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Hygroscopicity of aerosol and its organic component at a coastal location

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Supplementary Information

1 Chemical speciation of the ambient aerosol

The inorganic components of the aerosol are determined by balancing the anionic and cationic charges of the ionic species that were reported by IC for the MOUDI size ranges (wet vacuum aerodynamic diameters) of 56 – 100 nm and 100 – 180 nm (see Table S1). For instance, if the concentrations of Na^+ and Cl^- were 1 mol/m^3 and 2 mol/m^3, respectively, 1 mol/m^3 of NaCl would have been produced and the remaining Cl^- concentration would have been balanced by another cation such as K^+ to produce, for example, 1 mol/m^3 of KCl. In order to calculate the organic concentrations, the mass concentrations of ionic bearing constituents are subtracted from the total particle mass concentrations for each of the two size bins as determined from SMPS data and estimated densities, ie. mass concentration of organics = total mass concentration – ionic mass concentration. However, because the MOUDI and SMPS classify particles according to their wet aerodynamic diameters ($d_{a,wet}$) and dry mobility diameters (d_m), respectively, the MOUDI's $d_{a,wet}$ values are converted into the corresponding d_m values to allow for comparison of the size-resolved ionic and total particle mass concentrations. This is done by:

1) Assuming the aerosol was only composed of inorganic molecules, and determining the water volume of the aerosol at 50% RH, which was representative of trailer conditions, using the aerosol ionic model (AIM, http://www.aim.env.uea.ac.uk/aim/aim.php/) by inputting Na^+, Cl^-, SO_4^{2-}, NH_4^+, and NO_3^- concentrations measured by IC, with the unbalanced negative charge balanced using H^+, and with the assumption that the organics did not affect the amount of water present (Chang, 2011). A sensitivity study demonstrated that when the amount of water present in the particles was doubled the resulting d_m values changed by less than 10 nm, which validates the aforementioned assumption.

2) Calculating the mass-weighted density of the wet aerosol (ρ_{wet}) at 50% RH according to Eq. S1:

$$\rho_{wet} = (\rho_{orgs})(f_{orgs}) + (\rho_{inorg,wet})(f_{inorg}), \quad \text{(S1)}$$

where ρ_{orgs} is the density of organics (assumed to be 1.3 g cm^{-3}), f_{orgs} is the mass fraction of organics in the aerosol (derived from the ACSM relationship of organic to sulfate mass concentrations), $\rho_{inorg,wet}$ is the density of the wet aerosol as calculated by AIM, and f_{inorg} is the fraction of inorganics in aerosol containing both the inorganic species included in AIM and the organic species derived in the calculation of f_{orgs};

3) calculating the total mass of the wet particle by taking the sum of the inorganic mass produced by AIM and the organic mass that was calculated using the average organic to sulfate ratio from the ACSM;

4) removing the water content in the wet aerosol by subtracting the mass of water (as indicated by the mass fraction of water calculated by AIM) from the total wet particle mass to convert the $d_{a,wet}$ into a dry vacuum aerodynamic diameter ($d_{a,dry}$);

5) converting $d_{a,dry}$ into d_m using Eq. S2 (DeCarlo et al., 2004):

$$d_m = \frac{d_{a,dry}}{\sqrt{\frac{\rho_{dry}}{\rho_0 \chi_c}}}, \qquad \text{(S2)}$$

where ρ_{dry} is the mass weighted particle density, ρ_0 is the standard density (1.0 g cm^{-3}), and χ_c is the shape factor (assumed to be 1).

Through this series of calculations, the d_m values of the two smallest size ranges of the MOUDI are determined to be: 42 – 75 nm and 78 – 141 nm.

The overall uncertainty in these values is hard to estimate. As an indication of uncertainty, we note that changing any one of these assumptions by 20% results in a change in d_m of less than 10 nm. There is no single calculation or assumption that is particularly more uncertain than the others.

Because particulate size distributions were missing for some periods during August 14 – 19 (see Fig. 3, top), a correlation (having an R^2 value of 0.3) between the remaining 78 – 141 nm particulate volume concentrations and the particulate mass concentrations, as measured by the ACSM throughout the entire campaign, was used to back-calculate the missing particulate volume concentrations. Because the back-calculated concentrations did not significantly affect the average two-day concentrations that were calculated using the original data, we feel confident in using the SMPS-measured concentrations to infer the chemical composition of the aerosol during August 13 – 17. However, because most of the SMPS data are missing during August 17 – 19, this time period was omitted when determining the aerosol's chemical composition.

2 Inferring κ_{org}

Using the two-day average chemical composition resulting from the comparison of the size-resolved ionic and particle concentrations, the corresponding hygroscopicity parameters of the ambient aerosol for the two size bins (42 – 75 nm and 78 – 141 nm) are inferred according to Eq. S3 (Petters and Kreidenweis, 2007).

$$\kappa_{inferred} = \sum_i \varepsilon_i \kappa_i, \qquad \text{(S3)}$$

where ε_i and κ_i are the volume fraction and hygroscopicity parameter of the i^{th} component of the aerosol. Literature values are used for the hygroscopicity parameters of the inorganic species (Christensen, 2012; Petters and Kreidenweis, 2007). The hygroscopicity parameter of KCl was assumed to be equal to that of NaCl, and that of $K_2C_2O_4$ was assumed to be equivalent to that of a continental organic species, as shown in Table S2. The calculations were not sensitive to these assumptions.

In order to determine κ_{org} for the two size bins, its value is varied from 0 to 1.0. The most accurate and precise κ_{org} value is one that results in the most accurate and precise average ratio of $\kappa_{ambient}$ to $\kappa_{inferred}$ from August 13 – 23 (see Table S3). While the average ratio's accuracy is represented by its estimated systematic error (±30%), the precision of the average ratio is represented by its standard deviation (σ). Therefore, the most accurate and precise average ratio is one that has a value of unity when considering both its systematic error and standard deviation. To conduct this comparison, the $\kappa_{ambient}$ values for 50 nm and 100nm particles are compared to the $\kappa_{inferred}$ values of 42 – 75 nm and 78 – 141 nm particles, respectively.

3 References

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Table S1. Two day average ionic mass concentrations of the MOUDI's six particle size ranges (aerodynamic diameters) as measured by ion chromatography. The start date represents the first day and time (PDT) of each two day particle collection period.

Start Date	**Particle Size (μm)**	**$\mu g/m^3$**								
		Cl^-	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**$C_2O_4^{2-}$**	**Na^+**	**NH_4^+**	**K^+**	**MSA^-**
Aug-13	>18	2E-03	1E-03	1E-03	8E-03	1E-03	2E-03	9E-04		2E-04
12:03	10-18	1E-03		6E-04	3E-03		1E-03	1E-03		6E-05
	0.32-0.56	6E-02	5E-04	2E-02	7E-01	2E-02	2E-01	1E-01	1E-02	7E-02
	0.18-0.32	5E-04	5E-04	2E-03	2E-01	4E-03	8E-03	6E-02	4E-03	2E-02
	0.10-0.18	2E-03		9E-04	4E-02	1E-03	2E-03	1E-02	1E-03	4E-03
	0.056-0.10	7E-04		4E-04	6E-03	0E+00	8E-04	2E-03	9E-04	1E-03
Aug-15	>18	1E-03			1E-03		1E-03	7E-04		6E-05
12:22	10-18	8E-04			7E-04	1E-03	1E-03	7E-04		3E-05
	0.32-0.56	2E-01		3E-02	3E-01	5E-03	2E-01	5E-02	5E-03	4E-02
	0.18-0.32	5E-04		1E-03	1E-01	3E-03	8E-03	4E-02	3E-03	2E-02
	0.10-0.18				4E-02		1E-03	1E-02	3E-03	6E-03
	0.056-0.10	5E-03		1E-03	9E-03	1E-03	2E-03	2E-03	1E-03	1E-03
Aug-17	>18	1E-03		1E-03	5E-03		1E-03	1E-03	0E+00	8E-04
12:44	10-18	1E-03		2E-04	5E-03		1E-03	1E-03	1E-03	4E-04
	0.32-0.56	1E-02	9E-04	1E-02	1E+00	1E-02	2E-01	2E-01	9E-03	2E-01
	0.18-0.32	5E-04		1E-03	3E-01	2E-03	5E-03	5E-02	3E-03	5E-02
	0.10-0.18	3E-04		1E-04	7E-02		1E-03	2E-02	3E-03	1E-02
	0.056-0.10	5E-04		2E-04	6E-03		6E-04	2E-03		8E-04
Aug-19	>18	2E-03		3E-04	2E-03		2E-03	1E-03	1E-03	2E-04
12:42	10-18	2E-03		4E-04	3E-03		2E-03	1E-03	9E-04	1E-04
	0.32-0.56	6E-01	2E-03	4E-02	1E+00	2E-02	6E-01	2E-01	2E-02	2E-01
	0.18-0.32	5E-04	4E-04		4E-01	2E-03	2E-02	9E-02	2E-03	4E-02
	0.10-0.18	7E-04		5E-04	5E-02	1E-03	2E-03	1E-02		8E-03
	0.056-0.10	2E-03		4E-04	6E-03		2E-03	2E-03		1E-03
Aug-21	>18	1E-03		1E-03	3E-03		8E-04	1E-03		2E-04
13:51	10-18	8E-04		1E-03	3E-03		5E-04	1E-03		2E-04
	0.32-0.56	2E-02	6E-04	1E-02	5E-01	8E-03	1E-01	1E-01	4E-03	5E-02
	0.18-0.32	9E-04	5E-04	2E-03	2E-01	2E-03	5E-03	5E-02	2E-03	2E-02
	0.10-0.18	5E-04		2E-03	4E-02	1E-03	1E-03	1E-02	2E-03	3E-03
	0.056-0.10	2E-03			9E-03	9E-04	1E-03	3E-03	8E-04	7E-04

Table S2. Hygroscopicity parameters of inorganic species (Christensen, 2012; Petters and Kreidenweis, 2007).

Compound	**κ**
$(NH_4)_2SO_4$	0.61
H_2SO_4	0.90
NaCl	1.28
KCl	1.28
$NaNO_3$	0.88
$NaHSO_4$	0.91
KNO_2	0.80
$K_2C_2O_4$	0.20
MSA^-	0.44

Table S3. Average ratios of $\kappa_{ambient}$ to $\kappa_{inferred}$ as κ_{org} is varied from 0 to 1.0 for 42 – 75 nm and 78 – 141 nm particles. Yellow shading highlights what are determined to be the most accurate and precise κ_{org} values for each size range, i.e. the ratio could potentially have a value of unity when considering both the systematic error and precision. Precision is represented by the standard deviation (σ) of the average ratio. The estimated systematic error is calculated to be ±30%, as based on estimated errors in the values of $\kappa_{ambient}$ and $\kappa_{inferred}$.

42 – 75 nm				78 – 141 nm			
κ_{org}	Avg $\kappa_{ambient}$ / $\kappa_{inferred}$	Systematic error	σ	κ_{org}	Avg $\kappa_{ambient}$ / $\kappa_{inferred}$	Systematic error	σ
0	4.66	1.40	0.77	0	2.88	0.86	1.31
0.1	2.33	0.70	0.23	0.1	1.27	0.38	0.45
0.2	1.56	0.47	0.12	0.2	1.75	0.52	0.66
0.3	1.17	0.35	0.08	0.3	1.00	0.30	0.35
0.4	0.89	0.27	0.01	0.4	0.83	0.25	0.29
0.5	0.78	0.23	0.04	0.5	0.71	0.21	0.25
0.7	0.58	0.18	0.03	0.7	0.54	0.16	0.19
1.0	0.43	0.13	0.02	1.0	0.41	0.12	0.14

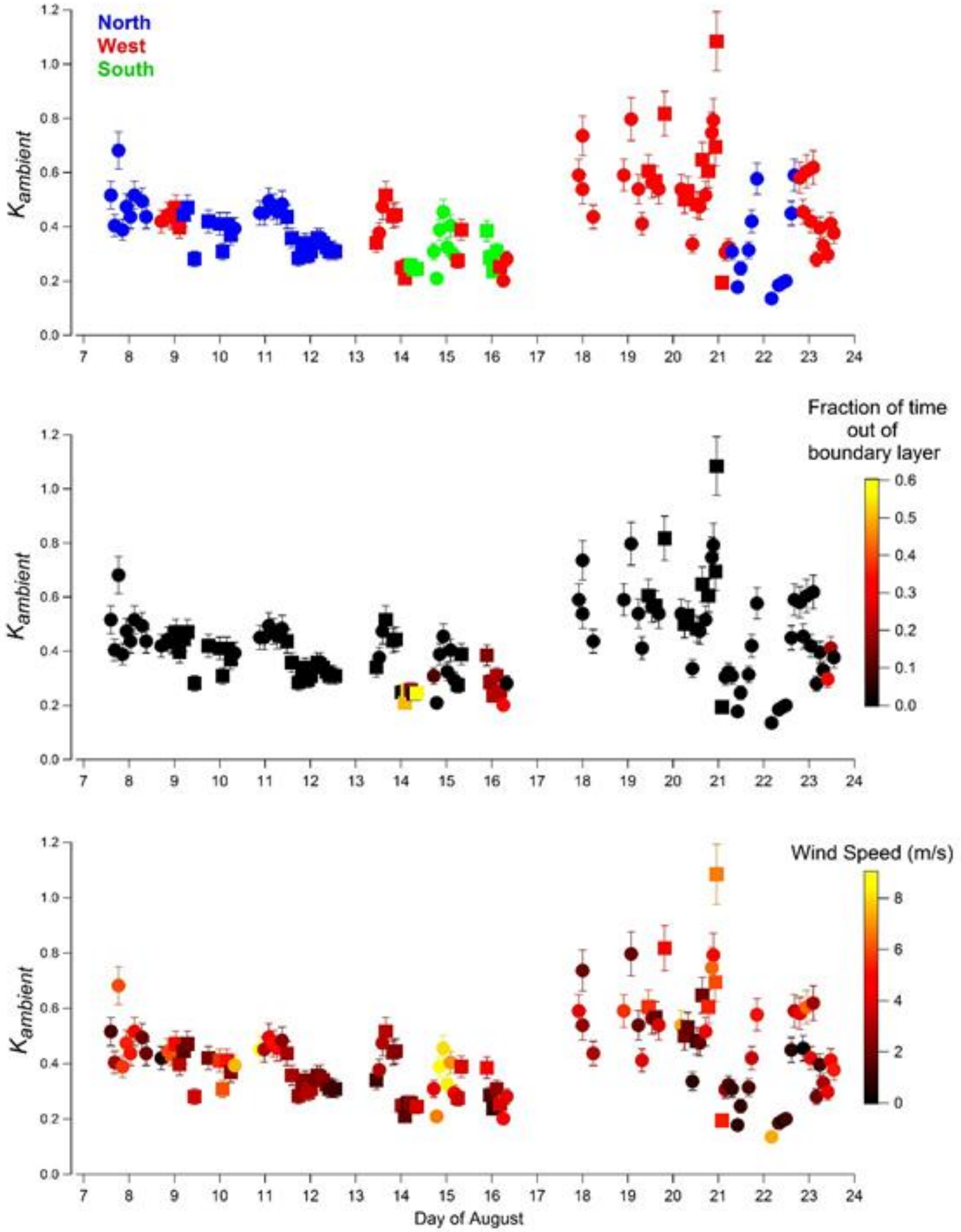

Figure S1. Time series of $\kappa_{ambient}$ colour coded according to the corresponding air mass origins (top), the fraction of time that the air masses (72 hour back trajectories) were out of the marine boundary layer or above 1000 m (middle), and the average wind speed (bottom).