Complex interplay between organic and secondary inorganic aerosols with ambient relative humidity implicates the aerosol liquid water content over India during wintertime”

Amar Krishna Gopinath[1,2], Subha S. Raj[2,3], Snehitha M. Kommula[2,3], Christi Jose[2,3], Upasana Panda[2,3,4], Yukti Bishambu[2,3], Narendra Ojha[5], R. Ravikrishna[1,2], Pengfei Liu[6], Sachin S. Gunthe[2,3]

[1]Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai,India

[2]Laboratory for Atmospheric and Climate Sciences, Indian Institute of Technology Madras,Chennai, India

[3]EWRE Division, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India

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

[5]Space and Atmospheric Sciences Division, Physical Research Laboratory, Ahmedabad 380 009, India

[6]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA,USA

Pengfei Liupengfei.liu@eas.gatech.edu

Sachin S. Gunthes.gunthe@iitm.ac.in

Contents of this file

1. Tables S1 to S4
2. Figures S1 to S8

Table S2. Summary of the average chemical composition of atmospheric aerosols at locations across India reported in literature.

Reference	Location	Type	Period	Duration	Mode	Species mass concentration in μg m^{-3} air (mass fraction)						
						NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	OC	Org	K^+
Gani et al. (2019)	New Delhi	Urban	Dec 2017 to Feb 2018	2.5 months	ACSM	20.0 (0.10)	16.0 (0.08)	24.0 (0.12)	23.1 (0.12)	-	112.0 (0.57)	-
Thamban et al. (2019)	Kanpur	Urban	1-31 Jan 2016	1 month	AMS	46.4 (0.11)	52.3 (0.13)	71.2 (0.18)	19.3 (0.05)	-	217.2 (0.053)	-
Kommula et al. (2021)	Chennai	Urban	5 Jan - 1 Feb 2019	1 month	ACSM	3.6 (0.12)	10.1 (0.33)	1.3 (0.04)	0.83 (0.03)	-	14.4 (0.48)	-
Mukherjee et al. (2018)	Mahabaleshwar	Rural	5 Jan- 1 Feb 2019	1 month	ACSM	1.28 (0.10)	3.0 (0.24)	0.96 (0.08)	0.11 (0.01)	-	7.02 (0.57)	-
Kompalli et al. (2020)	Bhubhaneshwar	Urban	Dec 2016–Feb 2017	3 months	AMS	2.08 (0.10)	5.47 (0.27)	2.1 (0.10)	0.52 (0.03)	-	9.82 (0.49)	-
Ajith et al. (2022)	Thiruvananthapuram	Urban	Winter 2017-2020	-	ACSM	3.45 (0.06)	10.90 (0.20)	1.69 (0.03)	0.24 (0.00)	-	37.5 (0.70)	-
Rastogi et al. (2016)	Patiala	Urban	Dec 2011- Feb 2012	3 months	Filter	16.5 (0.12)	24.87 (0.18)	22.34 (0.16)	3.9 (0.03)	42.58	68.13 (0.50)	2.73
Rengarajan et al. (2011)	Ahmedabad	Urban	8 Dec 2006- 7 Jan 2007	1 month	Filter	3.2 (0.07)	9.7 (0.22)	1.2 (0.03)	0.08 (0.00)	18.3	29.28 (0.67)	0.9
S. Kumar and Raman (2016); Samiksha et al. (2021)	Bhopal	Urban	Jan-Feb 2012,2013	2 months	Filter	7.54 (0.09)	23.25 (0.08)	5.99 (0.13)	1.08 (0.03)	31.48	50.37 (0.67)	2.85
S. Kumar et al. (2018)	Amritsar	Urban	Dec 2011- Feb 2012	3months	Filter	4.08 (0.09)	3.95 (0.26)	6.08 (0.07)	1.3 (0.01)	19.56	31.29 (0.57)	0.81
A. Kumar and Sarin (2010)	Mount Abu	Rural	Jan-Feb,Oct-Dec 2007	5 months	Filter	1.83	4.98	0.34	0	-	-	0.36
Agarwal et al. (2020)	Sikandarpur	Rural	Dec-Feb 2015-17	3 months	Filter	13.12	13.25	13.03	13.25	-	-	3.36
A. Kumar et al. (2020)	Patna	Urban	Jan-Feb, Dec	3 months	Filter	6.21	3.73	3.34	0.43	-	-	1.08

Table S1. Quantitative parameters used to identify the dominance of NH_4^+ in aerosol chemical composition.

Location	NH_4^+ equivalent fraction	NH_4^+/SO_4^{2-}
Patiala	0.90	3.55
Ahmedabad	0.72	1.76
Amritsar	0.73	1.73
Bhopal	0.75	5.51
Mount Abu	0.80	1.96
Sikandarpur	0.71	5.28
Patna	0.77	8.88

Table S3. Estimates of κ_{inorg} and overall κ for all locations. The fit parameter R^2 for κ estimates are also shown.

Location	κ_{inorg}	κ_{org}	κ
New Delhi	0.59	0.08	0.28
Kanpur	0.55	0.08	0.28
Chennai	0.37	0.08	0.22
Mahabaleshwar	0.42	0.13	0.24
Bhubhaneshwar	0.33	0.08	0.20
Thiruvananthapuram	0.39	0.08	0.17
Patiala	0.51	0.08	0.28
Ahmedabad	0.41	0.08	0.18
Amritsar	0.36	0.08	0.19
Bhopal	0.58	0.08	0.23

Table S4. Regimes of salt species modelled in ISORROPIA2.1 (considering only NH_4^+)

Regime	$R_{SO_4} = NH_4^+/SO_4^{2-}$	Aerosol type	Salt species
(i)	$R_{SO_4} < 1$	Sulphate super rich	H_2SO_4, NH_4HSO_4
(ii)	$1 \leq R_{SO_4} < 2$	Sulphate rich	NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$
(iii)	$R_{SO_4} \geq 2$	Ammonium rich	$(NH_4)_2SO_4$, NH_4NO_3, NH_4Cl

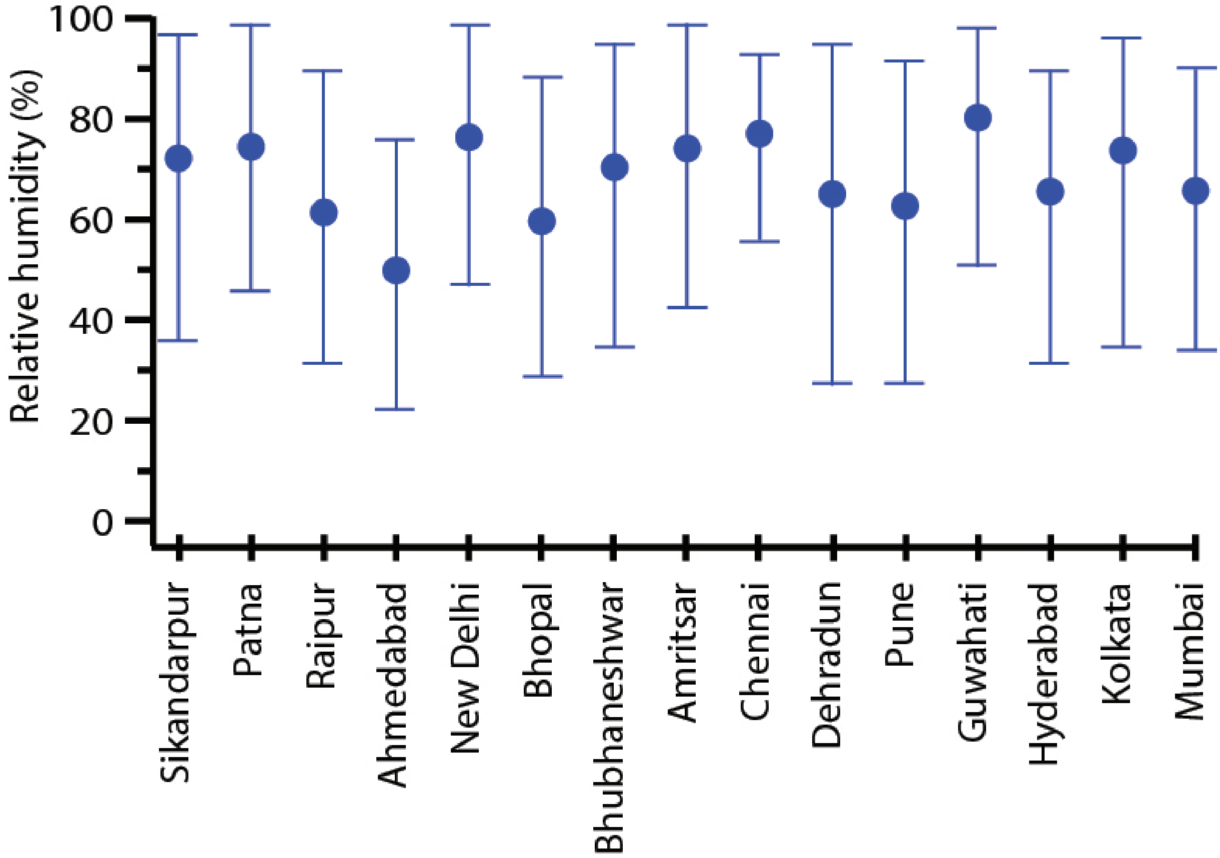

Figure S1. Overview of the atmospheric RH over Indian locations during wintertime. The dots represent the average RH while the whiskers represent the maximum and minimum RH for the corresponding locations.

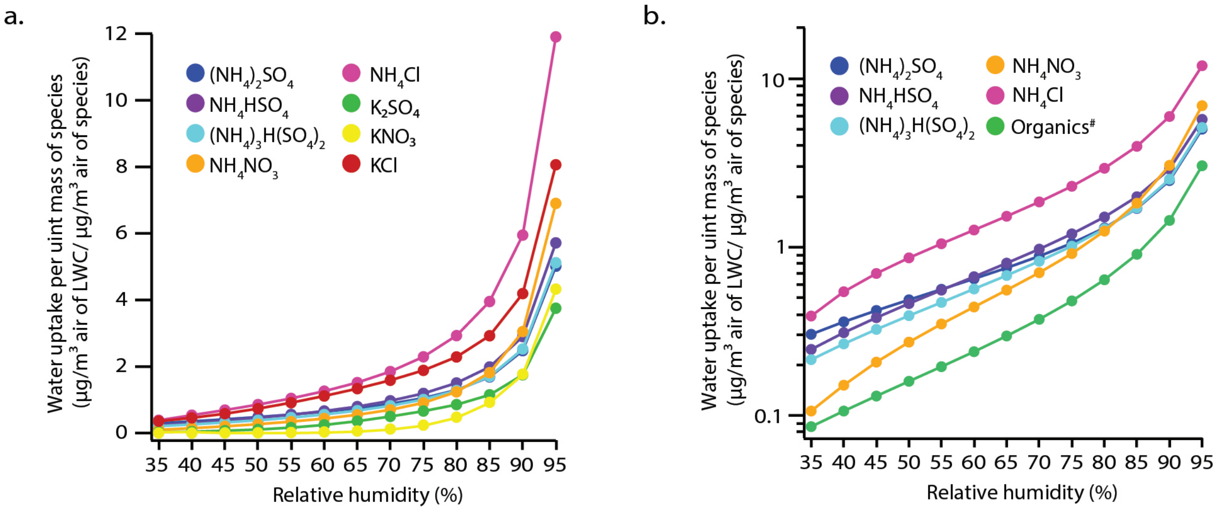

Figure S2. The water uptake per unit mass of species (μg/m^3 air of LWC/ μg/m^3 air of species) over a range of RH (35-95%) of (a) major salts of NH_4^+ and K^+ on linear scale (b) major salts of NH_4^+ and organic matter on log scale

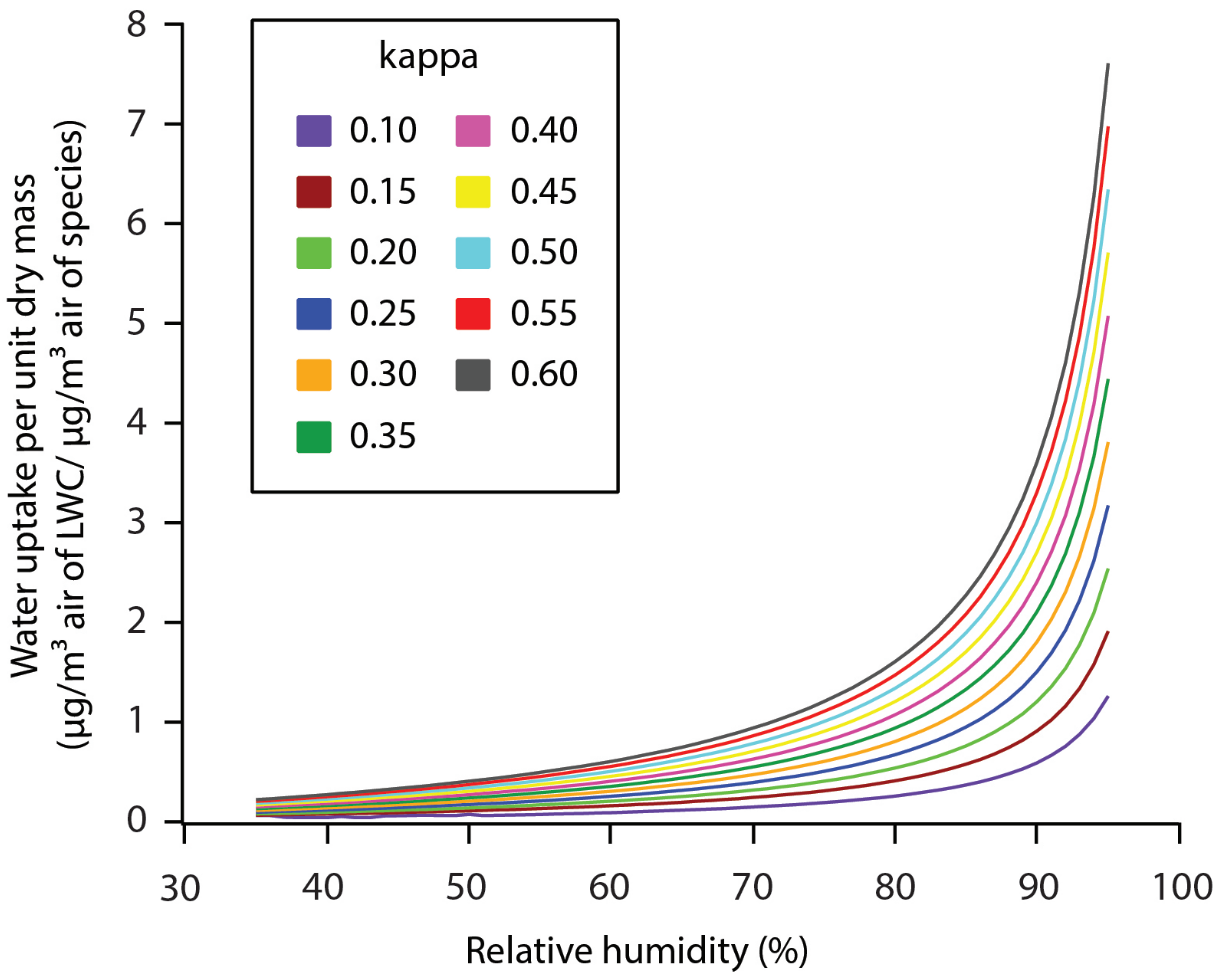

Figure S3. Variation of water uptake per unit dry mass (μg/m^3 air of LWC/ μg/m^3 air of species) with RH for κ ranging from 0.1 to 0.6.

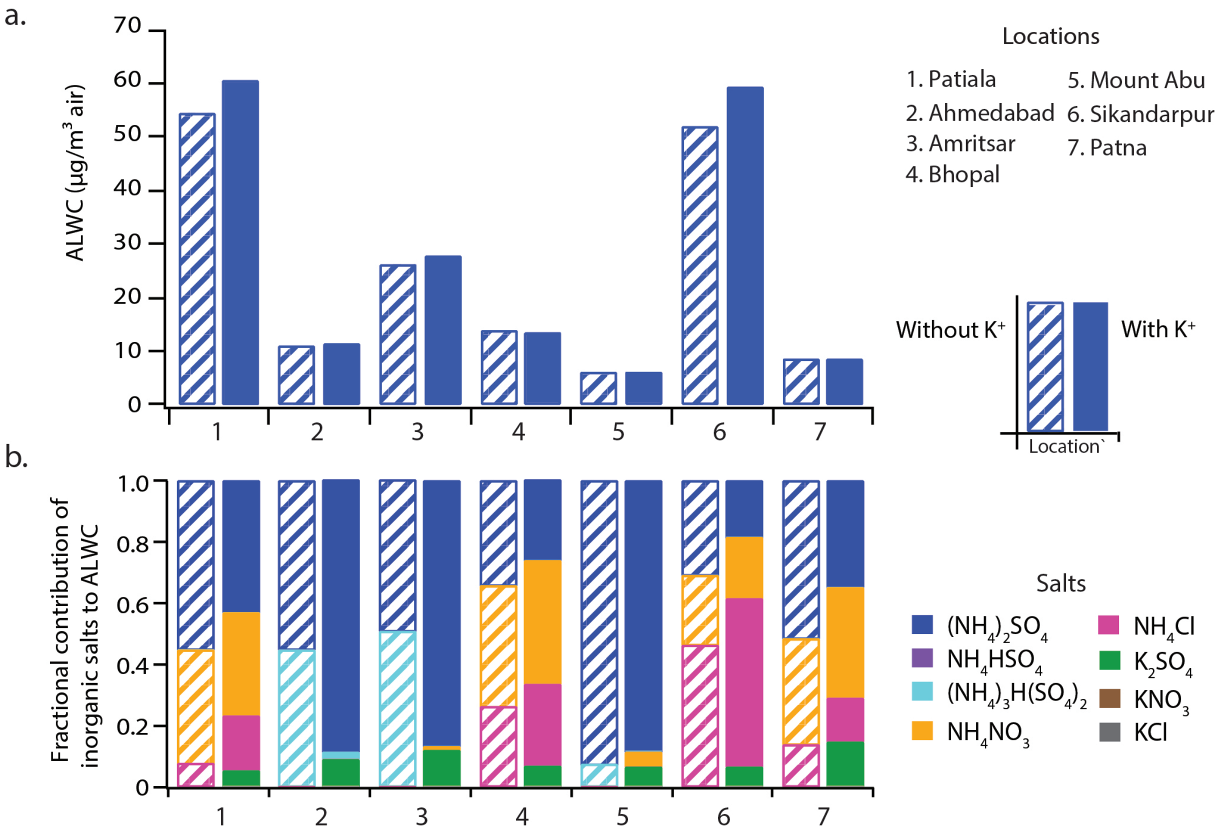

Figure S4. Sensitivity analysis of the effect of including K^+ in the ALWC calculations. For every location, two bars represent data without and with K^+. (a) Comparison of the absolute ALWC (μg/m^3 air) contributed by inorganic species without and with K^+. (b) The fractional composition of inorganic species (represented as salts) without and with K^+.

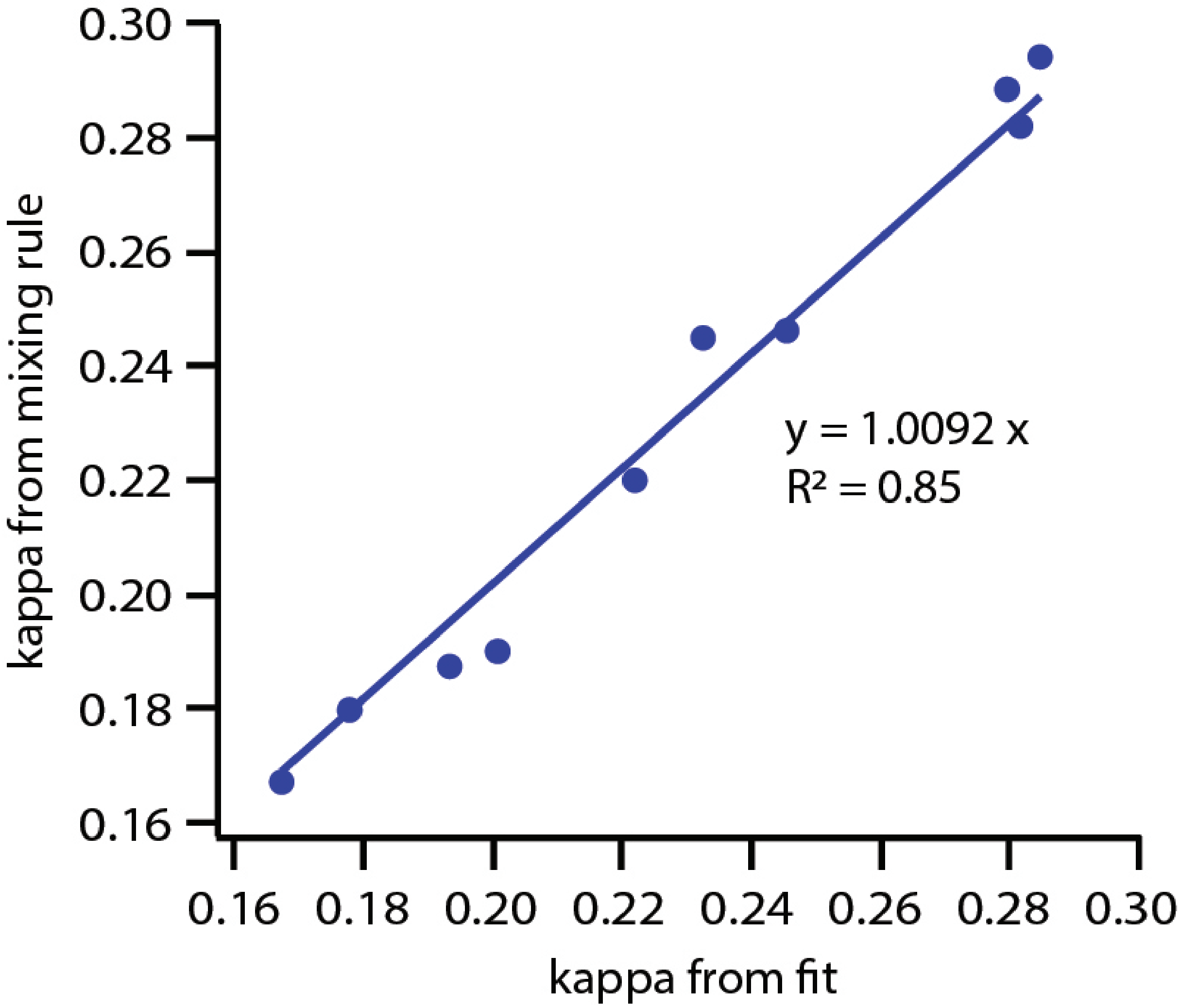

Figure S5. Comparison of the overall kappa from fit with kappa from mixing rule.

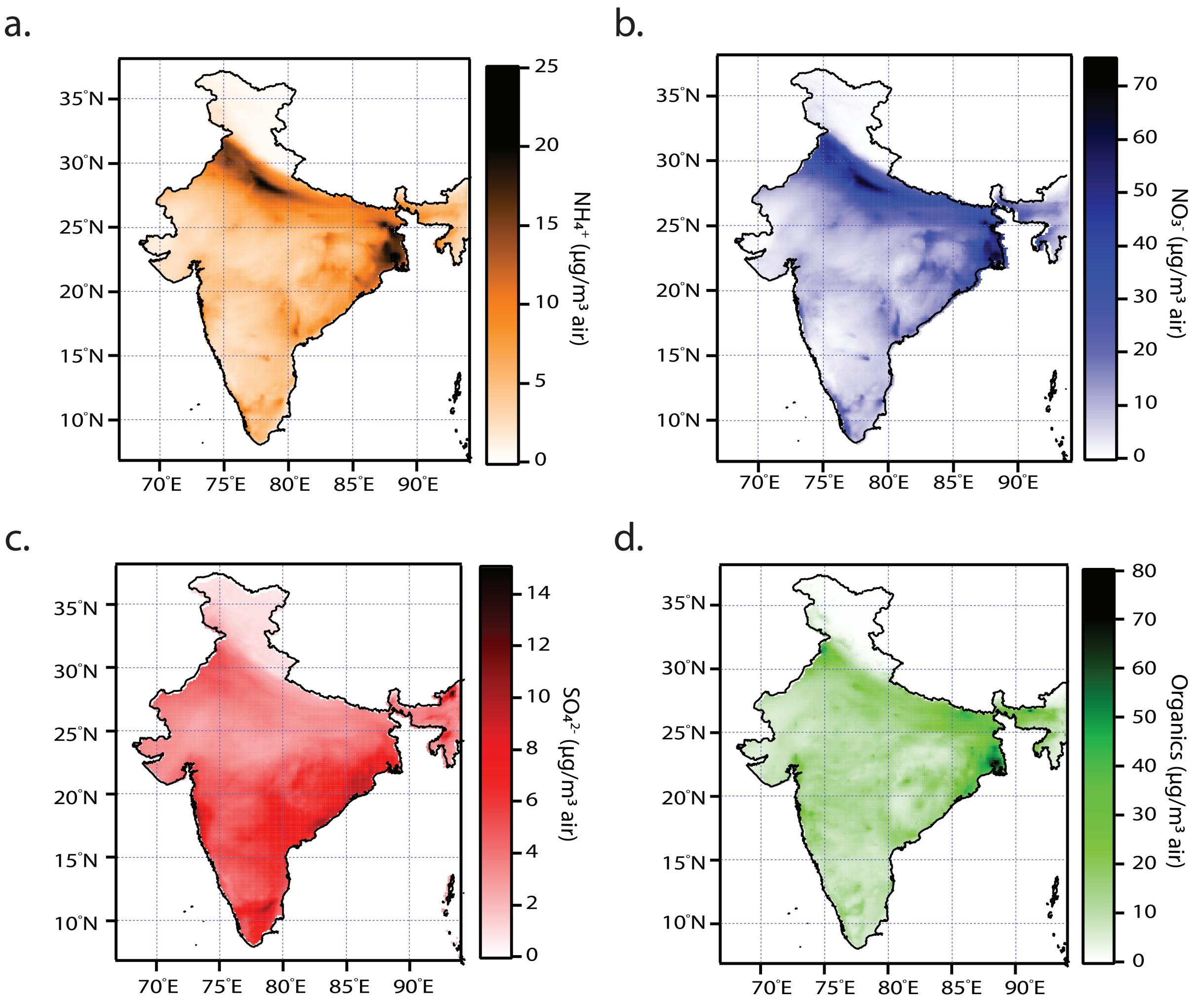

Figure S6. Spatial variation of the mass concentration of the chemical species (a) NH_4^+ (b) NO_3^- , (c) SO_4^{2-} and (d) organic matter over India using data from WRF CHEM model (concentrations in μg/m^3 air).

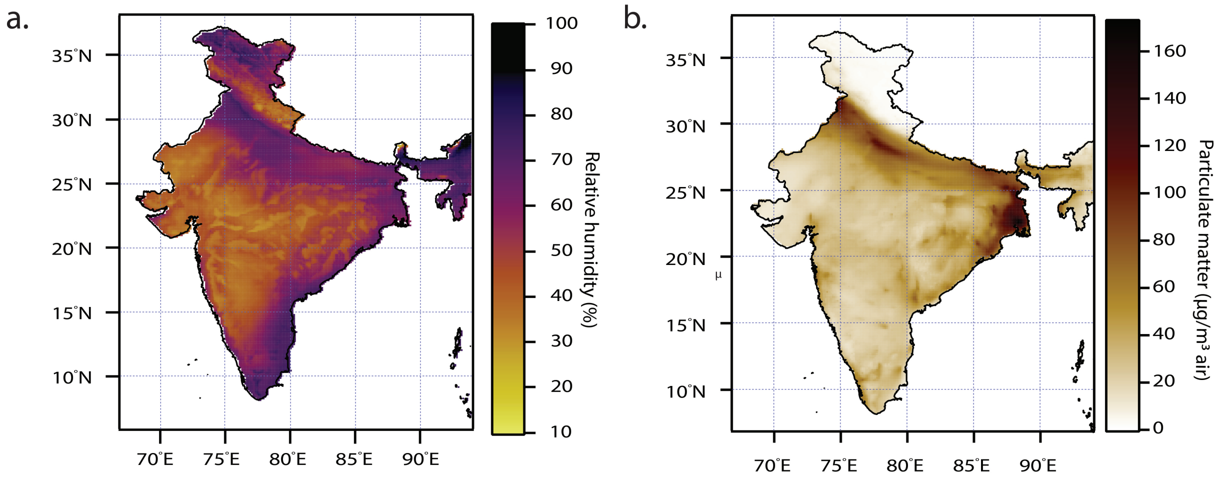

Figure S7. Spatial variation of various parameters calculated from WRF CHEM model for the month of January (a) Relative humidity (%) (b) Total dry aerosol mass (μg/m^3 air).

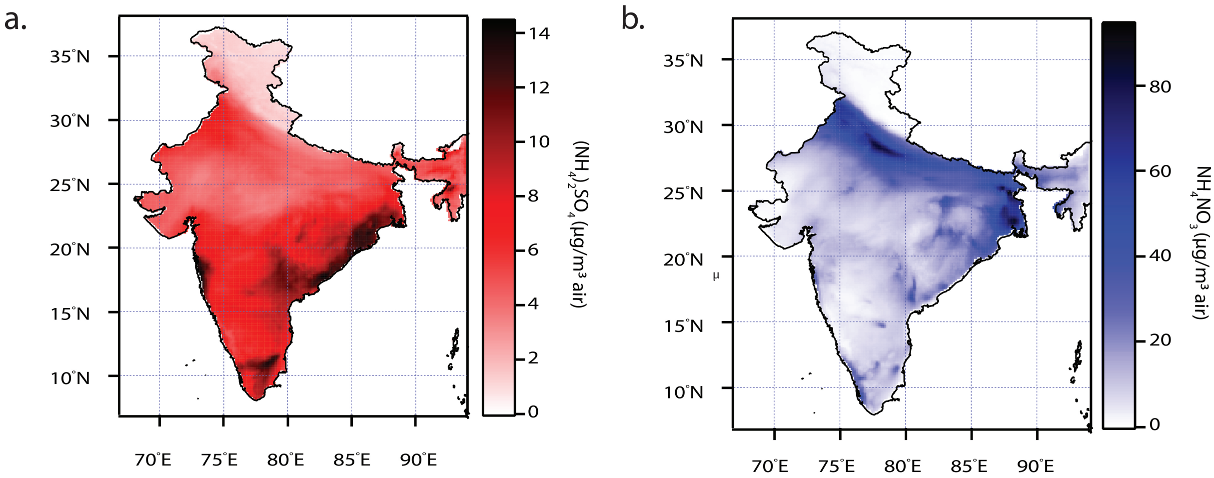

Figure S8. Spatial variation of the mass concentration of the chemical species (a) $(NH_4)_2SO_4$ (b) NH_4NO_3 over India predicted by ISORROPIA2.1 using data from WRF CHEM model (concentrations in μg/m^3 air) for the month of January.

References

Agarwal, A., Satsangi, A., Lakhani, A., & Kumari, K. M. (2020). Seasonal and spatial variability of secondary inorganic aerosols in PM2.5 at Agra: Source apportionment through receptor models. *Chemosphere*, *242*, 125132. doi: https://doi.org/10.1016/j.chemosphere.2019.125132

Ajith, T., Kompalli, S. K., Nair, V. S., & Babu, S. S. (2022). Mesoscale variations of the chemical composition of submicron aerosols and its influence on the cloud condensation nuclei activation. *Atmospheric Environment*, *268*, 118778. doi: https://doi.org/10.1016/j.atmosenv.2021.118778

Gani, S., Bhandari, S., Seraj, S., Wang, D. S., Patel, K., Soni, P., Arub, Z., Habib, G., Hildebrandt Ruiz, L., & Apte, J. S. (2019). Submicron aerosol composition in the world's most polluted megacity: the Delhi Aerosol Supersite study. *Atmospheric Chemistry and Physics*, *19*(10), 6843–6859. doi: 10.5194/acp-19-6843-2019

Kommula, S. M., Upasana, P., Sharma, A., Raj, S. S., Reyes-villegas, E., Liu, T., Allan, J. D., Jose, C., Pöhlker, M. L., Ravikrishna, R., Liu, P., Su, H., Martin, S. T., Pöschl, U., Mcfiggans, G., Coe, H., & Gunthe, S. S. (2021). Chemical Characterization and Source Apportionment of Organic Aerosols in the Coastal City of Chennai, India: Impact of Marine Air Masses on Aerosol Chemical Composition and Potential for Secondary Organic Aerosol Formation. *ACS Earth and Space Chemistry*, *5*(11), 3197-3209. doi: 10.1021/acsearthspacechem.1c00276

Kompalli, S. K., Suresh Babu, S. N., Satheesh, S. K., Krishna Moorthy, K., Das, T., Boopathy, R., Liu, D., Darbyshire, E., Allan, J. D., Brooks, J., Flynn, M. J., & Coe, H. (2020). Seasonal contrast in size distributions and mixing state of black carbon and its association with $PM_{1.0}$ chemical composition from the eastern coast of India. *Atmospheric Chemistry and Physics*, *20*(6), 3965–3985. doi: 10.5194/acp-20-3965-2020

Kumar, A., & Sarin, M. (2010). Atmospheric water-soluble constituents in fine and coarse mode aerosols from high-altitude site in western India: Long-range transport and seasonal variability. *Atmospheric Environment*, *44*(10), 1245-1254. doi: https://doi.org/10.1016/j.atmosenv.2009.12.035

Kumar, A., Yadav, I., Shukla, A., & Devi, N. (2020, 08). Seasonal Variation of PM2.5 in the Central Indo-Gangetic Plain (Patna) of India: Chemical Characterization and Source Assessment. *Journal of Applied Sciences*. doi: 10.1007/s42452-020-3160-y

Kumar, S., Nath, S., Bhatti, M., & Yadav, S. (2018, 06). Chemical Characteristics of Fine and Coarse Particles during Winter Time over Two Urban Cities in North India. *Aerosol and Air Quality Research*, *18*. doi: 10.4209/aaqr.2018.02.0051

Kumar, S., & Raman, R. (2016, 08). Inorganic ions in ambient fine particles over a National Park in central India: Seasonality, dependencies between SO42, NO3, and NH4+, and neutralization of aerosol acidity. *Atmospheric Environment*, *143*. doi: 10.1016/j.atmosenv.2016.08.037

Mukherjee, S., Singla, V., Pandithurai, G., Safai, P., Meena, G., Dani, K., & Anil Kumar, V. (2018). Seasonal variability in chemical composition and source apportionment of sub-micron aerosol over a high altitude site in Western Ghats, India. *Atmospheric Environment*, *180*, 79-92. doi: https://doi.org/10.1016/j.atmosenv.2018.02.048

Rastogi, N., Singh, A., Sarin, M., & Singh, D. (2016). Temporal variability of primary and secondary aerosols over northern India: Impact of biomass burning emissions. *Atmospheric Environment*, *125*, 396-403. (South Asian Aerosols And Anthropogenic Emissions: Regional And Global Climate Implications) doi: https://doi.org/10.1016/j.atmosenv.2015.06.010

Rengarajan, R., Sudheer, A., & Sarin, M. (2011). Wintertime PM2.5 and PM10 carbonaceous and inorganic constituents from urban site in western India. *Atmospheric Research*, *102*(4), 420-431. doi: https://doi.org/10.1016/j.atmosres.2011.09.005

Samiksha, S., Kumar, S., & Raman, R. (2021, 04). Two-year record of carbonaceous fraction in ambient PM2.5 over a forested location in central India: temporal characteristics and estimation of secondary organic carbon. *Air Quality Atmosphere Health*, *950*. doi: 10.1007/s11869-020-00951-2

Thamban, N. M., Joshi, B., Tripathi, S. N., Sueper, D., Canagaratna, M. R., Moosakutty,

S. P., Satish, R., & Rastogi, N. (2019). Evolution of Aerosol Size and Composition in the Indo-Gangetic Plain: Size-Resolved Analysis of High-Resolution Aerosol Mass Spectra. *ACS Earth and Space Chemistry*, *3*(5), 823-832. doi: 10.1021/acsearthspacechem.8b00207