



The effect of organic composition on N₂O₅ reactive uptake

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Reactive uptake of N₂O₅ to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations

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Abstract

We measured N_2O_5 reactive uptake onto mixed organic/inorganic submicron particles using organic compounds with a variety of oxidation states (using mainly atomic O : C ratios as a proxy) and molecular weights. The organic mass fraction, organic molecular composition, and relative humidity (RH) were varied to separately assess their effect on the N_2O_5 uptake coefficient, $\gamma(\text{N}_2\text{O}_5)$. At a constant RH, mixtures of organic components having an O : C < 0.5 with ammonium bisulfate (ABS) significantly suppressed the uptake of $\text{N}_2\text{O}_{5(\text{g})}$ compared to pure ABS, even at small organic mass fractions (e.g., $\leq 15\%$). The effect of the organic component became less pronounced at higher RH. In general, highly oxygenated organic components (O : C > 0.8) had a smaller or even negligible impact on N_2O_5 uptake at all RHs probed; however, a few exceptions were observed. Notably, $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ABS with polyethylene glycol (PEG), PEG-300 (O : C = 0.56), decreased nearly linearly as the PEG mass fraction increased at constant RH until leveling off at the value measured on pure PEG. The response of $\gamma(\text{N}_2\text{O}_5)$ to increasing PEG mass fraction was similar to that measured on ambient atmospheric particles as a function of organic mass fraction. The effects of the organic mass fraction on $\gamma(\text{N}_2\text{O}_5)$, for mixtures having an O : C $< \sim 0.8$, were best described using a standard resistor model of reactive uptake assuming the particles had a RH dependent inorganic core-organic shell morphology. This model suggests that the N_2O_5 diffusivity and/or solubility in the organic layer is up to a factor of 20 lower compared to aqueous solution particles, and that the diffusivity, solubility, and reactivity of N_2O_5 within organic coatings and particles depend upon both RH and the molecular composition of the organic medium. We use these dependencies and ambient measurements of organic aerosol from the global aerosol mass spectrometry (AMS) database to show that the typical impact of organic aerosol components is to both uniformly decrease $\gamma(\text{N}_2\text{O}_5)$, by up to an order of magnitude depending on the RH, organic mass fraction, and O : C ratio, and to induce a stronger dependence of $\gamma(\text{N}_2\text{O}_5)$ upon RH compared to purely inorganic aqueous solutions.

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1 Introduction

Heterogeneous reactions between gases and atmospheric particles play an important role in air quality and global climate (Abbatt et al., 2012; Chang et al., 2011; Liao and Seinfeld, 2005; Poschl, 2005; Solomon, 1999). The reactive uptake of N_2O_5 , a major nighttime NO_x ($\equiv \text{NO} + \text{NO}_2$) reservoir species, onto particles is one such reaction that is known to be potentially important on regional and global scales (Dentener and Crutzen, 1993), but remains poorly described in atmospheric models, in part due to a lack of detailed understanding of the reaction rate and mechanism in atmospheric particles. The reactive uptake of N_2O_5 to aerosol particles is a terminal sink of NO_x and source of photolabile Cl-atoms (Finlayson-Pitts et al., 1989), and thus impacts ozone formation and the lifetime of greenhouse gases such as methane (Alexander et al., 2009; Dentener and Crutzen, 1993; Osthoff et al., 2008; Shindell et al., 2009; Thornton et al., 2010). Laboratory measurements have probed the reactive uptake coefficient, $\gamma(\text{N}_2\text{O}_5)$, defined as the probability that a colliding gas molecule (N_2O_5 in this case) will react with a particle. Measurements focused on purely inorganic aerosols tend to find relatively high values of $\gamma(\text{N}_2\text{O}_5)$ ranging from 0.015–0.2 so long as the particles are deliquesced (Hallquist et al., 2003; Hu and Abbatt, 1997; Kane et al., 2001; Mentel et al., 1999; Mozurkewich and Calvert, 1988; Thornton and Abbatt, 2005). However, measurements of ambient aerosols have consistently shown the presence of internally mixed inorganic and organic components (Murphy et al., 2006; Zhang et al., 2007) highlighting the need to assess N_2O_5 reactivity on these mixtures.

Studies probing the effect of pure organic aerosol as well as inorganic particle seeds coated with organics have shown that even a monolayer coating can suppress the heterogeneous uptake of N_2O_5 . However, the magnitude of this surface effect is highly dependent on molecular structure and likely not broadly relevant for the majority of submicron atmospheric particles, which tend to have large organic mass fractions (χ_{OA}) (Badger et al., 2006; Cosman and Bertram, 2008; Folkers et al., 2003; McNeill et al., 2006; Riemer et al., 2009; Thornton and Abbatt, 2005; Thornton et al., 2003).

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Chamber-derived secondary organic aerosol (SOA) coatings on sulfate seed particles produced from the ozonolysis of α -pinene, with minimal photochemical aging, showed strong suppression of $\gamma(\text{N}_2\text{O}_5)$ even with small mass loadings of biogenic SOA (Anttila et al., 2006; Escorcía et al., 2010; Folkers et al., 2003). In spite of these studies, laboratory measurements of $\gamma(\text{N}_2\text{O}_5)$ have not been able to match ambient observations, even when organic aerosol is taken into account (Abbatt et al., 2012; Bertram et al., 2009; Brown et al., 2009; Riedel et al., 2012). As suggested in a recent modeling study by Riemer et al. (2009), these discrepancies are likely due to the formation of organic coatings that can affect $\gamma(\text{N}_2\text{O}_5)$; however, the magnitude of this effect will likely depend on organic aerosol composition, particle phase, and/or morphology. As such, a systematic study of the effect of organic molecular composition on N₂O₅ uptake, though necessary, has been lacking.

In the absence of halides, hydrolysis is expected to be the dominant driver of N₂O₅ reactive uptake, and the rate of N₂O₅ reactive uptake even on halide salt particles depends on whether the particle is crystalline or deliquesced (Finlayson-Pitts et al., 1989; Griffiths et al., 2009; Thornton and Abbatt, 2005; Thornton et al., 2003). As such, properties of organic compounds thought to affect particle water content and thus $\gamma(\text{N}_2\text{O}_5)$ include the polarity and molecular weight (Griffiths et al., 2009; Jimenez et al., 2009; Thornton et al., 2003). These properties are also thought to determine particle phase and morphology as some organics when mixed with inorganic compounds can undergo RH-dependent liquid-liquid phase separations due to a “salting-out” effect wherein the lower polarity organic components partition into an organic coating (Bertram et al., 2011; Ciobanu et al., 2009; Erdakos and Pankow, 2004; Marcolli and Krieger, 2006; Song et al., 2012; You et al., 2012, 2013). At < 70 % RH, humidity-induced liquid-liquid phase separations are predicted to occur for particles containing organics with a low oxidation state (e.g., low O : C) (Bertram et al., 2011; You et al., 2013). Additionally, certain organics facilitate the formation of amorphous phases comprised of liquid, semi-solid, and solid (glassy) states (Koop et al., 2011; Renbaum-Wolff et al., 2013; Saukko et al., 2012; Virtanen et al., 2010; Zobrist et al., 2008). The average carbon oxidation

state, which scales with the O : C ratio, and molecular weight of organic components are proposed to be predictors for these phase transitions (Bertram et al., 2011; Saukko et al., 2012).

Here we present measurements of $\gamma(\text{N}_2\text{O}_5)$ on laboratory generated particles that are mixtures of organics with ammonium bisulfate. The organic compounds, used in mixtures or as single components, spanned a range in molecular weights, water solubility, and O : C ratios, which we use as a proxy for the average carbon oxidation state and thus organic aerosol age (Kroll et al., 2011). We show the response of $\gamma(\text{N}_2\text{O}_5)$ to variations in the mass fraction, the chemical composition of different organics, and relative humidity (RH). We discuss the results in terms of: (i) which properties of the particles' organic composition are most important for accurately predicting $\gamma(\text{N}_2\text{O}_5)$; (ii) the role of phase separations and morphology; and (iii) the extent to which these laboratory measurements on synthetic mixed organic/inorganic particles are comparable to ambient measurements.

2 Methods

Measurements of $\gamma(\text{N}_2\text{O}_5)$ were made using an entrained aerosol flow tube coupled to a chemical ionization mass spectrometer (CIMS) and a combination of experimental approaches similar to those described previously (Bertram and Thornton, 2009; McNeill et al., 2006; Thornton et al., 2003). Both standard decays of N_2O_5 as a function of interaction time (Thornton et al., 2003) and modulation of particle concentration at constant interaction time (Bertram and Thornton, 2009) were used in this experiment. Mixed organic/inorganic aerosol were generated using a constant output atomizer using dilute solutions similar to the approach of McNeill et al. (2006). Supplement Fig. S1 shows the experimental set-up used for this work.

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2.1 Aerosol generation and characterization

The solutions used in this manuscript are summarized in Table 1 along with the corresponding χ_{OA} (in the aerosol) and $\gamma(\text{N}_2\text{O}_5)$ values. Three types of aqueous solutions were used to generate aerosol: (1) single component solutions (e.g., ammonium bisulfate (ABS) or polyethylene glycol, PEG); (2) solutions of ABS and a single organic component (e.g., ABS + azelaic acid); (3) and ABS solutions containing a mix of organic components with either a high average O : C atomic ratio of 1.13 or a low average O : C atomic ratio of 0.48. ABS was chosen as the inorganic component because it does not crystallize at RHs used in this work (e.g., 30–70 % RH) ensuring a deliquesced inorganic solution (Martin, 2000; Tang and Munkelwitz, 1977; Tang and Munkelwitz, 1994). ABS (Alfa Aesar, 99.9 % purity), azelaic acid (Acros Organics, 98 % purity), (1,2,9)-nonanetriol (Sigma, purity unknown), poly (ethylene glycol) with an average molecular weight of 300 g mol^{-1} (PEG-300) (Aldrich), citric acid, (2,5)-dihydroxy benzoic acid (gentisic acid), D-(+)-glucose, malonic acid, and succinic acid (all Sigma-Aldrich with a purity of 98 % or higher) were used as the aerosol components. Citric acid, glucose, malonic acid, and succinic acid were used to create the high O : C mixture while azelaic acid, gentisic acid, 1,2,9-nonanetriol, and PEG were used to generate the low O : C mixture, as denoted in Table 1.

Particles were generated using a constant output atomizer (TSI Inc., Model 3076). The atomizer output was diluted and conditioned for approximately 1 min by mixing 3.3 to 4 standard liters per minute (slpm) of humidified ultra-high purity (UHP) N_2 with the atomizer output. The humidity of the dilution flow was adjusted so that the aerosol flow was at the desired RH determined with a Vaisala humidity probe (accuracy $\pm 2\%$) just upstream of the flow reactor.

Approximately 2.3–3 slpm of the conditioned aerosol flow was continuously drawn through the flow reactor via a side-arm at the top of flow tube by means of a critical orifice on the CIMS inlet. Particle size distributions and total surface area concentrations (S_a) at the flow tube exit were measured using a scanning mobility particle

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sizer (SMPS) consisting of a differential mobility analyzer and condensation particle counter (TSI Inc. or Grimm Technologies; both instruments gave similar distributions). S_a typically ranged from $0.8\text{--}7.0 \times 10^{-4} \text{ cm}^2 \text{ cm}^{-3}$. Example surface area-weighted size distributions resulting from atomizing an ABS solution containing various amounts of PEG (i.e., mixture type 2 above) are shown in Fig. 1. The single mode, and a mean diameter that increases monotonically with increasing PEG content at constant ABS, suggests particles are internal mixtures of PEG and ABS. To ensure the measured S_a was representative of the flow tube conditions, the DMA sheath flow was conditioned to the appropriate RH by sampling from the flow reactor for ~ 1 h prior to the start of the experiment.

2.2 N₂O₅ generation and detection

The method used to generate N₂O₅ has been discussed previously (Bertram and Thornton, 2009; Bertram et al., 2009; Lopez-Hilfiker et al., 2012; Riedel et al., 2012). As shown in Figure S1, NO₃ is generated by reaction of NO₂ and O₃. NO₃ is then allowed to react further with excess NO₂ to produce N₂O₅ in equilibrium with NO₂ and NO₃ at room temperature (298 K). The N₂O₅ is introduced axially down the center of the flow reactor in a 0.1 slpm UHP N₂ carrier flow through a Teflon-lined movable stainless steel injector (Bertram and Thornton, 2009). N₂O₅ was detected using iodide adduct CIMS (Kercher et al., 2009) and the identical instrument described in Lopez-Hilfiker et al. (2012).

2.3 Determination of $\gamma(\text{N}_2\text{O}_5)$

N₂O₅ and the conditioned aerosol interacted within a pyrex, halocarbon wax coated flow tube with an inner diameter (ID) of 3 or 6 cm and a length of 90 cm. Measurements were limited to the central 60 cm to maintain well-mixed, laminar flow conditions. The injector was moved to the top and bottom of the flow tube, altering the interaction time between N₂O₅ and the generated particles. The first-order rate loss (k_{het}) was deter-

mined using a pseudo-particle modulation technique (Bertram and Thornton, 2009):

$$k_{\text{het}} = - \left(\frac{1}{t_{\text{res}}} \right) \ln \left(\frac{[\text{N}_2\text{O}_5]_{\text{top}}}{[\text{N}_2\text{O}_5]_{\text{bottom}}} \right) \quad (1)$$

t_{res} is the resulting interaction time between the gases and particles. Wall losses of N_2O_5 to the flow tube (k_{wall}) were determined for each experiment in the same manner as k_{het} except in the absence of particles. The uptake efficiency $\gamma(\text{N}_2\text{O}_5)$ was then determined from the equation:

$$\gamma(\text{N}_2\text{O}_5) \approx \frac{4(k_{\text{het}} - k_{\text{wall}})}{\omega S_a} \quad (2)$$

ω represents the mean molecular velocity of N_2O_5 (Bertram and Thornton, 2009; McNeill et al., 2006; Riedel et al., 2012). This equation neglects gas-phase diffusion limitations to reactive uptake, which are small ($< 10\%$) for the typical $\gamma(\text{N}_2\text{O}_5)$ and particle sizes used here (Fuchs and Sutugin, 1971). The $\gamma(\text{N}_2\text{O}_5)$ reported here are the mean of 5 independent determinations and the quoted uncertainties are the respective 95% confidence intervals. Most $\gamma(\text{N}_2\text{O}_5)$ measurements are shown normalized to that measured on ABS at 50% RH, which varied between 0.036 and 0.030, for comparison to other ambient and chamber data sets (Anttila et al., 2006; Bertram et al., 2009; Escorcia et al., 2010), and to account for drifts in sources of systematic errors related to flow rates, SMPS transmission and humidification, and CIMS detection efficiency. Moreover, the relative trends in $\gamma(\text{N}_2\text{O}_5)$ as a function of RH, χ_{OA} , and oxidation state are the primary focus of these measurements. Normalized measured values of $\gamma(\text{N}_2\text{O}_5)$ for all experiments are summarized in Table 1; absolute values can be obtained by multiplying the normalized values by the absolute $\gamma(\text{N}_2\text{O}_5)$ for ABS.

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3 Results and discussion

3.1 ABS and PEG experiments: evidence for the role of liquid–liquid phase separations

Figure 2a shows $\gamma(\text{N}_2\text{O}_5)$ measured on pure PEG particles vs. RH. The $\gamma(\text{N}_2\text{O}_5)$ increased with particle water content from 0.003 ± 0.003 , 0.007 ± 0.003 , to 0.017 ± 0.011 . These values start \sim a factor of 10 lower than that for ABS particles and with increasing RH reach a value that is a factor of 2 lower than ABS suggesting an additional limitation to reactive uptake of N_2O_5 on PEG compared to ABS. Also shown in Fig. 2a are predicted values of $\gamma(\text{N}_2\text{O}_5)$ derived from the model of Bertram and Thornton (2009) (see black dashed line), which uses the particulate water, nitrate, and chloride content in addition to the total particle volume and surface area to predict $\gamma(\text{N}_2\text{O}_5)$; the model assumes that N_2O_5 reacts throughout the bulk of the particle without any additional solubility or diffusion limitations compared to pure water. The water content of the PEG particles was calculated with the AIM II model and using the ethylene oxide (CH_2OCH_2) and the hydroxyl (OH) functional groups in UNIFAC, which has been previously shown to accurately predict the water activity of PEG solutions (Marcolli and Peter, 2005; Ninni et al., 1999, 2000). The predicted $\gamma(\text{N}_2\text{O}_5)$ values are within error of the measured values despite the fact that we assume the solubility and diffusivity of N_2O_5 in PEG is the same as that for aqueous inorganic solutions.

In Fig. 2b, we show normalized $\gamma(\text{N}_2\text{O}_5)$ measured on particles that are mixtures of ABS and PEG (labeled ABS/PEG from here). At 50% RH, the $\gamma(\text{N}_2\text{O}_5)$ decreased nearly linearly from the ABS value as the PEG mass fraction increased until a PEG mass fraction of ~ 0.6 , beyond which the normalized $\gamma(\text{N}_2\text{O}_5)$ plateaued at ~ 0.20 . As shown in Fig. 3, using particles with a PEG mass fraction of 0.2, where only minimal suppression of reactivity was observed at RH = 50%, and decreasing the RH from 50 to 30% resulted in a 70% decrease in $\gamma(\text{N}_2\text{O}_5)$. In contrast, using particles with a PEG mass fraction of 0.56, where significant suppression of reactivity was observed at RH = 50%, and increasing the RH from 50 to 70% led to a factor of 5 increase in $\gamma(\text{N}_2\text{O}_5)$.

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Both of these sensitivities to RH are far stronger than that of pure ABS (Bertram and Thornton, 2009). Also shown in Fig. 2b are the predicted values of $\gamma(\text{N}_2\text{O}_5)$ obtained from the Bertram and Thornton (2009) parameterization (black dashed line), assuming the particles are homogeneous (a single phase) internal mixtures, and allowing the PEG to partition between aqueous and hydrophobic phases in the AIM II model. The predicted values capture the measured $\gamma(\text{N}_2\text{O}_5)$ well for the two extremes, where the particles are composed of either 100% ABS or 100% PEG. However, the model fails to capture the observed behavior of $\gamma(\text{N}_2\text{O}_5)$ on ABS/PEG particles, likely because the model does not account for organic coatings formed due to liquid-liquid phase separations, which have been shown to occur in mixtures of PEG and ammonium sulfate (Ciobanu et al., 2009; Marcolli and Krieger, 2006).

To investigate the role of particle morphology on N₂O₅ uptake, a slightly modified version of the core-shell resistivity model of Anttila et al. (2006) was also used to predict experimental results presented herein with the following equation:

$$\frac{1}{\gamma} = \frac{\omega R_p}{4D_{\text{gas}}} + \frac{1}{\alpha} + \frac{\omega R_p}{4RT H_{\text{org}} D_{\text{org}} (q_{\text{org}} F - 1)} \quad (3)$$

R_p is the particle radius (m), D_{gas} is the gas phase diffusion coefficient for N₂O₅ taken to be $1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (Anttila et al., 2006), α is the dimensionless mass accommodation coefficient, H_{org} is the Henry's law coefficient for N₂O₅ in the organic layer ($\text{mol m}^{-3} \text{ atm}^{-1}$), D_{org} is the diffusion coefficient of N₂O₅ in the organic layer ($\text{m}^2 \text{ s}^{-1}$), and q_{org} is the dimensionless diffusio-reactive parameter, which describes the competition between diffusion and reaction in the organic layer:

$$q_{\text{org}} = R_p \sqrt{\frac{k_{\text{org}}}{D_{\text{org}}}} \quad (4)$$

where k_{org} is the pseudo first-order reaction rate constant of N₂O₅ in the organic layer (s^{-1}). The parameter F , which we show in the Supplement, also contains the dimen-

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sionless diffuso-reactive parameter in the aqueous core of the particle (q_{aq}) similar to q_{org} , however, the reaction rate constant of N_2O_5 in the aqueous layer (k_{aq}) and the diffusion coefficient in the aqueous core (D_{aq}) are used instead. The model of Anttila et al. (2006) considers k_{aq} a tunable parameter; however, the model of Bertram and Thornton (2009) explicitly parameterizes the equivalent rate constant (k'_{2f}) as a function of liquid water, nitrate, and chloride content using the RH and inorganic composition of the particle in the AIM II model. We therefore use the Bertram and Thornton parameterization for k_{aq} to better capture the dependence of $\gamma(\text{N}_2\text{O}_5)$ on the liquid water content. Further information regarding the model of Anttila et al. (2006) and equations used can be found in the Supplement. We note that this parameterization does not factor in temperature dependencies of $\gamma(\text{N}_2\text{O}_5)$, which may also be important (Abbatt et al., 2012; Wagner et al., 2013).

The water activity and diffusivity of PEG solutions are reasonably well-constrained by independent data, and thus the ABS/PEG particles provide a useful test case for the reactive uptake model. Table 2 shows the values of each variable used in the model of Anttila et al. (2006) for PEG and mixtures of ABS/PEG. The N_2O_5 rate constant in the organic coating (k_{org}) for pure PEG particles was determined to be $2.0 \times 10^5 \text{ s}^{-1}$ at 50 % RH, increasing by a factor of ~ 1.6 to $3.2 \times 10^5 \text{ s}^{-1}$ as the RH was increased to 70 %, and decreasing by a factor of ~ 3 to $7.0 \times 10^4 \text{ s}^{-1}$ as the RH was decreased to 30 %. Values of k_{org} can be used to probe the particle liquid water content assuming that k_{org} is equivalent to the rate constant of N_2O_5 in water derived from Bertram and Thornton (2009) (k'_{2f}) multiplied by the liquid water content in the PEG. The liquid water content of PEG predicted using the values of k_{org} at each RH matched the predicted liquid water content using the AIM II model to within 40 % or better at all RHs suggesting that N_2O_5 uptake kinetics can provide an additional metric to assess the liquid water content of both inorganic and organic aerosol. In addition to k_{org} , ε , the factor used to scale the product of D_{aq} and H_{aq} to account for the decrease in diffusion and solubility of N_2O_5 in the organic layer compared to the aqueous core, was also found to be important for achieving agreement between experimental and predicted

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values. The best agreement was found by setting $\varepsilon = 0.06$ for ABS/PEG at 30 % RH, $\varepsilon = 0.3$ at 50 % RH, and $\varepsilon = 1$ at 70 % RH. Using the constraints from the observed dependence of $\gamma(\text{N}_2\text{O}_5)$ on the PEG mass fraction, and the model sensitivity to q_{org} , we conclude that the changes in ε represent mostly changes in D_{org} relative to D_{aq} and less so changes in H_{org} compared to H_{aq} (see Supplement), a similar finding to Antilla et al. (2006). Assuming that the largest changes in $\gamma(\text{N}_2\text{O}_5)$ for ABS/PEG particles compared to ABS particles are driven by changes in diffusivity and reactivity, we find the best model-measurement agreement with $D_{\text{org}} = 3$ to $5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 50 % RH. For comparison, assuming the PEG mass fraction in pure PEG particles is ~ 0.85 at 50 % RH (Ninni et al., 1999) and using an estimated dynamic viscosity of $\sim 14.7 \text{ mPa s}^{-1}$ (Rahbari-Sisakht et al., 2003) for PEG-300, yields a value of D_{org} of $\sim 10^{-10} \text{ m}^2 \text{ s}^{-1}$ using the Stokes–Einstein equation. At 70 % RH, best agreement between the observed $\gamma(\text{N}_2\text{O}_5)$ and that predicted by the resistor model was obtained when D_{org} was equal to D_{aq} ($1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and $H_{\text{org}} = H_{\text{aq}}$ for both pure PEG and ABS/PEG particles, suggesting the presence of internally mixed systems at this higher RH and the lack of phase separations.

The modified Antilla et al. (2006) resistor model predictions of $\gamma(\text{N}_2\text{O}_5)$ generally match measured values for both pure PEG (assuming a single-phase) and mixtures of ABS/PEG (assuming a 2-phase system), see Fig. 2a and b. As noted above, the parameterization of Bertram and Thornton (2009) also achieved good agreement for pure PEG particles despite the fact that it does not account for diffusion limitations of N_2O_5 in PEG. Bertram and Thornton (2009) use a lower value for H_{aq} than Antilla et al. (2006), while Antilla et al. (2006) use a lower value for D_{org} than that used by Bertram and Thornton (2009) who conclude that the diffusion limitation in aqueous solution particles was negligible. These differing values of H_{aq} likely cancel the effects of the different approaches to diffusion limitations. Thus, while there is good agreement between both models and measured values of $\gamma(\text{N}_2\text{O}_5)$ for pure PEG, the two models are not directly comparable as they are based on different assumptions. In contrast, for ABS/PEG mixtures, the model of Antilla et al. (2006) clearly predicts values of $\gamma(\text{N}_2\text{O}_5)$ with much

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higher accuracy than that of Bertram and Thornton (2009) likely due to the fact that only modest decreases in the overall liquid water content of mixed ABS/PEG particles are predicted for an internally mixed system; however, these modest decreases in liquid water content cannot fully explain the behavior of $\gamma(\text{N}_2\text{O}_5)$. Instead, the formation of organic coatings of PEG through liquid-liquid phase separations likely further decrease the liquid water content in the coating and additional decreases in N_2O_5 solubility and diffusivity in a coating of PEG likely impact $\gamma(\text{N}_2\text{O}_5)$ as well; these decreases are more accurately represented by the core-shell resistivity model of Anttila et al. (2006).

We conclude this section by noting that $\gamma(\text{N}_2\text{O}_5)$ on ABS/PEG particles show strikingly similar dependencies on χ_{OA} to $\gamma(\text{N}_2\text{O}_5)$ measured on ambient atmospheric particles (Bertram et al., 2009), as shown in Fig. 3. We note that the χ_{OA} in the ambient particles is mostly secondary in nature (e.g., most of the organic aerosol is oxidized organic aerosol, OOA) (Bertram et al., 2009). In both the laboratory and field measurements, a similar nearly linear decrease in $\gamma(\text{N}_2\text{O}_5)$ with increasing χ_{OA} was observed, with linear fits to the normalized $\gamma(\text{N}_2\text{O}_5)$ vs. χ_{OA} having slopes of -1.6 and -1.7 , respectively (see Supplement Fig. S2). Due to the similar response of the normalized $\gamma(\text{N}_2\text{O}_5)$ to increases in χ_{OA} , a comparison of these two systems was made. The O : C of PEG-300 is 0.56, while the average O : C of the organic content in the ambient particles was estimated to be ~ 0.45 as measured by an Aerodyne aerosol mass spectrometer (AMS) with unit-mass resolution (see Supplement Fig. S3 and Supplement for this calculation). However, this latter value may be an under-estimate as recent measurements have shown the AMS can under-predict O : C by up to $\sim 25\%$; this observations holds for both the unit-mass resolution and high resolution AMS (Canagaratna, 2013). Further, the average RH during ambient sampling conditions was 65 %, which is higher than most of the ABS/PEG experiments that were primarily conducted at 50 % RH. At 70 % RH, $\gamma(\text{N}_2\text{O}_5)$ on ABS/PEG particles were found to roughly match $\gamma(\text{N}_2\text{O}_5)$ on ambient particles with similar χ_{OA} .

Several possibilities exist for why laboratory measurements of N_2O_5 uptake onto particles composed of ABS and PEG mimic uptake experiments on ambient aerosol

so well. First, the polymeric nature of PEG may be similar to SOA found in ambient aerosols, which have been found to contain oligomers in certain environments (Denkenberger et al., 2007; Kalberer et al., 2004; Surratt et al., 2006); however, the presence of liquid-liquid phase separations is an additional possibility. While speculative, the similar behavior of $\gamma(\text{N}_2\text{O}_5)$ observed on ABS/PEG mixtures, which are known to exhibit liquid-liquid phase separations (Ciobanu et al., 2009; Marcolli and Krieger, 2006), and on ambient aerosol is certainly consistent with the idea that ambient organic aerosol constituents undergo humidity-dependent liquid-liquid phase separations, thereby inhibiting heterogeneous losses of N_2O_5 .

3.2 ABS and organic compounds with low O : C

N_2O_5 uptake onto mixtures of ABS and organic compounds with low O : C ratios (mean O : C ratio = 0.48 for the mixture) as a function of χ_{OA} is shown in Fig. 4; a mixture of several organic components, including organic acids and polyols, was used to minimize the chance of crystallization (Marcolli et al., 2004). In contrast to the experiments using organics with a high O : C ratio described below, $\gamma(\text{N}_2\text{O}_5)$ decreased by ~ 70–80 % with an χ_{OA} of as little as ~ 15 %, beyond which $\gamma(\text{N}_2\text{O}_5)$ remained at a nearly constant suppressed value. Similar trends in $\gamma(\text{N}_2\text{O}_5)$ were found for mixtures of ABS and azelaic acid only (see Supplement Fig. S4 and Supplement). Azelaic acid, one of the components used in the low O : C mixture that has the same O : C ratio as the mixture, has been shown to exhibit a salting out effect in the presence of inorganic salts (Reid et al., 2011). Observations of a rapid decrease in $\gamma(\text{N}_2\text{O}_5)$ with small amounts of organics are in agreement with previous laboratory studies using surface-active compounds (McNeill et al., 2006; Thornton and Abbatt, 2005), humic acids (Badger et al., 2006), and secondary organic aerosol (SOA) from α -pinene ozonolysis (Anttila et al., 2006; Escorcia et al., 2010; Folkers et al., 2003), which independent measurements by an AMS suggest has an O : C ratio similar to that of semi-volatile oxygenated organic aerosol (SV-OOA, O : C = 0.35 ± 0.14) (Ng et al., 2010). As noted previously, this O : C ratio may be biased low by up to ~ 25 % (Canagaratna, 2013). As shown in Fig. 4,

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the change in $\gamma(\text{N}_2\text{O}_5)$ we observe with the low O : C mixture were similar to, though somewhat smaller than, that measured using α -pinene ozonolysis SOA deposited on ammonium sulfate seed particles (Anttila et al., 2006; Escorcia et al., 2010; Folkers et al., 2003) suggesting our low O : C ratio mixture mimics the properties of α -pinene ozonolysis SOA that affect N_2O_5 reactive uptake. The similarity between the two systems could be due to similarities in the O : C ratios for the two systems, particularly if the correction to the AMS-derived O : C ratio is taken into account, or due to other similarities between the two systems, such as the properties of the polyols and organic acids found in our low O : C mixture.

Also shown in Fig. 4 are normalized $\gamma(\text{N}_2\text{O}_5)$ measurements at 30% RH and 70% RH with χ_{OA} of $\sim 15.6\%$ and $\sim 63.5\%$, respectively. Normalized values of $\gamma(\text{N}_2\text{O}_5)$ are nearly a factor of 3 lower at 30% RH, and coincidentally match N_2O_5 uptake onto chamber-derived biogenic SOA. This sensitivity to lower RH is far larger than for pure ABS (Bertram and Thornton, 2009), and, given the relatively small χ_{OA} (15%), again suggests the presence of an organic coating having a different hygroscopicity (and thus water content) and viscosity than pure ABS. Increasing RH from 50% to 70% leads to more than a doubling of the $\gamma(\text{N}_2\text{O}_5)$, though it remains suppressed compared to pure ABS particles by more than a factor of 2.

3.3 ABS and organic compounds with high O : C

The uptake of N_2O_5 onto mixtures of ABS and organic compounds with high O : C ratios (mean O : C ratio = 1.13 for the mixture) as a function of RH and χ_{OA} is shown in Fig. 5. The normalized $\gamma(\text{N}_2\text{O}_5)$ decreased nearly linearly as the χ_{OA} increased, but this decrease (slope of -0.78 see Figure S5 in the Supplement) was modest compared to the other systems investigated (e.g., ABS + low O : C mixtures and ABS/PEG). As shown in Fig. 5, at an χ_{OA} of 10%, decreasing the RH from 50 to 30% leads to a 40% decrease in $\gamma(\text{N}_2\text{O}_5)$, less of an RH dependence compared to the ABS-low O : C mixture, but stronger than that for pure ABS (Bertram and Thornton, 2009). At an χ_{OA} of

56 %, increasing RH from 50 % to 70 % leads to a 33 % increase in $\gamma(\text{N}_2\text{O}_5)$, again less than for the ABS – low O : C mixture.

Previous measurements have shown that water soluble organic carbon is likely to have a high O : C ratio (Duong et al., 2011), and that higher O : C organic aerosol has higher hygroscopicity (Jimenez et al., 2009). Thus, these more modest decreases in $\gamma(\text{N}_2\text{O}_5)$ with increasing organic mass fraction likely indicate that appreciable water content and/or fewer diffusion limitations are associated with organics with a higher O : C ratio compared to those with lower O : C ratios. Further, these modest decreases in $\gamma(\text{N}_2\text{O}_5)$ compared to those measured on ABS particles are in line with previous measurements of $\gamma(\text{N}_2\text{O}_5)$ on particles composed of dicarboxylic acids having O : C ratios of 0.8–2 (Griffiths et al., 2009; Thornton et al., 2003). We found significant differences in $\gamma(\text{N}_2\text{O}_5)$ when using mixtures of ABS and individual high O : C organic components. For example, $\gamma(\text{N}_2\text{O}_5)$ on particles composed of ABS and succinic acid alone showed little change with increasing succinic acid mass fraction (see Supplement Fig. S6). In contrast, decreases in $\gamma(\text{N}_2\text{O}_5)$ were observed for mixtures of ABS and citric acid alone that were similar to the decrease observed using the high O : C mixture. Citric acid was one of the components used in the high O : C mixture, representing 32 % of the organic mass, that has the same O : C ratio as the mixture, and may be responsible for the decrease in N_2O_5 uptake with an increasing mass fraction of the high O : C mixture used here. Both citric acid and glucose can form amorphous phases, which may also play a role in the observed dependence of normalized $\gamma(\text{N}_2\text{O}_5)$ on the χ_{OA} (Koop et al., 2011). These results illustrate the challenge associated with faithfully reproducing the properties of atmospheric organic aerosol using individual compounds.

3.4 Role of organic O : C ratio on $\gamma(\text{N}_2\text{O}_5)$

Figure 6 shows normalized $\gamma(\text{N}_2\text{O}_5)$ vs. the O : C ratio of particles that are mixtures of organic components and ABS. The response at a single organic mole fraction of 0.5 is shown; more data points were taken at this mole fraction, and the effect of the

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O : C ratio on $\gamma(\text{N}_2\text{O}_5)$ at different mole fractions was similar, albeit weaker. Because the carbon oxidation state followed the same trend as the organic O : C ratio, only the dependence of $\gamma(\text{N}_2\text{O}_5)$ on the O : C ratio is shown. In addition to PEG, low O : C and high O : C mixtures, $\gamma(\text{N}_2\text{O}_5)$ on particles that are two-component mixtures of ABS and azelaic, glutaric, succinic, citric, or malonic acids are also shown. For organics with an O : C of ~ 0.45 , significant suppression in N_2O_5 uptake occurs at low organic mole fractions (e.g., $\gamma(\text{N}_2\text{O}_5)$ drops by 70–80 % relative to pure ABS at organic mole fractions of only 0.1) with little changes observed after the initial suppression. In general, for organics with high O : C ratios (e.g., O : C > 0.7), relatively little suppression of $\gamma(\text{N}_2\text{O}_5)$ was observed. An unexpected result was the observation that mixtures of ABS with citric acid and with the high O : C mixture showed more suppression than mixtures of ABS with other organics having O : C > 0.7 . As shown in Fig. 6, $\gamma(\text{N}_2\text{O}_5)$ increases as the O : C ratio increases above 0.56. Together with the different responses to RH exhibited by the lower O : C mixtures compared to the higher O : C, the dependence upon O : C observed here is consistent with the observation that liquid-liquid phase separations most readily occur for organic compounds with O : C ratios of ≤ 0.7 (Bertram et al., 2011; You et al., 2013) and $\text{RH} < 70\%$. However, our results also show that the O : C ratio is not the only controlling factor for the effect of organic components on $\gamma(\text{N}_2\text{O}_5)$. Moreover, even if phase separations occurred for all systems studied here, a dependence upon O : C is still expected due to its correlation with higher hygroscopicity and thus a greater water content within an organic phase that would promote N_2O_5 reactivity.

3.5 Model predictions of $\gamma(\text{N}_2\text{O}_5)$ for low and high O : C mixtures with ABS

In addition to the pure PEG and ABS/PEG mixtures described above, mixtures of ABS and other organics were also modeled using the modified version of the Anttila et al. (2006) resistor model of reactive uptake described above. Figure 7 shows a comparison of $\gamma(\text{N}_2\text{O}_5)$ measured from mixtures of ABS and organic compounds with different oxidation states vs. predicted values. Although we cannot rule out the possibility

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of organic lenses (e.g., incomplete organic coatings) (Reid et al., 2011), for simplicity, we assume each particle is completely coated. This assumption is likely valid since predicted values of $\gamma(\text{N}_2\text{O}_5)$ obtained from the assumption of an organic lens were found to consistently over-predict the measured $\gamma(\text{N}_2\text{O}_5)$ with the possible exception of the high O : C mixture. For the core-shell model, excellent agreement (slope = 0.98, $R^2 = 0.91$) is found for all systems at all RH values used in this work. Table 2 shows the values of each model variable used. Predicted values of $\gamma(\text{N}_2\text{O}_5)$ were less sensitive to values of α , the mass accommodation coefficient, than for other parameters in agreement with the findings of Anttila et al. (2006) and Riemer et al. (2009). The k_{org} required to bring observed and predicted $\gamma(\text{N}_2\text{O}_5)$ into agreement differed by more than an order of magnitude, ranging from 3.5×10^4 to $2 \times 10^5 \text{ s}^{-1}$ for the low O : C and high O : C mixtures, respectively, at 50 % RH.

For the high O : C mixture at both 50 % and 70 % RH, reasonable agreement was achieved by simply lowering k_{org} compared to k_{aq} and lowering ε from 1 to 0.3 without necessarily invoking any changes in the diffusivity of N_2O_5 in the organic layer compared suggesting that solubility limitations and differences in the liquid water content between the aqueous and organic components are primarily responsible for the behavior of $\gamma(\text{N}_2\text{O}_5)$ as a function of the organic content for the high O : C mixture. At 30 % RH, best agreement is achieved when D_{org} is lowered to half the value of D_{aq} for the high O : C mixture.

In contrast, poor agreement was observed for the low O : C mixture when only differences in the liquid water content (k_{org}) and solubility of N_2O_5 in the organic layer are accounted for. Instead, better agreement is achieved when D_{org} is lowered to $5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, a value approaching a viscous liquid (Koop et al., 2011; Shiraiwa et al., 2011). At 70 % RH, best agreement was obtained when D_{org} was equal or close to D_{aq} (8×10^{-10} to $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) suggesting the presence of internally mixed systems at this higher RH. At 50 % RH, the best agreement was found by setting $\varepsilon = 0.05$ for ABS + low O : C mixture, which is similar to the value of $\varepsilon = 0.03$ used to achieve agreement between measured and predicted values of $\gamma(\text{N}_2\text{O}_5)$ onto biogenic SOA

derived from α -pinene ozonolysis (Anttila et al., 2006; Riemer et al., 2009). Our results further support findings that suggest that changes in diffusion and/or solubility can result in large reductions in the N_2O_5 uptake efficiency, even for thin coatings, without having to invoke changes in α . The fact that ε is the similar for the low O : C mixture used in this work and biogenic SOA suggests that similar diffusion limitations exist for these two systems.

4 Atmospheric implications and conclusions

Measured values of $\gamma(\text{N}_2\text{O}_5)$ were well-predicted using a model that accounts for liquid-liquid phase separations into a core-shell morphology given suitable adjustments to the water content and N_2O_5 diffusivity and solubility within the organic shell. As expected, these parameters were dependent upon organic composition and humidity. Moreover, the dependence of $\gamma(\text{N}_2\text{O}_5)$ on χ_{OA} observed in these laboratory studies is remarkably similar to that observed on ambient aerosol particles, indicating that similar parameterizations could be used to predict $\gamma(\text{N}_2\text{O}_5)$ on ambient aerosol at least in some cases. Below, we use these insights into the effects of organic aerosol mass fraction and composition on N_2O_5 developed in this work and field measurements of these quantities to illustrate the impact of organic aerosol on N_2O_5 reactivity.

4.1 Model predictions of $\gamma(\text{N}_2\text{O}_5)$ applied to ambient aerosol

We extend our predictions of $\gamma(\text{N}_2\text{O}_5)$ to ambient aerosol using global measurements of submicron, non-refractory aerosol composition using AMS ambient data sets. The O : C ratio was determined for 25 data sets ranging from urban to remote environments from f (fraction of m/z 44 to total organics in the mass spectrum) (Aiken et al., 2008; Ng et al., 2010); details of the data sets can be found in Jimenez et al. (2009) and the Supplement. To parameterize the impact of RH, the organic aerosol mass fraction (χ_{OA}), and the O : C ratio, we first model the impact of RH (e.g., liquid water content)

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on the $\gamma(\text{N}_2\text{O}_5)$ for pure ABS using the model of Bertram and Thornton (2009) (see Fig. 8, dashed black line). We then factor in the effect of organic aerosol using the model of Anttila et al. (2006), the average χ_{OA} (0.48 ± 0.12), and the average O : C ratio (O : C = 0.46 ± 0.14) determined from all 25 data sets. The average O : C ratio is low enough that liquid-liquid phase separations can potential form, particularly at RH \leq 70 % (Bertram et al., 2011; Renbaum-Wolff et al., 2013; Saukko et al., 2012). PEG was used as a model organic compound, which is appropriate when considering that the dependence of $\gamma(\text{N}_2\text{O}_5)$ on the mass fraction of PEG for ABS/PEG mixtures was found to resemble the dependence of $\gamma(\text{N}_2\text{O}_5)$ on the χ_{OA} exhibited by ambient aerosol that had a similar average O : C ratio (O : C = 0.45). The dotted orange line in Fig. 8 shows the impact of factoring in organic coatings using PEG as the model compound and the database average χ_{OA} (0.48). Compared to pure ABS, the normalized value of $\gamma(\text{N}_2\text{O}_5)$ was found to be lower by 40 % at 70 % RH, by \sim 60 % at 50 % RH, and by 85 % at 30 % RH.

We also use 95 % confidence intervals, taken as 2 standard deviations, for the organic aerosol mass fraction and use organics that exhibit a wide-range of influence on $\gamma(\text{N}_2\text{O}_5)$ (e.g., from near complete suppression to almost no impact) to predict the range of different possible effects organic coatings will have on $\gamma(\text{N}_2\text{O}_5)$. For the case where the organic coating would have the largest impact on $\gamma(\text{N}_2\text{O}_5)$, we use the upper limit of the 95 % confidence interval for the typical χ_{OA} , which is 0.72, and an organic composition similar to the low O : C mixture, which suppressed $\gamma(\text{N}_2\text{O}_5)$ the most. The corresponding prediction for $\gamma(\text{N}_2\text{O}_5)$ is shown in Fig. 8 as a dotted red line; $\gamma(\text{N}_2\text{O}_5)$ decreases by an order of magnitude or more at 30 and 50 % RH. For the case where the organic coating would have a minimal effect on $\gamma(\text{N}_2\text{O}_5)$, we use the lower limit of the 95 % confidence interval for the typical χ_{OA} , which is 0.24 from the database, and the ABS/succinic acid mixture. We choose succinic acid because, as shown in Fig. 6 and Table 1, even at a high χ_{OA} , succinic acid has a minimal impact on $\gamma(\text{N}_2\text{O}_5)$. The corresponding predictions of $\gamma(\text{N}_2\text{O}_5)$ are shown in Fig. 8 as a dotted blue line; $\gamma(\text{N}_2\text{O}_5)$ only decreases by \sim 33 % at 30 % RH and only by \sim 15 % at 50 and 70 % RH.

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While the estimates of the impact of organics on $\gamma(\text{N}_2\text{O}_5)$ will depend on phase (e.g., whether an organic coating forms) in addition to coating thicknesses, particle surface area, and humidity, the predictions presented in Fig. 8 capture a uniformly suppressing effect of organic aerosol on N_2O_5 reactivity observed in previous studies (Bertram et al., 2009; Brown et al., 2009; Riedel et al., 2012) and illustrate that significant variability in the degree of suppression is expected. To the extent which averaging over multiple data sets from different regions and seasons yields a reasonable estimate of the “typical” organic aerosol, these calculations suggest that N_2O_5 reactivity on ambient particles should be significantly suppressed (by factors of 2 to 10) with a stronger dependence on RH compared to that expected for aqueous inorganic solution particles. While outside the scope of this paper, including the “nitrate effect”, the well-known suppression of N_2O_5 reactivity by particle nitrate aerosol (Bertram and Thornton, 2009; Brown et al., 2009; Mentel et al., 1999; Riedel et al., 2012), only enhances the effect of RH.

4.2 Conclusions

Failing to account for organic components has consistently over-predicted uptake rates of N_2O_5 compared to measured values, even when the nitrate effect is taken into account (Abbatt et al., 2012; Brown et al., 2009; Riedel et al., 2012). Previous studies have shown that organic aerosol has varied effects on N_2O_5 uptake, from near complete suppression of reactive uptake at small mass fractions (Badger et al., 2006; Cosman and Bertram, 2008; Escorcía et al., 2010; Folkers et al., 2003; Knopf et al., 2007; McNeill et al., 2006; Thornton and Abbatt, 2005), to allowing the same reactivity as inorganic aqueous solutions (Bertram and Thornton, 2009; Griffiths et al., 2009; Thornton et al., 2003). Our results suggest differences in organic composition, such as oxidation state and molecular weight, and the related responses of particle phase, morphology and liquid water content to RH, can explain the different effects of the bulk organic aerosol on N_2O_5 reactivity, and should be factored into parameterizations that account for the presence of organic coatings or variations in particle hygroscopicity.

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The key variables for predicting N₂O₅ uptake in the organic coating or pure organic particles are the organic mass fraction in the particles, the diffusivity of N₂O₅ and the liquid water content in the organic layer, the latter two correspond to the viscosity and hygroscopicity of the organic content (Renbaum-Wolff et al., 2013; Shiraiwa et al., 2011; Virtanen et al., 2010). We show that for constraining the effects of organic aerosol on N₂O₅ reactivity, the degree of oxidation of the organic aerosol is a useful, but not complete, indicator of these properties, and it is now widely measured during field campaigns and even as part of long-term monitoring activities. We anticipate that our results presented herein together with a growing understanding of organic aerosol properties will help better quantify N₂O₅ reactive uptake onto mixtures of organic and inorganic aerosol in and downwind of polluted regions, thereby, further improving predictions made by air quality and climate models. Moreover, N₂O₅ hydrolysis is likely just one of many possible heterogeneous and multiphase processes that may depend similarly on the viscosity, hygroscopicity and mixing state of organic aerosol.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys-discuss.net/13/32053/2013/acpd-13-32053-2013-supplement.pdf>.

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Table 1. Relative humidity (RH), solution types and weight percentages, organic mass fractions (χ_{OA}) and organic molar ratios, and $\gamma(\text{N}_2\text{O}_5)$ values (both absolute and normalized). The stated uncertainty in both the absolute and normalized values of $\gamma(\text{N}_2\text{O}_5)$ are 95 % confidence intervals.

RH (%)	Solution type	Wt %	Components	χ_{OA}	Organic O : C ratio	$\gamma(\text{N}_2\text{O}_5)$	Normalized $\gamma(\text{N}_2\text{O}_5)$
50	1	0.085	ABS	N/A	N/A	0.036 ± 0.002	1.00 ± 0.058
30	1	0.300	PEG	1.000	0.56	0.003 ± 0.003	0.08 ± 0.07
50	1	0.300	PEG	1.000	0.56	0.007 ± 0.003	0.20 ± 0.07
70	1	0.300	PEG	1.000	0.56	0.017 ± 0.011	0.47 ± 0.30
30	2	0.107	ABS + PEG	0.210	0.56	0.009 ± 6.5 e-4	0.24 ± 0.02
50	2	0.107	ABS + PEG	0.210	0.56	0.028 ± 0.002	0.77 ± 0.04
50	2	0.129	ABS + PEG	0.340	0.56	0.017 ± 0.004	0.47 ± 0.10
50	2	0.140	ABS + PEG	0.390	0.56	0.016 ± 0.002	0.45 ± 0.05
50	2	0.159	ABS + PEG	0.460	0.56	0.011 ± 0.002	0.31 ± 0.05
50	2	0.195	ABS + PEG	0.560	0.56	0.004 ± 0.006	0.12 ± 0.17
70	2	0.195	ABS + PEG	0.560	0.56	0.023 ± 0.003	0.62 ± 0.08
50	2	0.306	ABS + PEG	0.720	0.56	0.007 ± 8.0 e-4	0.20 ± 0.02
50	2	0.092	ABS + Azelaic Acid	0.076	0.44	0.023 ± 0.006	0.64 ± 0.17
30	2	0.099	ABS + Azelaic Acid	0.140	0.44	0.004 ± 0.005	0.10 ± 0.12
50	2	0.099	ABS + Azelaic Acid	0.140	0.44	0.019 ± 0.004	0.52 ± 0.10
50	2	0.113	ABS + Azelaic Acid	0.250	0.44	0.017 ± 0.007	0.48 ± 0.18
50	2	0.131	ABS + Azelaic Acid	0.350	0.44	0.012 ± 0.001	0.33 ± 0.04
50	2	0.154	ABS + Azelaic Acid	0.450	0.44	0.010 ± 0.005	0.27 ± 0.13
70	2	0.154	ABS + Azelaic Acid	0.450	0.44	0.016 ± 0.003	0.44 ± 0.07
50	2	0.215	ABS + Azelaic Acid	0.620	0.44	0.007 ± 0.005	0.20 ± 0.13
50	2	0.363	ABS + Azelaic Acid	0.760	0.44	0.008 ± 0.002	0.21 ± 0.04
30	2	0.094	ABS + Succinic Acid	0.097	1.0	0.019 ± 0.007	0.42 ± 0.16
50	2	0.094	ABS + Succinic Acid	0.093	1.0	0.045 ± 0.016	1.00 ± 0.35
50	2	0.102	ABS + Succinic Acid	0.170	1.0	0.035 ± 0.006	0.78 ± 0.14
50	2	0.114	ABS + Succinic Acid	0.254	1.0	0.037 ± 0.018	0.81 ± 0.41
50	2	0.129	ABS + Succinic Acid	0.340	1.0	0.036 ± 0.007	0.80 ± 0.15
70	2	0.129	ABS + Succinic Acid	0.340	1.0	0.040 ± 0.003	0.89 ± 0.06
50	2	0.172	ABS + Succinic Acid	0.500	1.0	0.036 ± 0.003	0.79 ± 0.06
50	2	0.260	ABS + Succinic Acid	0.670	1.0	0.026 ± 0.003	0.58 ± 0.06
30	2	0.099	ABS + Citric Acid	0.146	1.17	0.011 ± 0.006	0.30 ± 0.15
50	2	0.099	ABS + Citric Acid	0.146	1.17	0.025 ± 0.011	0.70 ± 0.31
50	2	0.113	ABS + Citric Acid	0.250	1.17	0.024 ± 0.005	0.65 ± 0.14
50	2	0.132	ABS + Citric Acid	0.360	1.17	0.019 ± 0.005	0.51 ± 0.13
50	2	0.156	ABS + Citric Acid	0.450	1.17	0.013 ± 0.005	0.35 ± 0.14
70	2	0.156	ABS + Citric Acid	0.450	1.17	0.035 ± 0.002	0.95 ± 0.05
50	2	0.226	ABS + Citric Acid	0.620	1.17	0.017 ± 0.005	0.46 ± 0.14
50	2	0.370	ABS + Citric Acid	0.770	1.17	0.013 ± 0.003	0.37 ± 0.08
50	1	0.085	ABS	N/A	N/A	0.030 ± 0.005	1.00 ± 0.15
50	2	0.183	ABS + Glutaric Acid	0.530	0.8	0.018 ± 0.003	0.6 ± 0.11
50	2	0.162	ABS + Malonic Acid	0.470	1.33	0.021 ± 0.003	0.68 ± 0.09
30	3	0.089	ABS + High O/C (Glucose, Malonic Acid, Citric Acid, Succinic Acid)	0.120	1.13	0.013 ± 0.006	0.42 ± 0.21
50	3	0.089	ABS + High O/C	0.120	1.13	0.021 ± 0.003	0.71 ± 0.11
50	3	0.122	ABS + High O/C	0.300	1.13	0.017 ± 0.004	0.57 ± 0.12
50	3	0.195	ABS + High O/C	0.559	1.13	0.010 ± 0.002	0.33 ± 0.05
70	3	0.195	ABS + High O/C	0.559	1.13	0.015 ± 0.003	0.50 ± 0.10
50	3	0.110	ABS + High O/C	1.000	1.13	0.005 ± 0.001	0.16 ± 0.04
30	3	0.091	ABS + Low O/C (Azelaic Acid, PEG, Genticic Acid, (1,2,9)-Nonanetriol)	0.156	0.48	0.003 ± 0.002	0.10 ± 0.06
50	3	0.091	ABS + Low O/C	0.156	0.48	0.008 ± 0.002	0.27 ± 0.08
50	3	0.135	ABS + Low O/C	0.370	0.48	0.007 ± 0.003	0.23 ± 0.10
50	3	0.236	ABS + Low O/C	0.635	0.48	0.006 ± 0.001	0.20 ± 0.03
70	3	0.236	ABS + Low O/C	0.635	0.48	0.013 ± 0.004	0.44 ± 0.13
50	3	0.151	ABS + Low O/C	1.000	0.48	0.002 ± 0.002	0.08 ± 0.06

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Table 2. Input parameters for the model of Anttila et al. (2006) used to predict $\gamma(\text{N}_2\text{O}_5)$.

RH	Compound	α	$[\text{H}_2\text{O}]_{\text{ABS}}$	$k_{\text{aq}} (k_{2f})$	k_{org}	ε	D_{org}
50%	ABS	0.1	25.7	1.11 E + 06	0.00 E + 00	1.00	1.00 E - 09
30%	PEG	0.1	13.6	9.50 E + 05	7.00 E + 04	0.06	6.00 E - 11
50%	PEG	0.1	25.7	1.11 E + 06	2.00 E + 05	0.30	5.00 E - 10
70%	PEG	0.1	36.5	1.14 E + 06	3.20 E + 05	1.00	1.00 E - 09
30%	ABS/PEG	0.1	13.6	9.50 E + 05	7.00 E + 04	0.06	6.00 E - 11
50%	ABS/PEG	0.1	25.7	1.11 E + 06	2.00 E + 05	0.30	5.00 E - 10
70%	ABS/PEG	0.1	36.5	1.14 E + 06	3.20 E + 05	1.00	1.00 E - 09
30%	ABS/Low OC	0.1	13.6	9.50 E + 05	1.23 E + 04	0.008	8.00 E - 12
50%	ABS/Low OC	0.1	25.7	1.11 E + 06	3.50 E + 04	0.05	5.00 E - 11
70%	ABS/Low OC	0.1	36.5	1.14 E + 06	5.60 E + 04	0.80	1.00 E - 09
30%	ABS/High OC	0.1	13.6	9.50 E + 05	7.00 E + 04	0.06	5.00 E - 10
50%	ABS/High OC	0.1	25.7	1.11 E + 06	2.00 E + 05	0.30	1.00 E - 09
70%	ABS/High OC	0.1	36.5	1.14 E + 06	3.20 E + 05	0.80	1.00 E - 09

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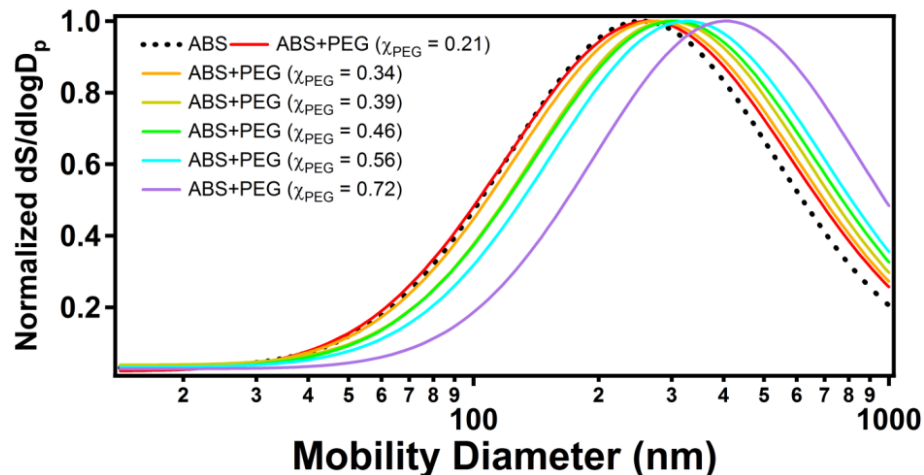


Fig. 1. Representative surface area-weighted size distributions for ABS (black dotted line) and ABS/PEG aerosols generated from solutions with increasing mass (mole) fractions of PEG (colored lines).

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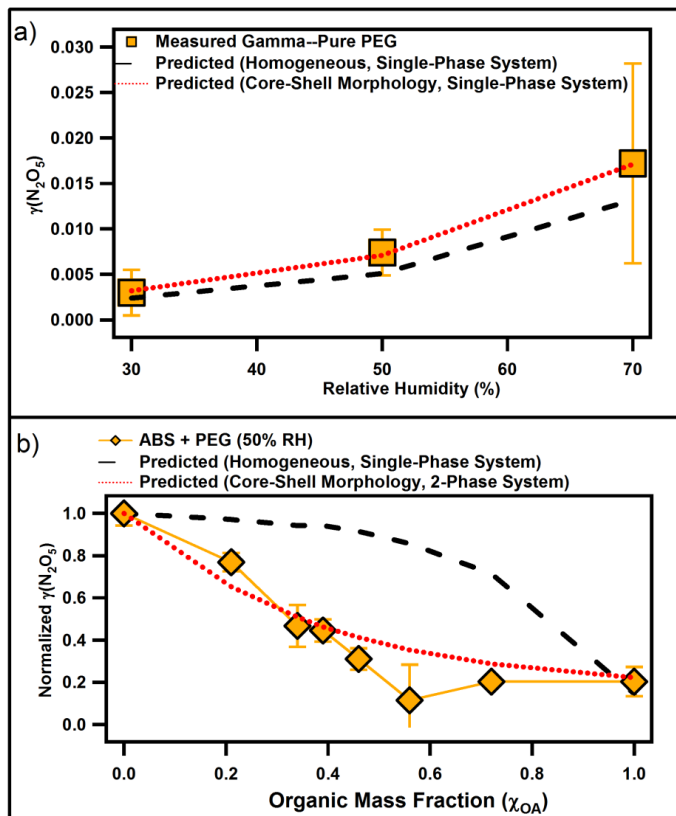


Fig. 2. (a) Experimentally measured $\gamma(\text{N}_2\text{O}_5)$ values of pure PEG at 30%, 50%, and 70% relative humidity (RH) (orange squares). (b) Experimentally measured normalized $\gamma(\text{N}_2\text{O}_5)$ values of particles generated from ABS and PEG as a function of PEG mass fraction at 50% RH (orange diamonds connected by orange line). Predicted values of $\gamma(\text{N}_2\text{O}_5)$ for pure PEG (top panel) and for ABS/PEG particles (bottom panel) using the parameterizations of Bertram and Thornton (2009) (dashed black lines) and Anttila et al. (2006) (dashed red lines) are also shown.

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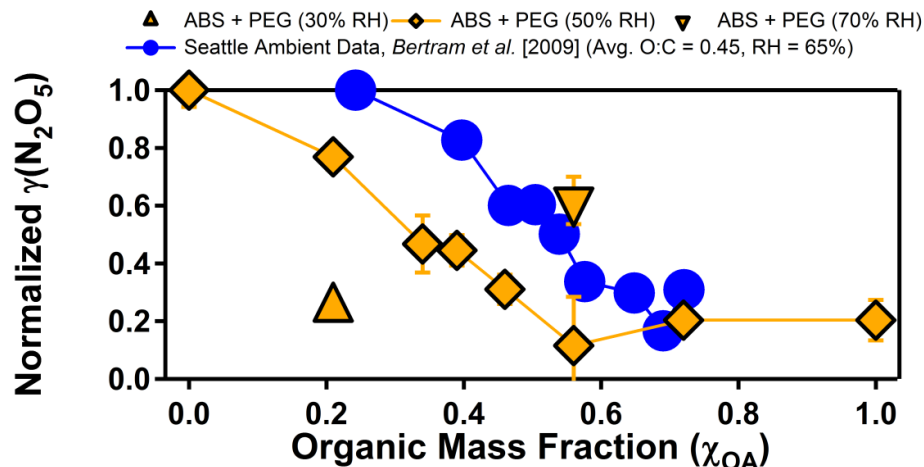


Fig. 3. Normalized $\gamma(N_2O_5)$ values of particles generated from ABS/PEG as a function of PEG mass fraction at 30% RH (orange, right-side up triangle), 50% RH (orange diamonds connected by orange line), and 70% RH (orange upside-down triangle). Normalized $\gamma(N_2O_5)$ for ambient particles measured in Seattle, WA during the summer of 2008 (Bertram et al., 2009b) are also shown (blue dots connected by blue line). The average RH in the sampling inlet was 65% RH and the average O : C ratio of the ambient organic aerosol was 0.45, estimated from an AMS operated simultaneously.

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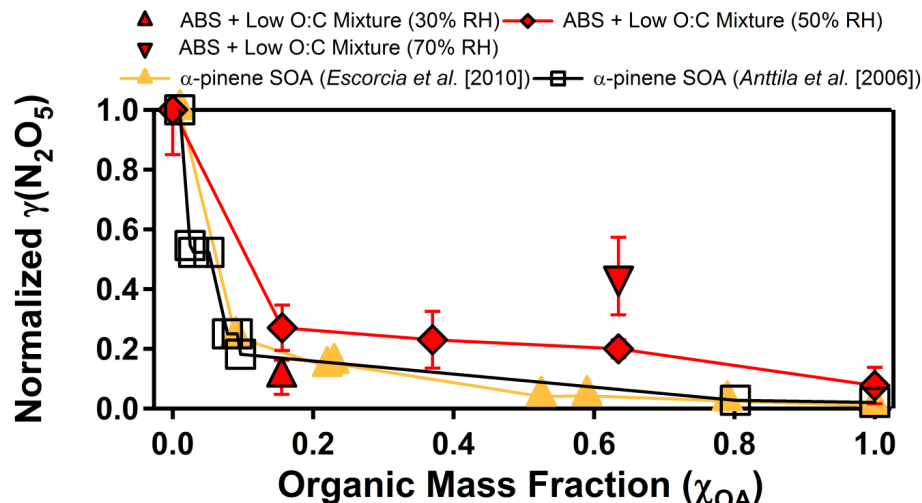


Fig. 4. Normalized $\gamma(\text{N}_2\text{O}_5)$ values for particles generated from ABS and a mixture of organic compounds with a low O:C ratio as a function of χ_{OA} at 30% RH (red, right-side up triangle), 50% RH (red diamonds connected by red line), and 70% RH (red upside-down triangle). Normalized $\gamma(\text{N}_2\text{O}_5)$ for particles containing chamber-derived SOA from α -pinene oxidation as measured by Escorcía et al. (2010) (solid, orange triangles with connecting line) and reported by Anttila et al. (2006) (open, black squares with connecting line) are also shown.

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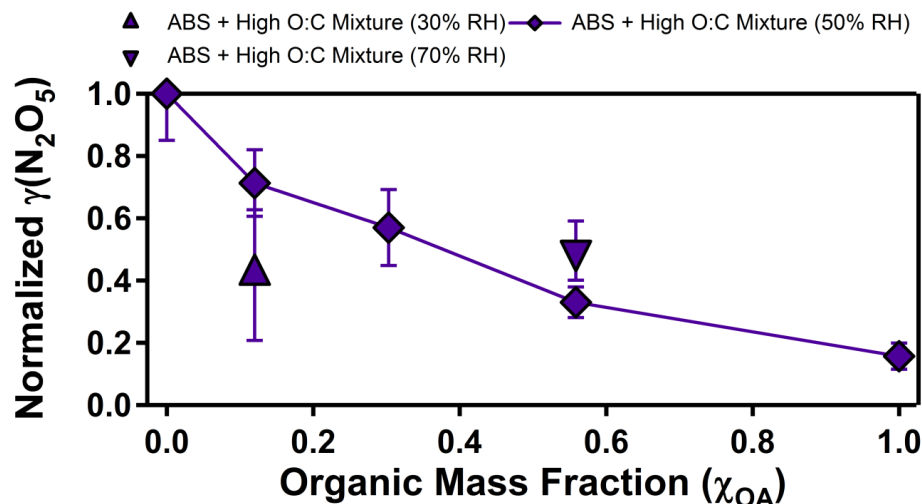


Fig. 5. Normalized $\gamma(\text{N}_2\text{O}_5)$ values for particles generated from ABS and a mixture of organic compounds with a high O : C ratio as a function of χ_{OA} at 30 % RH (purple, right-side up triangle), 50 % RH (purple diamonds connected by purple line), and 70 % RH (purple upside-down triangle).

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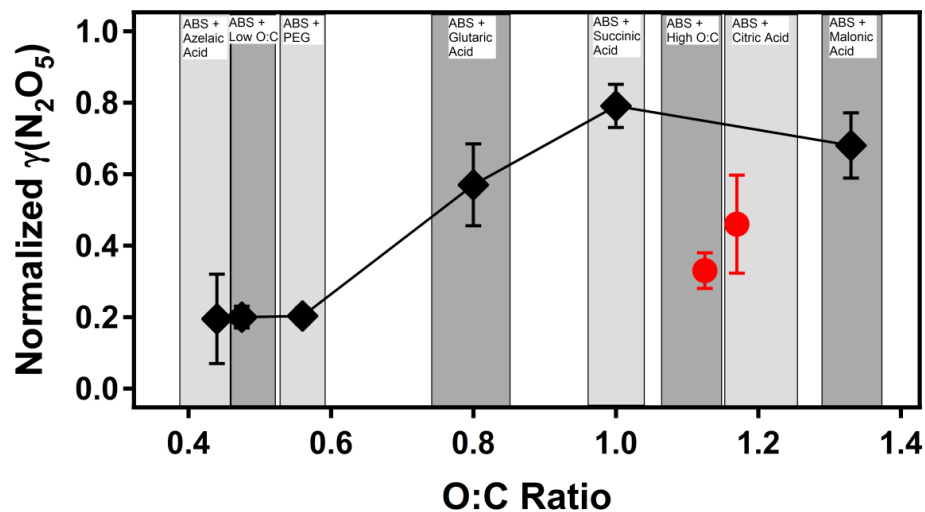


Fig. 6. Normalized $\gamma(\text{N}_2\text{O}_5)$ values for ABS and organic mixtures as a function of organic O : C ratio at an organic mole fraction of 0.5 and RH of 50 % (black markers). Red markers denote values for mixtures of ABS and citric acid and ABS and the high O : C mixture.

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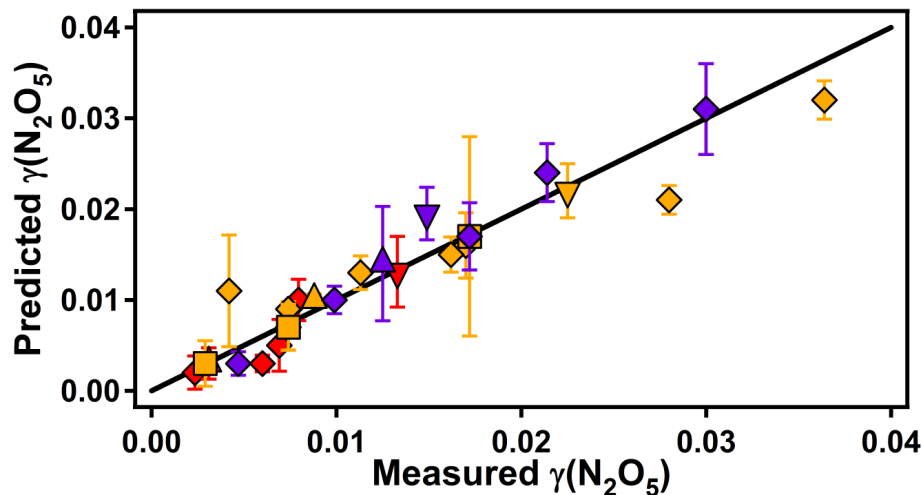


Fig. 7. Measured $\gamma(\text{N}_2\text{O}_5)$ and predicted $\gamma(\text{N}_2\text{O}_5)$ using the model of Anttila et al. (2006) for particles composed of ABS + low O : C organic mixture (red markers), ABS + PEG (orange markers), pure PEG (orange squares), and ABS + high O : C organic mixture (markers) at all χ_{OA} . Values at 30 % RH are shown as right-side up triangles, those at 50 % RH are shown as diamonds, and those at 70 % RH are shown as upside-down triangles. The black line represents a 1 : 1 ratio between the measured and predicted uptake values fit through the origin.

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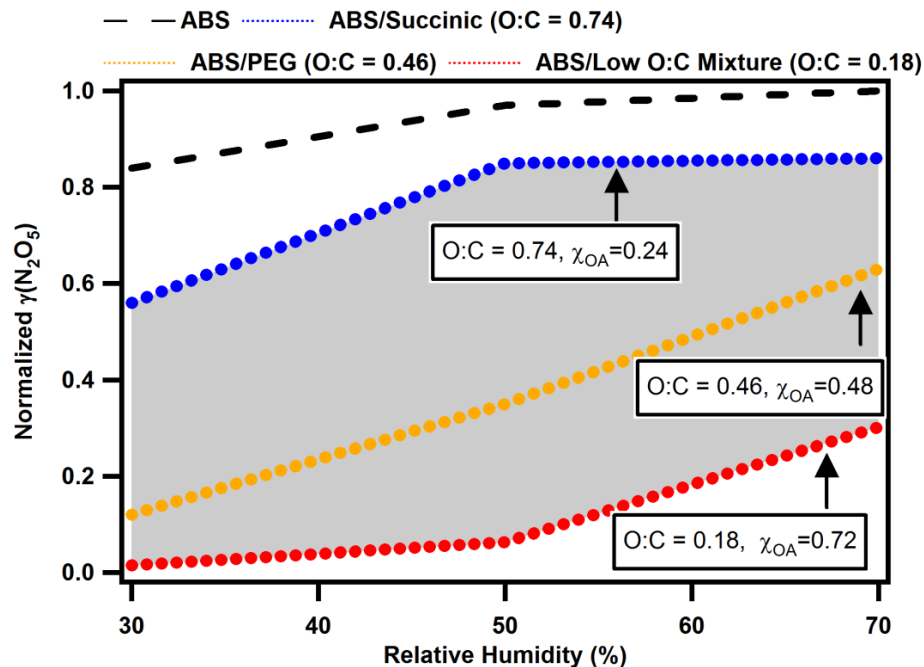


Fig. 8. Predicted $\gamma(\text{N}_2\text{O}_5)$ for pure ABS (dashed black lines) as a function of RH, normalized to RH > 50 % values. The effect of organic aerosol on $\gamma(\text{N}_2\text{O}_5)$ under atmospheric conditions is shown using trends observed in this study and ambient organic aerosol abundance and composition obtained from AMS data sets. See text for details.