P1, was added in the multicomponent system, and a hygroscopicity κ
699 value of 0.1 was used in the calculations of water uptake for organic PM. These values used in
700 the simulations are consistent with the measurements during the high chloride period of Delhi,
701 with uncertainty and variability taken into account (Extended Data Fig. 2). A campaign-averaged
702 temperature of $17 \text{ }^\circ\text{C}$ in Delhi was used in the simulations. Thermodynamic equilibrium states
703 were calculated for different RH values, and the RH-dependent PM composition for the
704 simulation with chloride is shown in Extended Data Fig. 9. Based on the calculated water uptake
705 for inorganic and organic PM components, we modelled the CCN activation for particles with an
706 initial dry diameter of 100 nm (Fig. 4b). We calculated the hygroscopicity κ value at $a_w=0.99$ (the
707 upper limit of the ISORROPIA model) for the mixed inorganic-organic particle. Hygroscopic
708 growth at higher a_w values were extrapolated using this constant κ value. This extrapolation is
709 valid because $>99\%$ of chloride partitions to the particle phase at $a_w=0.99$, and further water
710 uptake at higher a_w values does not significantly enhance the hygroscopicity. A surface tension
711 value of pure water (0.072 N m^{-1}) was used in the calculations of CCN activation.

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

718 **4. Light-Extinction Enhancement factor**

719 Following the work of Wang and Chen¹⁸, we derived the measured light-extinction
720 enhancement factor ($f(\text{RH})$) of aerosol hygroscopic growth from ambient observations. We
721 selected the period of winter (December to mid-February) to spring (mid-February to March)
722 with high concentrations of chloride reported², to investigate the effect of chloride
723 co-condensation. Hourly observations during 2015-2019, including PM_{2.5} from the U.S. Embassy
724 in Delhi (<https://www.airnow.gov/>), along with visibility and meteorological parameters from the
725 Indira Gandhi International Airport (DEL, only 7 km away from the U.S. Embassy,
726 <https://www.ncdc.noaa.gov/>) were used in the analysis. The PM_{2.5} and visibility observations
727 were well calibrated and quality-controlled according to the protocols of the U.S. Environmental
728 Protection Agency^{64, 65}, and the National Oceanic and Atmospheric Administration, National
729 Climatic Data Center⁶⁶, respectively. The RH values were calculated from dew point temperature
730 and temperature using the Magnus formula⁶⁷. The periods with wind speed larger than 6.5 m/s or
731 RH higher than 95% were excluded from analysis, to minimize the uncertainties induced by dust
732 and the low accuracy of the RH sensor under high RH conditions¹⁸. We projected the data pairs
733 of RH, PM_{2.5}, and visibility into eight RH-bins (with borders of 30%, 40%, 50%, 60%, 70%,
734 80%, 85%, 90% and 95%), with more than 400 pairs within each bin. The light extinction
735 coefficient of aerosol particles was derived from visibility data using the Koschmieder's
736 equation⁶⁸. Then, the mass extinction efficiency for each RH-bin, $E(\text{RH})$ with units of m²/g, was
737 derived as the slope between light extinction coefficient and PM_{2.5} concentration with least
738 squares fit linear regression. By normalizing the $E(\text{RH})$ with $E(30\%-40\%)$, we derived the $f(\text{RH})$
739 for each RH bin. The uncertainty of $f(\text{RH})$ was estimated using bootstrapping⁶⁹ by resampling 1
740 million times from the observations within each RH bin.

741 The modeled $f(\text{RH})$ was calculated for two scenarios with and without chloride (Fig. 4a).
742 Thermodynamic equilibrium and water uptake were calculated following the methods described
743 in Section 3. Hygroscopicity parameter κ_{chem} values for PM₁ were derived from the modeled
744 chemical composition and water uptake. The chemical composition-derived κ_{chem} was then
745 linked with $f(\text{RH})$ following a physical-based empirical approach^{18, 49, 70, 71}. In this approach, the
746 $f(\text{RH})$ was parameterized in the form of κ -Kohler theory⁷⁰:

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

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

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

749 where the ratio R_{κ} is determined by the particle number size distribution and chemical
750 composition. The values of R_{κ} ranged 0.58-0.77 based on the study for Beijing⁷¹. An average
751 value of 0.69 was used in the present study following the work by Wang and Chen¹⁸.

752 5. Factor analysis

753 Source apportionment of the OA mass spectra obtained from ACSM for both the sites has been
754 performed using the unconstrained positive matrix factorization (PMF) algorithm implemented
755 in Multilinear Engine (ME-2) developed by ref.⁷² utilizing source finder tool (SoFi v4.8) in Igor
756 pro⁷³. Further, the PMF is a bilinear unmixing receptor model for factor analysis developed by
757 ref.^{72, 74} that simplifies the complex data sets to a linear combination of source types and their
758 time dependent concentration. In PMF, the measured organic mass spectra represented in the
759 form of a matrix $\mathbf{X}_{m \times n}$ (organic mass spectra in m rows and ion fragments in n columns) is
760 factorized into two sub matrices, the time series $\mathbf{G}_{m \times p}$ and the factor profiles $\mathbf{F}_{p \times n}$, where p is the
761 number of factors/OA sources selected.

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

762 Here, $\mathbf{E}_{m \times n}$ is the residual matrix containing the fraction of the matrix X that is unexplained by
763 the model solution. The model then uses a least square algorithm to minimize the object function
764 Q as given in the below equation:
765

$$Q = \sum_{i=1}^m \sum_{j=1}^n (e_{ij} / \sigma_{ij})^2$$

766 where e_{ij} represents the squared residuals and σ_{ij} are the respective measurement uncertainties.
767 The extraction procedure of organic mass spectra, corresponding error matrices, time and m/z
768 values as model input has been adopted from ref.^{57, 75}. The input data were created up to m/z 120
769 and analyzed while increasing the number of factors from two to eight. The optimum number of
770 factors was obtained after careful evaluation of several parameters including residuals, time
771 series, Q/Q_{exp} values of various solutions gained by running the model from different initial
772 conditions (SEED run). For Delhi, a five-factor solution profile was found to be the most
773 suitable. The factors were assigned after comparing the mass spectra profiles with some known
774 references from published literature⁷³ including 1-hydrocarbon-like OA (HOA), 2-biomass
775

776 burning related OA (BBOA), 3-cooking OA (COA), 4-oxygenated primary OA (OPOA), and
777 5-oxygenated OA (OOA)

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

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

784 We used the Stochastic Time-Inverted Lagrangian Transport (STILT) model, version 2.0, to
785 simulate the transport of an ensemble of 10,000 air particles to the receptor site, 72 hours back in
786 time⁷⁶. We performed a total of 1,830 simulations, one for each ACSM measurement instance for
787 available meteorological data. While the meteorology from the Global Data Assimilation System
788 (GDAS) we use to drive STILT is coarse, at 0.5°x0.5° spatial resolution, STILT can resample the
789 influence footprint to a finer spatial resolution. STILT-v2.0 uses a Gaussian kernel density
790 estimator with modified vertical dilution in the hyper near field (1-10 km from the receptor) to
791 allocate the influence of air particles according to a user-specified footprint grid, which we
792 define as a regional domain (72-82°E, 23-33°N) at 0.01°x0.01° spatial resolution. We use the
793 STILT footprints to determine the average sensitivity of the receptor to nearby polluting sources
794 for low Cl and high Cl modes.

795

796 **Data availability**

797 The non-refractory PM₁ species from literature shown in Fig. 1 are available in Extended Data
798 Table 1. All other data displayed in figures, including concentrations of non-refractory PM₁
799 species measured by the ACSM in Delhi and Chennai in this study, and aerosol liquid water
800 modeled by ISORROPIA II, are available in the figshare repository:
801 <https://doi.org/10.6084/m9.figshare.13277486>

802

803 **Code availability**

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

808

809

810 **Methods references**

811

812 55. Panwar RM, Ahmed S. Assessment of contamination of soil and groundwater due to
813 e-waste handling. *Current Science* 2018, **114**(1): 166-173.

814 56. Sharma G, Sinha B, Pallavi, Hakkim H, Chandra BP, Kumar A, *et al.* Gridded Emissions
815 of CO, NO_x, SO₂, CO₂, NH₃, HCl, CH₄, PM_{2.5}, PM₁₀ BC, and NMVOC from Open
816 Municipal Waste Burning in India. *Environmental Science & Technology* 2019, **53**(9):
817 4765-4774.

818 57. Ng NL, Herndon SC, Trimborn A, Canagaratna MR, Croteau PL, Onasch TB, *et al.* An
819 Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the
820 Composition and Mass Concentrations of Ambient Aerosol. *Aerosol Science and*
821 *Technology* 2011, **45**(7): 780-794.

822 58. Freney E, Zhang Y, Croteau P, Amodeo T, Williams L, Truong F, *et al.* The second
823 ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM):
824 Calibration protocols and instrument performance evaluations. *Aerosol Science and*
825 *Technology* 2019, **53**(7): 830-842.

826 59. Middlebrook AM, Bahreini R, Jimenez JL, Canagaratna MR. Evaluation of
827 Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass
828 Spectrometer using Field Data. *Aerosol Science and Technology* 2012, **46**(3): 258-271.

829 60. Nenes A, Pandis SN, Pilinis C. ISORROPIA: A new thermodynamic equilibrium model
830 for multiphase multicomponent inorganic aerosols. *Aquatic Geochemistry* 1998, **4**(1):
831 123-152.

832 61. Nenes A, Pandis SN, Pilinis C. Continued development and testing of a new
833 thermodynamic aerosol module for urban and regional air quality models. *Atmospheric*
834 *Environment* 1999, **33**(10): 1553-1560.

835 62. Stokes RH, Robinson RA. Interactions in Aqueous Nonelectrolyte Solutions. I.
836 Solute-Solvent Equilibria. *The Journal of Physical Chemistry* 1966, **70**(7): 2126-2131.

837 63. Liu PF, Song MJ, Zhao TN, Gunthe SS, Ham SH, He YP, *et al.* Resolving the
838 mechanisms of hygroscopic growth and cloud condensation nuclei activity for organic
839 particulate matter. *Nature Communications* 2018, **9**.

840 64. (EPA) EPA. List of designated reference and equivalent methods. 2015 (last access
841 20.Nov.2018).

842 65. (EPA) EPA. Standard operating procedure for the continuous measurement of particulate
843 matter. 2009 (last accessed on 8.Nov.2018).

844 66. Neal Lott J. The Quality Control of the Integrated Surface Hourly Database. 2004 (Last
845 accessed on 8.Nov.2018).

846 67. Magnus G. Versuche über die Spannkkräfte des Wasserdampfs. *Annalen der Physik* 1844,
847 **137**(2): 225-247.

-
- 848 68. Visibility in meteorology: The theory and practice of the measurement of the visual
849 range. By W. E. Knowles Middleton, M.Sc. University of Toronto Press, Toronto, 1935.
850 Pp. 8 + 104. illus. *Quarterly Journal of the Royal Meteorological Society* 1936, **62**(263):
851 154-155.
- 852 69. Efron BT, R. J. . An Introduction to the Bootstrap. 1993.
- 853 70. Brock CA, Wagner NL, Anderson BE, Attwood AR, Beyersdorf A, Campuzano-Jost P, *et*
854 *al.* Aerosol optical properties in the southeastern United States in summer - Part 1:
855 Hygroscopic growth. *Atmospheric Chemistry and Physics* 2016, **16**(8): 4987-5007.
- 856 71. Kuang Y, Zhao CS, Tao JC, Bian YX, Ma N, Zhao G. A novel method for deriving the
857 aerosol hygroscopicity parameter based only on measurements from a humidified
858 nephelometer system. *Atmospheric Chemistry and Physics* 2017, **17**(11): 6651-6662.
- 859 72. Paatero P. The multilinear engine - A table-driven, least squares program for solving
860 multilinear problems, including the n-way parallel factor analysis model. *Journal of*
861 *Computational and Graphical Statistics* 1999, **8**(4): 854-888.
- 862 73. Canonaco F, Crippa M, Slowik JG, Baltensperger U, Prevot ASH. SoFi, an IGOR-based
863 interface for the efficient use of the generalized multilinear engine (ME-2) for the source
864 apportionment: ME-2 application to aerosol mass spectrometer data. *Atmospheric*
865 *Measurement Techniques* 2013, **6**(12): 3649-3661.
- 866 74. Paatero P, Tapper U. Positive matrix factorization - a nonnegative factor model with
867 optimal utilization of error-estimates of data values. *Environmetrics* 1994, **5**(2): 111-126.
- 868 75. Sun Y, Wang Z, Dong H, Yang T, Li J, Pan X, *et al.* Characterization of summer organic
869 and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor.
870 *Atmospheric Environment* 2012, **51**: 250-259.
- 871 76. Fasoli B, Lin JC, Bowling DR, Mitchell L, Mendoza D. Simulating atmospheric tracer
872 concentrations for spatially distributed receptors: updates to the Stochastic Time-Inverted
873 Lagrangian Transport model's R interface (STILT-R version 2). *Geoscientific Model*
874 *Development* 2018, **11**(7): 2813-2824.
875