Seven Years of Aerosol Optical Hygroscopic Growth Measurements from SGP
Factors influencing aerosol water uptake

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Abstract On average H_2O comprises ~ 50% of aerosol mass. Variation in the ambient RH and aerosol H_2O uptake have a large effect on the aerosol extinction, size, radiative forcing, aqueous phase oxidation, CCN and gas-to-particle partitioning of chemical species. DOE ARM has conducted long term measurements of the aerosol scattering hygroscopic growth at SGP since 1999. We report on the last 7 years of those measurements after the AOS system design was reconfigured. Seasonal changes in chemical emissions and ambient RH strongly influence the aerosol optical properties and hygroscopic growth. Higher aerosol organic and lower nitrate composition contribute to lower summertime hygroscopic growth. Cold temperatures and high nitrate composition promote higher hygroscopic growth during winter months.

Method The AOS scattering hygroscopic growth measurement is comprised two TSI nephelometers in series . A humidifier between the two nephelometers ramps the RH between 40-80% in hourly cycles. Impactors in the sample air flow alternate the aerosol size between sub 1*um and sub 10um* aerosol every 30 minutes. We define the aerosol hygroscopic fit at set RH values for comparison to other studies,

$$fRH = \sigma_w(85\%) / \sigma_o(40\%)$$, where σ_w and σ_o are the wet and dry scattering coefficients.

Algorithm Data is fit to the following 2 algorithms to calculate fit parameters, gamma (γ) and kappa (κ). The kappa algorithm has slightly better goodness of fit and works better at low RH. The gamma parameterization works better at high RH. Both algorithms assume a metastable behavior with continuous growth with RH.

gamma: $$\sigma_w(RH_w) / \sigma_o(RH_o) = a(1-RH_w/100)^{-\gamma}$$

kappa: $$\sigma_w(RH_w) / \sigma_o(RH_o) = (1+ \kappa\, RH/(100-RH))$$

Seasonal Trends

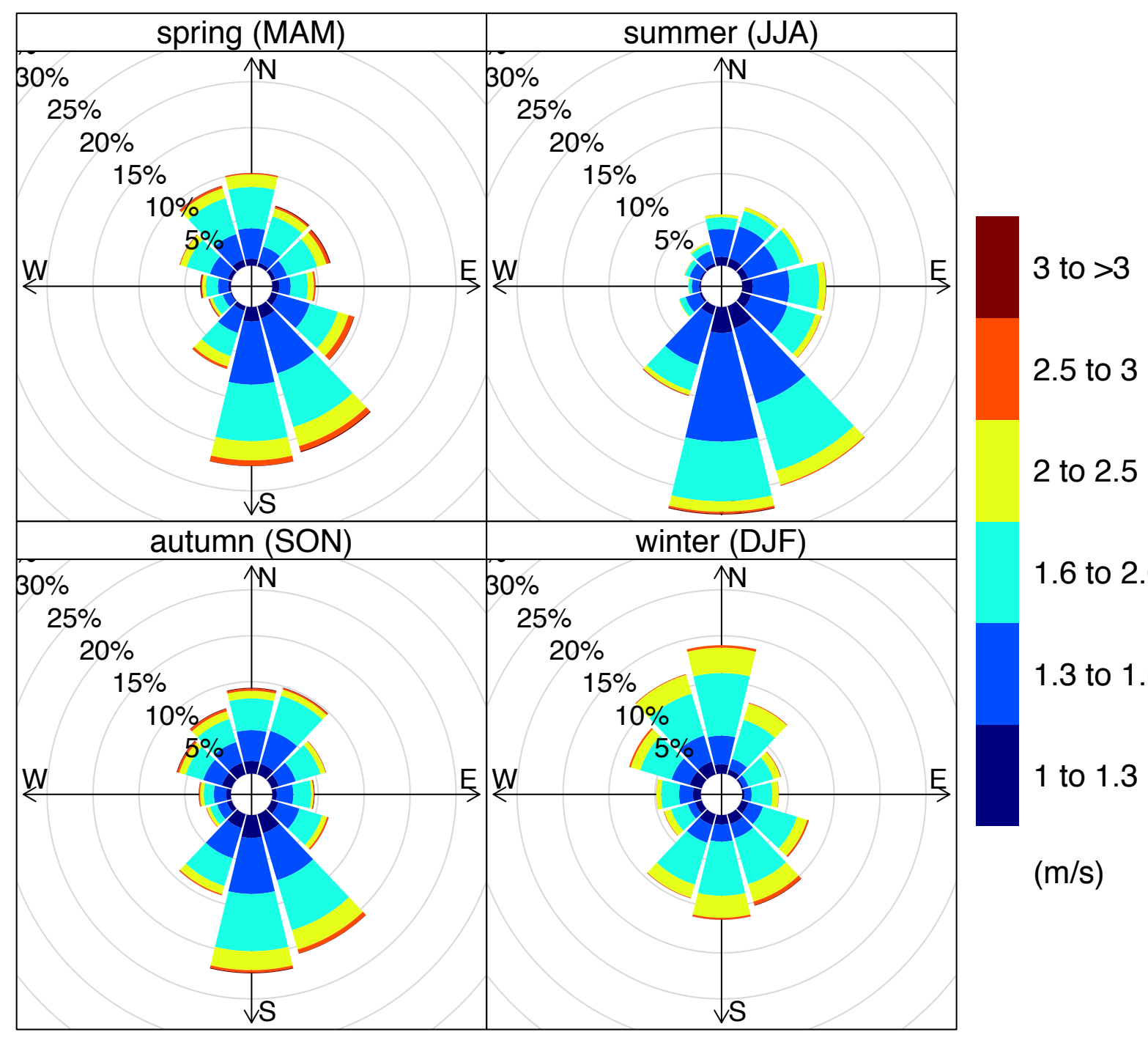

Fig. 2 Seasonal wind rose plots of aerosol *fRH*

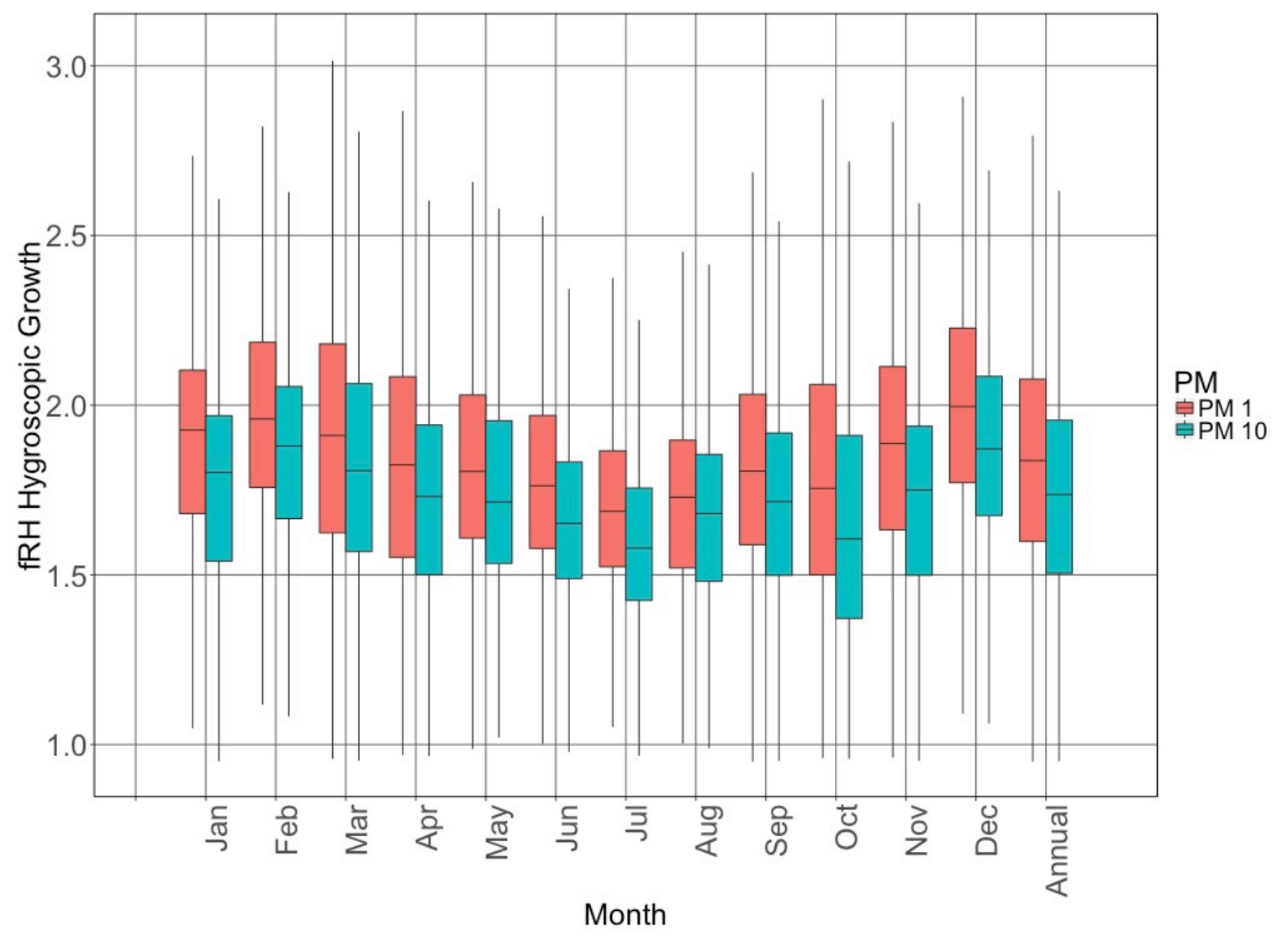

Fig. 1 Box plot showing monthly 5, 25, 50, 75 and 95th percentiles of the PM1 and PM10 aerosol hygroscopic growth factor, *fRH*

Table 1. Seasonal average (standard deviation) of aerosol hygroscopic growth fit parameters and calculated *fRH (85%/40%)*

Parameter	Spring (MAM)	Summer (JJA)	Fall (SON)	Winter (DJF)	Annual
fRH (γ) sub *um*	1.91 (0.46)	1.74 (0.30)	1.85 (0.42)	1.96 (0.41)	1.87 (0.41)
fRH (γ) sub 10*um*	1.80 (0.39)	1.65 (0.27)	1.72 (0.38)	1.82 (0.37)	1.75 (0.37)
γ sub *um*	0.45 (0.16)	0.39 (0.12)	0.42 (0.16)	0.47 (0.16)	0.44 (0.16)
γ sub 10 *um*	0.41 (0.15)	0.35 (0.12)	0.0.37 (0.16)	0.42 (0.15)	0.39 (0.15)
fRH (κ) sub *um*	2.00 (0.36)	1.88 (0.26)	1.91 (0.40)	2.11 (0.34)	1.98 (0.36)
fRH (κ) sub 10 *um*	1.89 (0.35)	1.76 (0.26)	1.78 (0.37)	2.00 (0.35)	1.87 (0.35)
κ sub *um*	0.24 (0.10)	0.20 (0.06)	0.21 (0.10)	0.26 (0.09)	0.23 (0.09)
κ sub 10 *um*	0.21 (0.09)	0.17 (0.06)	0.18 (0.09)	0.23 (0.09)	0.20 (0.09)

Seasonal aerosol hygroscopic growth

The aerosol hygroscopic growth parameter, *fRH,* shows a small seasonal trend with higher values in winter and lower values in summer. Sub um aerosol has higher *fRH* values than sub 10um aerosol.

Wind Rose plots show that aerosol source regions are primarily from the S-SE during the summer in the direction of Oklahoma City. Autumn –Spring emissions switch to the NW-NE sector which contain Wichita and more rural regions. Note that there is little sector variance in *fRH* within a given season, indicating that emissions are less dependent on wind direction and have a stronger seasonal signature.

Variance with Aerosol Chemistry

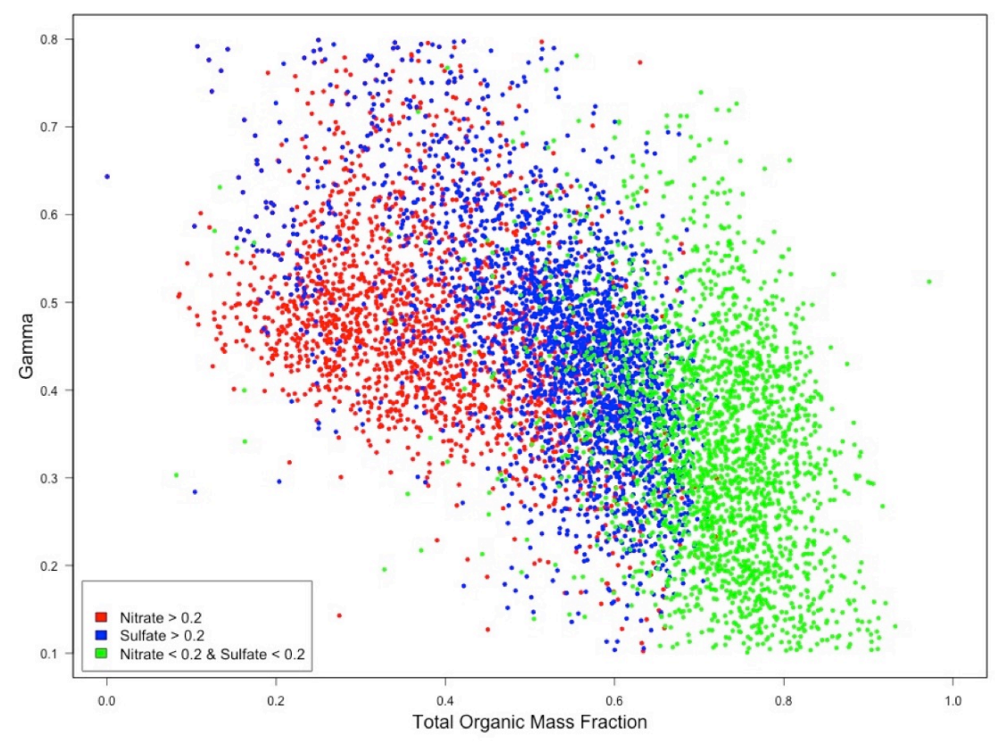

Fig. 3 Gamma vs the organic mass fraction color by the nitrate and sulfate mass fractions

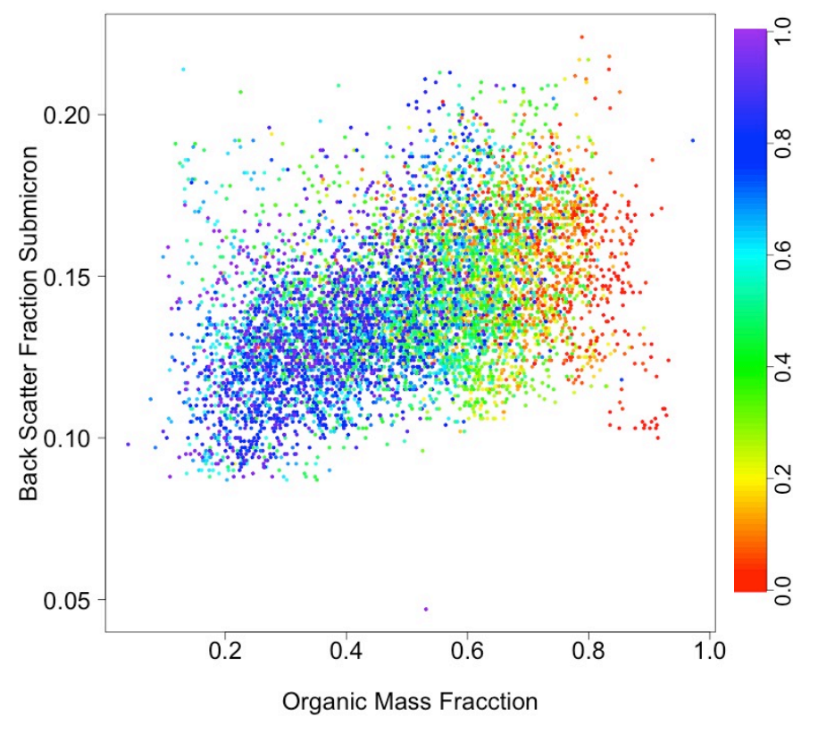

Fig. 4 Sub*um* backscatter fraction vs the organic mass fraction color by gamma

The aerosol hygroscopic fit parameter has 3 distinct regions of growth that vary with the sub um aerosol composition:

High OMF (organic mass fraction):low SO_4^{2-}: low NO_3^-
The high OMF region displays a high range of water uptake, despite low inorganic composition, which suggests the presence of highly oxidized organics.
Moderate OMF: high SO_4^{2-}: low NO_3^-
The high SO_4^{2-} aerosol has a steep increase in hygroscopic growth with declining OMF. This growth rates is slightly higher than other studies of pollution aerosol (Quinn et al.,2005 and Beyersdorf et al., 2016)
Low OMF: low SO_4^{2-}: high NO_3^-
High NO_3^- is present primarily when both SO_4^{2-} and OC are low. The hygroscopic growth rate with OMF for high NO_3^- aerosol is lower than times with higher OMF and SO_4^{2-}. As NO_3^- has a relatively high vapor pressure, high NO_3^- aerosol was present in the winter at low ambient temperatures and high ambient RH. NO_3^- mass fractions are a lower limit as instrument heating will result in $(NH_4)NO_3$ evaporation.

Size-dependent aerosol composition

Figure 4 shows the aerosol backscatter fraction (BSF) with OMF. Larger aerosol (smaller BSF) have lower OMF and higher hygroscopic growth parameter, gamma. Smaller aerosol (higher BSF) have a higher OMF and lower gamma.

Ambient RH and aerosol hygroscopic growth rate

Figure 5 shows a steep increase in hygroscopic growth with ambient RH. Note that ambient RH and instrument RH are poorly correlated as the latter varies with dew point. Ambient RH is higher at low temperatures (night and winter) when aerosol NO_3^- are highest. Ambient RH may also play a role in aqueous phase oxidation, which would also enhance the aerosol hygroscopic growth rate. This is a topic for further study.

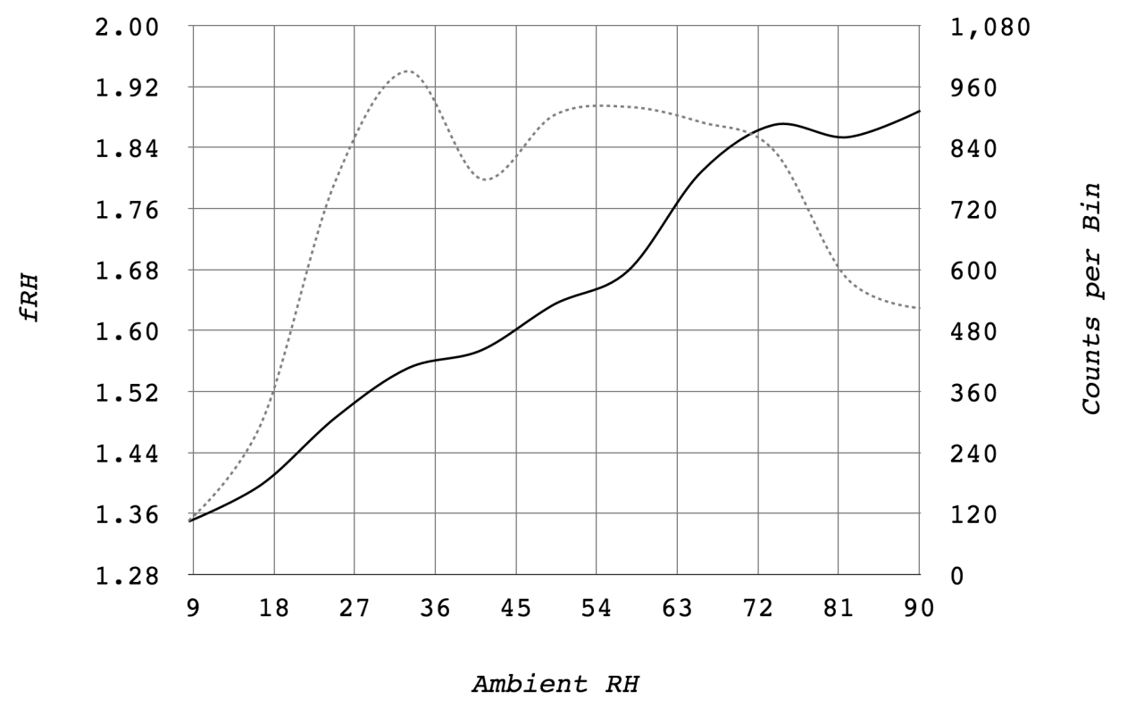

Fig. 5 Hygroscopic growth *fRH(85/40)* vs the ambient RH showing data distribution

Variance with optical properties

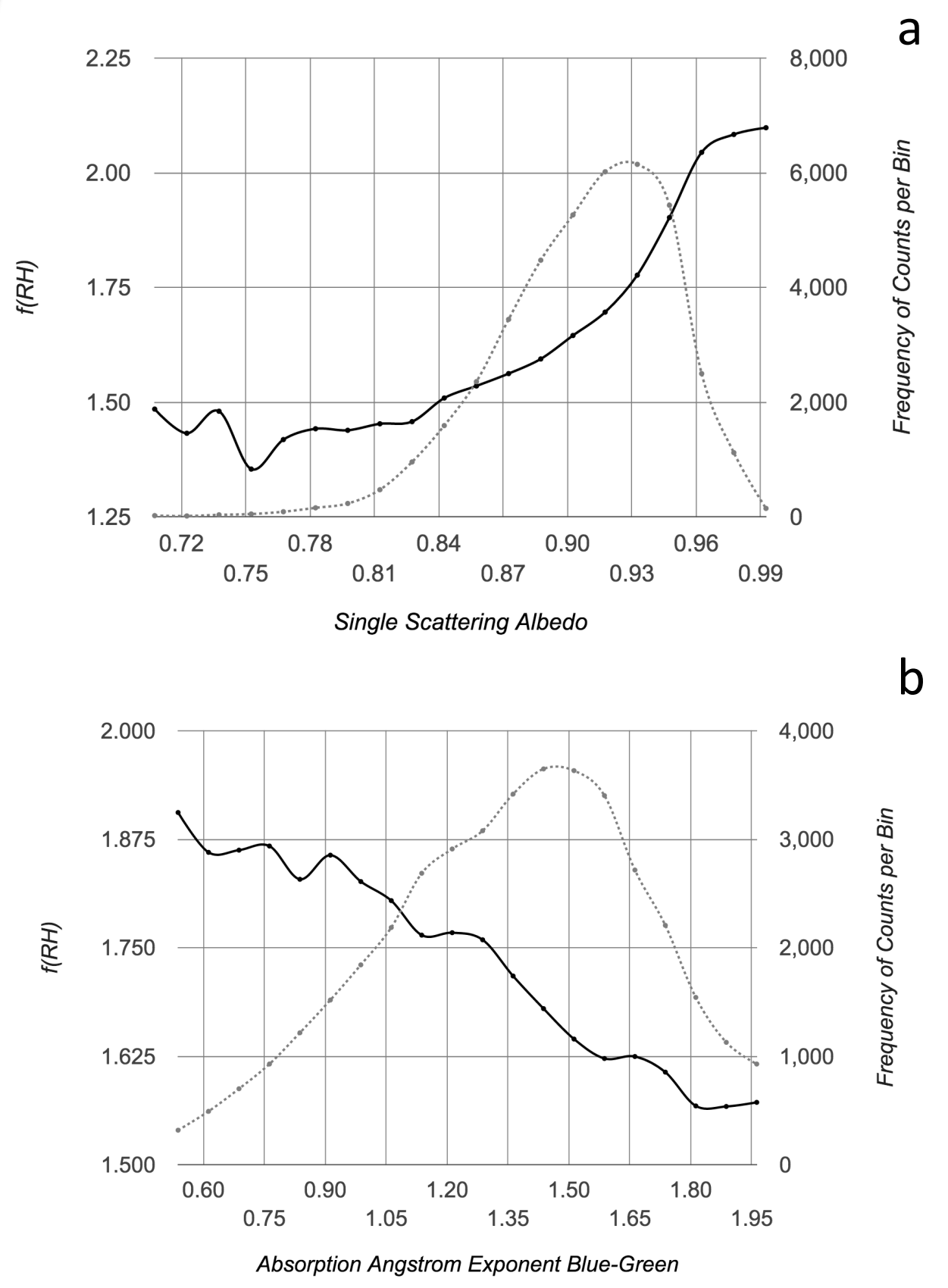

Fig 6. a) *fRH* vs the single scatter albdeo at 550 nm and b) Absorption Ångstrom (461nm/562nm)

Composition-dependent optical properties

Hygroscopic growth increases with single scatter albedo as the aerosol becomes less absorbing and OC and BC concentrations decline. The hygroscopic growth declines with increasing brown carbon or absorption Ångstrom. Absorption Ångstrom values <1.0 could be an indication of enhanced lensing of coated aerosol and/or the presence of nonabsorbing, highly oxidized OC.

Size-dependent optical properties

The backscatter fraction is sensitive to aerosol < 0.1 *um*, while the scattering Ångström exponent is sensitive to aerosol >0.1um. The aerosol hygroscopic growth behavior of these two size regimes is quite different. For sub 0.1 um aerosol the hygroscopic growth increases with size as observed with the backscatter fraction in Figure 7a. In Figure 7b the hygroscopic growth behavior declines with increasing size or Ångström exponent. Some of this behavior may be attributed to black carbon being present in fine mode aerosol and dust being present in larger accumulation mode aerosol.

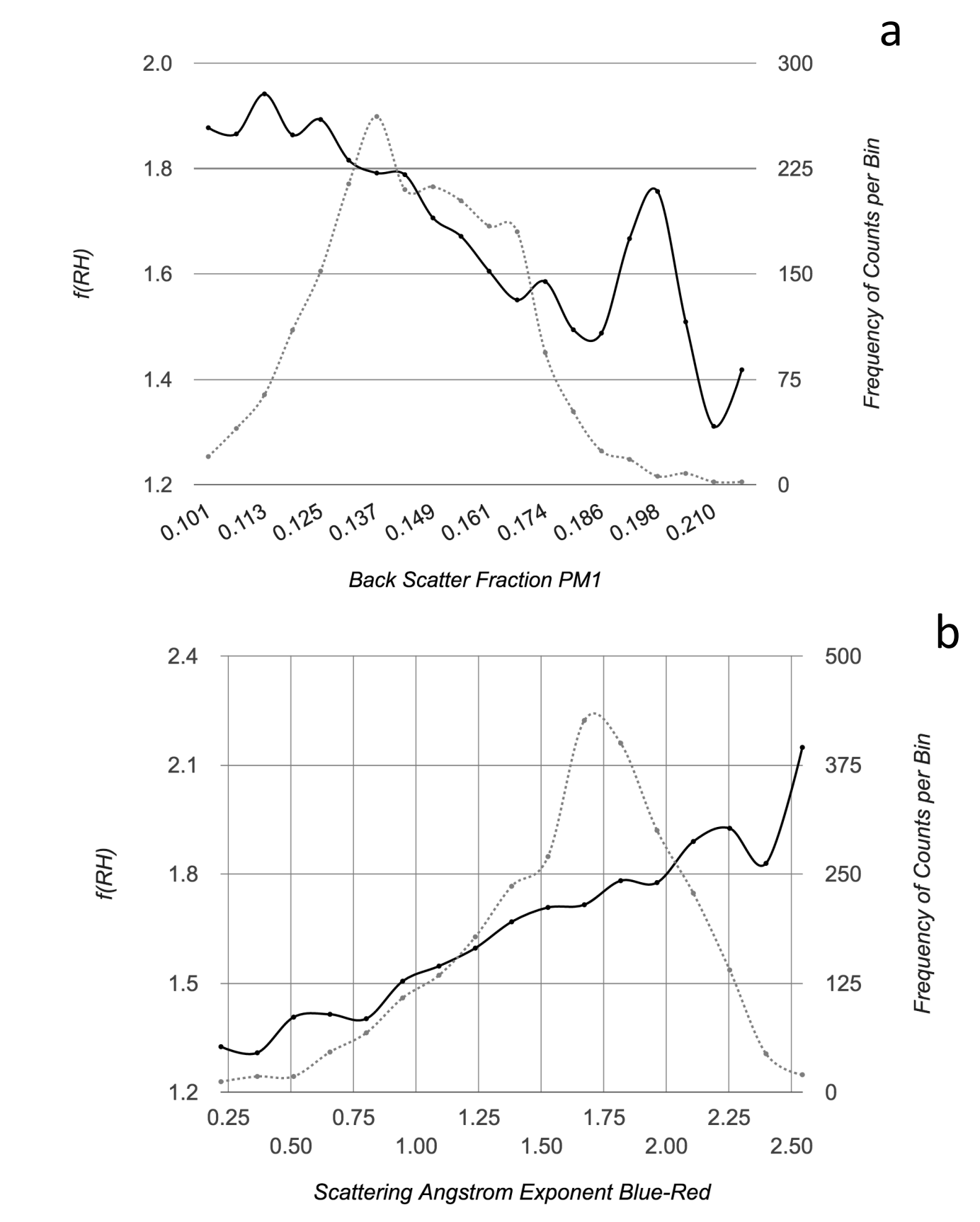

Fig 7. a) *fRH vs the ba*ckscatter fraction at 500 nm
b) *fRH* vs the aerosol Ångstrom Exponent (450nm/700nm)

Summary The aerosol hygroscopic growth varies seasonally with higher values in winter. The seasonal behavior is reflected in the aerosol composition with high organic mass fraction in the summer months and higher nitrate composition in the winter months (Parworth et al., 2015). The aerosol composition varies with size with higher organic mass fractions at higher values of the aerosol backscatter fraction. The hygroscopic growth decreases with aerosol size and corresponding higher organic mass fractions. This size and composition dependence of the aerosol hygroscopic growth is evident in the aerosol optical properties, where *fRH* increases with single scatter albedo and declines with increased absorption Ångström. *fRH* displays opposing trends with aerosol size with increasing values with increasing scattering Ångström and decreasing values with increasing backscatter fraction.

References Parworth et al., *Atmos. Environ., 2015, (106) 43-55;* Quinn et al., *Geophys. Res.Lett., (32), L22809, 2005; Beyersdorf et al.,* Atmos. Chem. Phys., *(16), 1003-1025, 2016.*

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