Hygroscopicity of organic compounds as a function of organic functionality, water solubility, molecular weight and oxidation level

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Abstract. Aerosol hygroscopicity strongly influences the number size distribution, phase state, optical properties as well as multiphase chemistry of aerosol particles. Due to the big number of organic species in atmospheric aerosols, the determination of the hygroscopicity of ambient aerosols remains challenging. In this study, we measured the hygroscopic properties of 23 organics including carboxylic acids, amino acids, sugars and alcohols using a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA). Earlier studies have characterized the hygroscopicity either for a limited number of organic compounds using similar techniques or for particles at sizes beyond the micro-scale range or even bulk samples by other methodologies. Here, we validate these studies and extend the data by measuring the hygroscopicity of a broader suite of organics for particles with size under the submicron range that are more atmospheric relevant. Moreover, we systematically evaluate the roles of related physico-chemical properties that play in organic hygroscopicity. We show that hygroscopicity of organics varies widely with functional groups and organics with the same carbon number but more functional groups show higher hygroscopicity. However, some isomers, which are very similar in molecular structures, show quite different hygroscopicity, demonstrating that other physico-chemical properties, such as water solubility may contribute to their hygroscopicity as well. If the organics are fully dissolved in water (solubility > 7×10^{-1} g/ml), we found that their hygroscopicity is mainly controlled by their molecular weight. For the organics that are not fully dissolved in water (slightly soluble: 5×10^{-4} g/ml < solubility < 7×10^{-1} g/ml), we observed that some of them show no obvious water uptake, which probably due to that they may not deliquesce under our studied conditions up to 90 % RH. The other type of slightly soluble organics is moderately hygroscopic and the larger their solubility the higher their hygroscopicity. Moreover, the hygroscopicity of organics generally increased with O:C ratios, although this relationship is not linear. Hygroscopicity of organic compounds were also predicted by two thermodynamic models, including the Extended Aerosol Inorganics Model (E-AIM), and the University of Manchester System Properties (UManSysProp). We show that hygroscopicity results of almost all organic compounds except those tricarboxylic acids were poorly represented by the UManSysProp and the E-AIM over-estimated the hygroscopicity of all amino acids. These discrepancies were likely due to that both models do not consider phase transition and intermolecular interactions of these selected compounds in the simulations. These results may further improve our understandings of the interactions between organics and water molecular and will benefit the estimate of the hygroscopicity and CCN (cloud condensation nuclei) activities of any mixtures, for instance, ambient mixtures based on known composition data.

1 Introduction

Atmospheric aerosol particles consist of numerous organic species with both anthropogenic and biogenic origins (Zhang et al., 2007; Jimenez et al., 2009; Zhang et al., 2015; Wang et al., 2018). These organic species often contribute a significant fraction to the mass of sub-micrometer aerosols, and have vital effects on air-quality and climate (McFiggans et al., 2006; Randall et al., 2007; Zheng et al., 2015). To obtain a systematic understanding of their effects, it is necessary to acquire correct information on the chemical composition and physico-chemical properties of these organics (Seinfeld and Pandis, 2016). Hygroscopicity is one of the most important physico-chemical properties and it describes the ability of particles to take up water and grow in size under sub- and supersaturated conditions (Petters and Kreidenweis, 2007). Thus, it strongly influences the number size distribution, phase state, optical properties as well as multiphase chemistry of aerosol particles (Cheng et al., 2008; Su et al., 2010; Hong et al., 2018; Tang et al., 2019).

Given the large number of organic species in atmospheric aerosols, the determination of their hygroscopicity is quite experimentally difficult. Current models normally use aggregate quantities, such as the atomic oxygen-to-carbon (O:C) ratio or the average oxidation state of organics to simply parameterize the hygroscopicity of organic species in ambient aerosols. However, recent studies show that the hygroscopicity of organic aerosols cannot be fully explained by their oxidation level and the empirical relationship between hygroscopicity and O:C might not be linear (Lambe et al., 2011; Kuwata et al., 2013; Rickards et al., 2013; Marsh et al., 2017). This suggests that this simplified approach to quantify organic hygroscopicity might be problematic and a more mechanistic understanding of the complex link between hygroscopicity and other physico-chemical properties such as molecular functionality, molecular weight and water solubility of organics should be examined.

Due to these challenges, prediction of the hygroscopicity of organic compounds sometimes relies on thermodynamic models which explicitly includes these properties, for instance molecular functionality, molecular weight, into simulations. These thermodynamic models, including the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) (Zuend et al., 2008; Zuend et al., 2011), the Extended Aerosol Inorganic Model (E-AIM), and the University of Manchester System Properties (UManSysProp) (Clegg et al., 1998; Topping et al., 2016) use group contribution methods to calculate water activity for organic species of atmospheric relevance. However, involving these thermodynamic simulations in transport or climate models to predict the hygroscopicity for such a large number of organic compounds in ambient aerosols is computationally expensive. Moreover, these models, based on parameterizations from measurements, are semi-empirical, and thus need more experimental data to constrain their predictions (Suda and Petters, 2013). Particularly, when it comes to very dry conditions, these models may perform even worse and cannot capture the non-ideality of the solutions accurately (Ohm et al., 2015). Therefore, quantifying the hygroscopicity of atmospheric relevant organic species through laboratory measurements by systematically varying the type of studied organics is an intrinsic necessity. Chan et al. (2008) studied the hygroscopic properties and CCN activities of a series of dicarboxylic acids and saccharides using an electrodynamic balance (EDB) and found that the CCN activities of highly water soluble organic compounds can be well predicted by the Köhler theory. Suda et al. (2014) examined the hygroscopicity of a few synthetic organic compounds that are atmospheric relevant but not commercially available using a CCN counter (CCNc). They found that the compounds with hydroxyl or carboxyl groups are the most hygroscopic, while the ones with nitrate or methylene are the least. Jing et al. (2016) investigated the hygroscopic properties of a series of dicarboxylic acids with levoglucosan using a HTDMA, but they mainly focused on the multicomponent interactions between organic compounds. Marsh et al. (2017) collected experimental hygroscopicity data for 23 organic compounds by a comparative kinetics EDB (CK-EDB) to compare with thermodynamic predictions and discussed that the hygroscopicity of organic compounds with increasing branching and chain length are poorly represented by models.

All these cases discussed above shows that there is already some_experimental hygroscopicity data for organics with high atmospheric abundance and relevance (Peng et al., 2001; Prenni et al., 2007; Chan et al., 2008; Lambe et al., 2011; Kuwata et al., 2013; Marsh et al., 2017; Lei et al., 2018). However, some of these measurements were conducted using different techniques rather than the HTDMA, all of which have different limitations. Measurements using a CCNc could only probe the hygroscopic properties or CCN activities at supersaturated conditions, where many compounds may already fully dissolve in water droplets. The EDB or CK-EDB approaches normally analyze the droplets in the micrometer size range, far beyond the size range of atmospherically relevant aerosols. In contrast, the HTDMA system allows direct measurement of particle hygroscopicity at subsaturated conditions and for particles at the size from tens to a few hundreds nanometers, which is a good complement closing the gaps beyond the reaches of other techniques. Furthermore, some of the aforementioned studies using similar HTDMA systems focused on quite a small number of organics discussing only one or two properties potentially influencing the hygroscopicity, leading to a limited coverage of the experimental datasets. Thus, a general picture in understanding the observed hygroscopicity among different organic species still remains unclear.

Therefore, in this work, we extend the compositional complexity and diversity of the studied organic compounds with varying functional groups, molecular structures and other relevant physico-chemical properties. We try to form a systematic matrix of experimentally- determined HTDMA data synthesizing a large suite of organics, providing unambiguous measurements of particles at atmospherically relevant size range. Combined with these experimental data, we aim to evaluate the roles of different physico-chemical properties that play in organic hygroscopicity and gain some insight on their limitations and applicability. In addition, predictions from two widely used thermodynamic models, E-AIM and the UManSysProp, are compared against our experimental data, which may benefit the validation and improvement of the fidelity of these models.

2 Measurements

Submicron aerosol particles were generated by nebulizing the aqueous solutions (0.1 g L^{-1}) of each compound using a constant output atomizer (TSI, 3076). The solutions were prepared by using ultrapure water (Millipore, resistivity ≥ 18.2 MΩ). The physico-chemical properties of the studied 23 compounds are summarized in Table 1.

After particle generation, the particles were introduced into a custom-made HTDMA system where their hygroscopic growth factor (GF(RH)) can be measured. GF(RH) is defined as Eq. (1):

$$GF(RH, D_0) = \frac{D(RH)}{D_0}, \tag{1}$$

where D(RH) and D_0 are the equilibrium mobility diameter of the particles at a given RH and under dry conditions (< 10 % RH), respectively. Figure S1 shows the schematic of the HTDMA system. The detailed schematic of the HTDMA system can be found in Tan et al. (2013). Residence time for humidication of the generated aerosols is around 2.7 seconds. Calibration of the system was performed using ammonium sulfate (AS) and the results shown in Fig. S2 display that the measured hygroscopic behaviour of AS agreed well with previous studies with the deliquescence RH around 78 %.

Swietlicki et al. (2008) summarized the potential sources of error in HTDMA measurements and concluded that the reliability of the measured data is strongly associated with the stability and accuracy of DMA2 RH as well as the accurate measurement of particle diameter by DMAs. According to Mochida and Kawamura (2004), the uncertainty in the measured GF can be calculated by Eq. (2):

$$\sqrt{\left(GF\frac{\sqrt{2}\varepsilon_{Dp}}{Dp}\right)^2 + \left(\varepsilon_{RH}\frac{dGF}{dRH}\right)^2}, \tag{2}$$

where GF is the measured growth factor with respect to any measured RH, ε_{Dp} and ε_{RH} are the errors in the measured Dp and RH. In our system, the accuracy of DMA2 RH was maintained to be ±1% and the uncertainty for the mobility diameter was ±1% according to PSL (Polystyrene Latex particles) calibration. Hence, for our system, ε_{RH} and ε_{Dp}/Dp are 1% and 0.01, respectively. The calculated uncertainty according to the above-mentioned method is added in the measured GF in the following section.

According to κ-Köhler theory, we converted the measured hygroscopic growth factor to the single hygroscopicity parameter κ (Eq. 3-6) to facilitate the comparison of the hygroscopic properties among different compounds (Petters and Kreidenweis, 2007):

$$\kappa = (GF^3 - 1)\left(\frac{Ke}{RH} - 1\right), \tag{3}$$

$$Ke = exp\left(\frac{4\sigma_{sol}M_w}{RT\rho_w D(RH)}\right), \tag{4}$$

$$RH/100\ \% = a_w Ke, \tag{5}$$

$$\kappa = \frac{(GF^3-1)(1-a_w)}{a_w}, \tag{6}$$

where a_w is the water activity, M_w and ρ_w are the molar mass and the density of pure water at temperature T, respectively; σ_{sol} is the solution droplet surface tension, which was assumed to be the surface tension of water (0.072 J m^{-2}) and R is the ideal gas constant.

3 Modeling

The E-AIM and UManSysProp are applied in this study to simulate the hygroscopic behaviour of the 23 organic species. E-AIM is a thermodynamic model for calculating gas, liquid and solid partitioning in aerosol systems (Clegg et al., 1998; Wexler, 2002), while UManSysProp (University of Manchester System Properties) is an online model to predict the hygroscopic growth factors of organic and inorganic species. Both models use the group contribution method of Universal quasi-chemical Functional group Activity Coefficients (UNIFAC) to characterize the subgroups of organic molecules and calculate activity coefficients based on the contributions from these subgroups (Fredenslund et al., 1975; Hansen et al., 1991). The detailed input setting and calculations for E-AIM and UManSysProp are given in Supplement.

4 Results and discussion

4.1 Hygroscopicity of individual organics

In this section, we summarized the measured and predicted hygroscopic properties of the 23 organic species, which are classified into three groups based on their functionality. Particles at the dry size of 200 nm were selected for analysis.

4.1.1 Carboxylic acids

Carboxylic acids are the most abundant water-soluble components identified in atmospheric aerosols (Chebbi and Carlier, 1996; Mochida et al., 2003; Kundu et al., 2010). Hygroscopic properties of straight-chain dicarboxylic acids have been extensively investigated in previous studies (Chan et al., 2008; Kuwata et al., 2013; Rickards et al., 2013), however, experimental data for dicarboxylic acids with additional substitutions and tricarboxylic acids are limited. To achieve a comprehensive overview of the hygroscopicity of carboxylic acids, we measured the water uptake of several common straight-chain dicarboxylic acids in the atmosphere and further extended the hygroscopic measurements for dicarboxylic acids with substitutions and tri-carboxylic acids. Figure 1 shows the measured and predicted humidograms of straight-chain dicarboxylic acids (Fig. 1a), dicarboxylic acids with substitutions (Fig. 1b) and tricarboxylic acids (Fig. 1c), respectively. Need to note that the E-AIM model cannot simulate the dissociation of tricarboxylic acids in aqueous phase. Hence, the hygroscopic growth of tricarboxylic acids was only modeled with the UManSysProp.

Among the studied straight-chain dicarboxylic acids, only malonic acid showed continuous hygroscopic growth with increasing RH and the measured GF at 90 % RH was 1.47, which agrees well with previous studies (Peng et al., 2001; Prenni et al., 2001; Wise et al., 2003). Figure 1a also shows that the hygroscopic behaviour of malonic acid was well represented by the E-AIM but overestimated by the UManSysProp. The other straight-chain dicarboxylic acids (i.e., succinic, adipic, pimelic, suberic and azelaic acids) did not show any water uptake at RH <= 90 %, which was not captured by the UManSysProp. Assuming a solid state of these dicarboxylic acids, the E-AIM was capable to predict their non-hygroscopicity. Similar results were also found in previous studies (Prenni et al., 2001; Kuwata et al., 2013; Rickards et al., 2013; Jing et al., 2016) and Chan et al. (2008) explained that these dicarboxylic acids have quite low-solubility in water and once they crystallized, they would not deliquesce even under high RH conditions (e.g., RH < 90 %). Moreover, we found that the measured GFs of these dicarboxylic acids were less than 1, which could be attributed to the adsorption of a small amount of water at the particle surface, leading to the rearrangements of the microstructure and compaction of the particle (Mikhailov et al., 2004; Mikhailov et al., 2009).

The humidograms of the three dicarboxylic acids with substitutions (i.e., double bond or hydroxy group) are illustrated in Fig. 1b. The continuous water uptake indicates that these particles may be at liquid state under dry conditions. We observed a small leap of the GFs from 80 % to 85 % RH, implying that these particles were only partially deliquesced and further dissolution occurred at elevated RH. However, considering the measurement uncertainties, the statement of the partial deliquescence could not be fully confirmed and thus further evidence from other measurements is needed. On the other hand, the E-AIM could well represent their hygroscopic properties at RH between 10 -90 %, while there are still some deviations between the measurements and the UManSysProp predictions, especially for malic and tartaric acids, even taking into account of their measurement uncertainties. This could be due to that the UManSysProp is a more simplified model taking into account less input data or parameterization. For instance, the phase state or the dissociation process of the studied compound at different conditions could not be assumed or considered in the simulation. Therefore, additional processes or properties should be included into this model for the further improvements of its predictions.

A similar gradual phase transition was observed for aconitic acid and citric acid (Fig. 1c), while the other tricarboxylic acid showed continuous hygroscopic growth over the studied RH range, indicating no obvious phase change for these particles upon hydration. However, it is quite interesting to note that predictions from the UManSysProp become more approaching to the experimental data, especially above 80 % RH, considering the measurement uncertainties.

4.1.2 Amino acids

Figure 2 shows the measured humidograms of the 5 amino acids and their corresponding thermodynamic predictions. Continuous water uptake was observed for particles of serine, glutamine and aspartic acid, indicating that there was no phase transition occurred during the hydration cycle. Considering the measurement uncertainties, no water uptake is observed for alanine particles, which has also been reported in previous works (Chan et al., 2005; Darr et al., 2018). For glycine, we observed a continuous shrink in wet particle size from 30 % RH to 80 % RH, and above 80 % RH the GFs increased slightly. Previous studies have reported that glycine particles started to absorb water above 60 % RH (Chan et al., 2005; Marsh et al., 2017; Darr et al., 2018) prior to deliquescence due to capillary effect, which could also be the potential reason for the shrinkage in particle size of glycine during hydration as a result of the microstructural rearrangement of particles upon humidification. The sizing of these structurally-rearranged particles, especially at lower RH range, will be erroneous as the volume change of the particles upon wetting may not only due to the water absorption but also the compaction of the original particles. This phenomena complicates the accurate estimation of the actual water amount absorbed by the particles due to their intrinsic hygroscopicity. In a recent study by Nakao et al. (2014), in order to avoid the influence from particle restructuring upon wetting, they sized wet particles without drying after generation and studied their droplet activation using a wet CCN. This approach they introduced might be an easier attempt, offering an unique solution for current problem from particle restructuring during the hydration processes.

Predictions of serine, glutamine, alanine and aspartic acid are generally in better agreement with measurements than that of glycine, although overestimation was observed for all the 5 amino acids. Luo et al. (2020) discussed that the UNIFAC ignored the intramolecular interactions between amine and carboxylic groups in both models, resulting in the observed difference in the measured and predicted GFs.

4.1.3 Sugars and Sugar alcohols

Two-stage-like gradual hygroscopic growth was also observed for particles of fructose, mannose, sucrose, xylitol and L-arabitol, shown in Fig. 3. The experimental results of those sugars and sugar alcohols are consistent with previous literature data (Chan et al., 2008; Estillore et al., 2017). Compared to other sugars and sugar alcohols, sucrose is slightly less hygroscopic with a mild downward trend in GFs at low RHs and the GF at 85 % RH was around 1.21, which is similar with the results of Estillore et al. (2017). Moreover, mannitol is the least hygroscopic or even hydrophobic with GF less than unity at 90 % RH, which also agrees with previous literature (Ohrem et al., 2014; Martău et al., 2020).

Similarly, phase transition or microstructural rearrangements of particles was not included in the models. Thus, these sugars and sugar alcohols were generally less hygroscopic than the values predicted by the E-AIM (except L-arabitol) under low RH conditions. However, at elevated RHs, whereas particles are fully dissolved, the E-AIM predictions agree well with most of the measured hygroscopic GFs within the measurement uncertainties.

4.2 Relating the hygroscopicity of organic compounds to their physico-chemical properties

In this section, we explore the effects from different physico-chemical properties such as molecular functionality, water solubility and organic oxidation level that potentially contribute to the observed hygroscopicity κ. Note that the hygroscopicity parameter κ discussed in this section was converted by using growth factor data measured at 90 % RH.

4.2.1 κ vs. organic functionality

Figure 4a shows the measured hygroscopicity of the 23 organics as a function of carbon number. The functional groups with their corresponding numbers are indicated with colors and symbols. In order to facilitate the comparison of the compounds with the same carbons, the carbons with only one compound are not illustrated. For the studied organic compounds with the same carbon number, the hygroscopicity was increased by the addition of extra functional groups to the carbon backbone. For instance, maleic, malic, tartaric and aspartic acid with extra functional groups (e.g., C=C, -OH and -NH2) with respect to succinic acid with only two -COOHs are more hygroscopic. For C7 compounds, adding an carboxylic acid group to the carbon backbone leads to an elevated hygroscopicity from pimelic to tricarboxylic acid. Moreover, organic compounds with the same carbon numbers but different molecular functionality presented quite distinct hygroscopicity. For example, for C3 compounds, if replacing the -CH3 with an -OH or replacing the -OH group by an -COOH in their parental molecules, the hygroscopicity was significantly increased. Taking another example from C4 compounds, the organics with a hydroxyl group (-OH) instead of an -NH2 or with a double bond (C=C) instead of the hydroxyl group in their carbon backbones were more hygroscopic. Similar difference in hygroscopicity was also observed between aconitic acid (C6) with a C=C and citric acid (C6) with a (-OH). By summarizing the results in current study, κ increased with the functionality in the following order: (-CH3 or -NH2) < (-OH) < (-COOH or C=C or C=O). However, it has to be noted that this comparison is quite qualitative, might be ambiguous and further evidence from other organic compounds is needed in order to drive a more general conclusion. Suda et al. (2012) and Chen et al. (2019) concluded that the hygroscopicity of organic compounds is closely related to their individual polarity and highly polar compounds are usually more hygroscopic. Kier (1981) ranked the polarity of different functional groups in the sequence of -CH3< -NH2< -OH< -CHO< -NH2OH< -COOH, which could explain the difference in the hygroscopicity of organics with various functionalities in our study.

Figure 4b shows that the measured hygroscopicity of the straight-chain dicarboxylic acids alternate with the parity of the carbon numbers. It has to be noted that data of glutaric acid (C5) is quoted from Chan et al. (2008). Bilde et al. (2003) observed an alternation in the volatility of dicarboxylic acids with the number of carbon atoms similar to the ones we observed for their hygroscopicity. They attributed this to the alternation in the molar enthalpies of fusion of those compounds. Moreover, we observed that some compounds (xylitol vs. L-arabitol and fructose vs. mannose) share the same molecular formular or functionality but vary differently in hygroscopicity as shown in Fig. 4c. Both findings suggest that other physico-chemical properties of organics besides molecular functionality may also contribute to the observed variation in their hygroscopicity. Previous studies (Marcolli and Peter, 2005; Petters et al., 2017) reported that the position of the functional groups could influence the hygroscopicity properties of organic compounds. For instance, Petters et al. (2017) suggested that organic molecules with the hydroperoxyl group close the end of carbon chain were more hygroscopic. Similarly, fructose observed in our study, with the hydroxyl group in the tail of the carbon chain and being far away from the C=O group, is more hygroscopic than mannose of which these two groups are much closer to each other.

4.2.2 κ vs. water solubility and molar volume

Previous studies suggested that for highly soluble compounds which are fully dissolved in the aqueous droplet, their hygroscopicity are mainly controlled by their molar volume (M_{org}/ρ_{org}); while for slightly soluble compounds, their hygroscopicity is limited by their low water solubility (Petters et al., 2009; Kuwata et al., 2013; Nakao, 2017; Wang et al., 2019). Hence, we considered two regimes in our study: (A) compounds that fully dissolved (highly soluble with solubility > 7×10^{-1} g/ml in this work or not saturated regime) and (B) compounds that are not fully dissolved (slightly or sparingly soluble compounds with solubility in the range between $1e^{-3}$ to $3e^{-1}$ g/ml or saturated regime) in the aqueous droplets under 90 % RH condition. In regime A, as shown in Fig. 5, the hygroscopicity decrease with increasing molar volume. Besides molar volume, the van't Hoff factor (i), which accounts for the degree of dissociation of a compound in water, could also contribute to the overall hygroscopicity for fully dissolved compounds. Sugars, as non-electrolytes with van't Hoff factor of 1, do not dissociate in aqueous solutions (Giebl et al., 2002; Koehler et al., 2006; Rosenørn et al., 2006) and thus are less hygroscopic than the dicarboxylic acids which can dissociate in water and contribute to the reduction in water activity. Frosch et al. (2010) related the van't Hoff factor with the pKa values for a series of carboxylic acids and found that the stronger the acid with smaller values of pKa, the larger the van't Hoff factor. This could explain why maleic acid, even with a larger molar volume but a smaller pKa value (1.8) is more hygroscopic than malonic acid (pKa = 2.4).

Organic compounds with low water solubility (regime B) could be obviously divided into two categories according to their hygroscopicity. One is non- or almost non-hygroscopic organics with κ close or equal to 0. These organics might present at solid or crystalline state and did not deliquesce at our measurement conditions during the whole RH range. Thus, their hygroscopicity is not only limited by their low water solubility but also their phase state and the energy that needed for the phase transition. Compared to these non-hygroscopic slightly/sparingly soluble organic compounds, there are some other slightly/sparingly soluble organics, showing moderately water uptake with κ values larger than 0.1. These organics with limited solubility may already partially deliquesce under our studied RH conditions (Hartz et al., 2006; Chan et al., 2008), and we found that their hygroscopicity increase with water solubility. This is physically reasonable that the aqueous droplet of these organics with limited solubility can be considered as being composed of an effectively insoluble core with a saturated solution. The organic with higher water solubility would dissolve more and have a higher molar concentration in the saturated solution. The higher molar concentration corresponds to a stronger reduction in water activity, which would lead the particles to become more hygroscopic.

4.2.3 κ vs. O:C ratio

Previous studies have suggested that the hygroscopicity parameter of organic species (κ_{org}) is closely related with their O:C ratios (Jimenez et al., 2009; Chang et al., 2010; Massoli et al., 2010; Cappa et al., 2011; Lambe et al., 2011; Kuwata et al., 2013; Rickards et al., 2013). In this study, we plotted our measured κ of the 23 organic compounds with their O:C ratios in Fig. 6, and for a wider atmospheric implication we compared them against previous results obtained from different atmospheric environments (Mei et al., 2013; Wu et al., 2013; Hong et al., 2015; Wu et al., 2016; Deng et al., 2018; Hong et al., 2018; Kuang et al., 2020). Clearly, ambient organics show much lower O:C value as seen in Fig. 6. Ng et al. (2010) compiled the measured O:C data from different environments and concluded that at most sites, ambient organic aerosols mainly consist of oxygenated organic material (OOA) and hydrocarbon-like organic material (HOA). HOA, which arises from vehicle emissions, is the least oxidized with the average O:C value less than 0.2 (Ng et al., 2010; Xu et al., 2015; Xu et al., 2016; Cao et al., 2019; Li et al., 2020). Hence, with the inclusion of HOA in ambient aerosols, the average O:C value of the bulk organic is less than 1, being generally lower than our laboratory-generated aerosols.

A general trend of the increase of κ_{org} with increasing O:C has also been observed for laboratory results but the correlation between κ and O:C falls into two categories. One is a non-hygroscopic organic group with a weak O:C-dependence as the blue shaded area in Fig. 6. We suggested these compounds with limited water solubility might not deliquesce yet under 90 % RH as discussed previously. The other slightly/sparingly soluble organics shaded in red area in Fig. 6 is a moderate-hygroscopic group with a slightly stronger O:C-dependence. However, the correlation of both categories is not good, which may be effected from the other properties which discussed above. Compared to those laboratory-generated pure organic compounds, ambient organics are more complex, with divergent O:C-dependent hygroscopicity among different environments. For instance, the hygroscopicity of urban aerosols in Beijing was almost constant, being less sensitive to the variations of the organic oxidation level, which is similar to our non-hygroscopic organics (Wu et al., 2016). On the contrast, the suburban aerosols in central Germany (Wu et al., 2013) and in Guangzhou (Hong et al., 2018) exhibit a slightly stronger influence from their O:C ratio, being close to the behaviour (slope ≈ 0.12) of the moderate hygroscopic organics with relative higher water solubilities in our study. As discussed in previous works (Rickards et al., 2013) some of the laboratory-generated pure organics share identical O:C ratio but differ widely in hygroscopicity. However, no molecular-specific information could be concluded further for those ambient organics. This, on the other hand, indicates that great uncertainties may arise from the approximation of organic hygroscopicity based on their atomic O:C ratio for ambient aerosols. The use of a simplified average property (i.e., O:C ratio) to describe the hygroscopicity of ambient organics, whose constitute may be complex, is quite risky as compounds with similar O:C ratio may vary considerably in hygroscopicity. Additional measurements of other properties (e.g., functionality or water solubility) may be difficult due to both the highly complex mixture of ambient aerosols and technique limitations. However, laboratory-generated surrogate mixtures representing the complexity of ambient aerosols at least should be examined to test the variety in the relationship between the O:C ratio and κ.

5 Atmospheric implication

Our laboratory observations reveal that current thermodynamic models may not always accurately simulate the hygroscopic behavior of organic compounds, despite their previous success. Phase transition may occur during the hydration cycle, which are not reasonably considered in the thermodynamic models. This will lead to significantly biased predictions of organic hygroscopic behaviour, as can be seen in the case of the slightly soluble organics in our study. Moreover, the interactions between functional group and water molecules were previously believed to dominate particle hygroscopicity rather than the interactions between functional groups. However, we found that the groups-groups interaction may be also important in water uptake processes. This effect is clearly revealed in our study by the discrepancy in the hygroscopicity of amino acids between measurements and model prediction. These limitations suggest that an improved mechanism with the inclusion of these processes (e.g., phase transition and intramolecular interactions) into these thermodynamic models is needed and require comprehensive data from empirical measurements to complement these models for validating predictions. Furthermore, extra care must be taken to deal with even more complex systems, such as multi-component mixtures with the presence of inorganic compounds in atmospheric particles.

Previous studies (Swietlicki et al; 2008; Duplissy et al., 2009; Wu et al., 2011; Suda et al., 2013) suggested that the residence time for humidification may also potentially influence the observed water uptake of particles as the measured particles, especially for some organic compounds, may not reach their equilibrium humidified sizes during a quite short time of wetting. However, extending the humidification time for hours using the EDB, no water uptake was also observed for most of our studied dicarboxylic acids (Chan et al., 2008) as well as for glycine and alanine particles (Chan et al., 2005), which was also confirmed by Darr et al., (2018), using another different measurement technique, i.e., ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared) with a residence time of 2 minutes. Estillore et al. (2017) reported a quite similar value of GF at 90% RH (1.24) for sucrose as ours using a different HTDMA with a much longer residence time (40s), similar as the one by Hodas et al. (2015) based on DASH-SP (Differential Aerosol Sizing and Hygroscopicity Spectrometer Probe) with a residence time of 4s. However, at intermediate RHs, our measured GF were much lower than theirs. Moreover, for glutamine and serine particles, no deliquescence was observed by Chan et al. (2005) even with a much longer residence time, while in our study a moderate water uptake for both compounds were observed. Using an STXM (Scanning Transmission X-ray Microscopy) with a residence time of 5-10 minutes, Piens et al. (2016) obtained a lower GF of fructose compared to ours, which should not be caused by the evaporation losses due to its low volatility. These aforementioned comparisons pointed out the influence of residence time on the observed water uptake of particles might not be conclusive. Therefore, other technical reasons should be raised for the measurement discrepancies between different instruments and studies using similar technique but different residence times should be suggested for understanding the effect from residence time on hygroscopicity."

In the previous section discussing the role of different physico-chemical properties of organics plays in aerosol hygroscopicity, the parameter κ was converted by the measured GF under 90 % RH. For those low or sparingly soluble organic compounds, the GF_derived κ (also known as apparent κ) is RH-dependent (see Fig. S3 as an example) and cannot express their intrinsic κ (expressed by fully dissolved compounds), when compounds are sufficiently soluble in water. As the RH increases, further dissolution of these organic compounds with promoted hygroscopicity is expected. In the real atmosphere, different RH conditions including both sub- and supersaturation can be reached. The measured GF or the apparent κ of ambient aerosols at a certain RH may not be able to reveal their real hygroscopicity under various atmospheric conditions. Further calculations of other variables, for instance the liquid water content (LWC), surface area of wet particles and number concentration of CCN associated with the apparent κ will be significantly biased. If possible, hygroscopicity measurements over large saturation range up to supersaturation, especially with the combination of CCN measurements provide an option to reduce the uncertainties, but requiring fast and stable scanning of RHs during the experiments. Technical improvement, for example in HTDMA system is essentially needed.

Data availability.

The details data can be obtained from the corresponding author upon request.

Supplement.

A detailed description of the HTDMA implementation, calibration of instrument by using ammonium sulfate, calculations for E-AIM and UManSysProp models, hygroscopicity parameter κ as a function of RH for sparingly soluble organics.

Author contributions.

SH contributed to investigation, data curation, visualization and writing original draft. JH and NM contributed to resources, writing review and editing. HBX contributed software, HBT, JCT, YQZ, LP, YH contributed to resources. QQW contributed to fund acquisition. JNS contributed to investigation. YFC, HS contributed to resources and fund acquisition.

Competing interests.

The authors declare no competing financial interest.

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References

Bilde, M., Svenningsson, B., Mønster, J., and Rosenørn, T.: Even− odd alternation of evaporation rates and vapor pressures of C3− C9 dicarboxylic acid aerosols, Environ. Sci. Technol., 37, 1371-1378, https://doi.org/10.1021/es0201810, 2003.

Cao, L.-M., Huang, X.-F., Wang, C., Zhu, Q., and He, L.-Y.: Characterization of submicron aerosol volatility in the regional atmosphere in southern China, Chemosphere, 236, 124383, https://doi.org/10.1016/j.chemosphere.2019.124383, 2019.

Cappa, C. D., Che, D. L., Kessler, S. H., Kroll, J. H., and Wilson, K. R.: Variations in organic aerosol optical and hygroscopic properties upon heterogeneous OH oxidation, J.Geophy.Res.Atmos., 116, https://doi.org/10.1029/2011JD015918, 2011.

Chan, M. N., Kreidenweis, S. M., and Chan, C. K.: Measurements of the hygroscopic and deliquescence properties of organic compounds of different solubilities in water and their relationship with cloud condensation nuclei activities, Environ. Sci. Technol., 42, 3602-3608, https://doi.org/10.1021/es7023252, 2008.

Chan, M. N., Choi, M. Y., Ng, N. L., and Chan, C. K.: Hygroscopicity of water-soluble organic compounds in atmospheric aerosols: Amino acids and biomass burning derived organic species, Environ. Sci. Technol., 39, 1555-1562, https://doi.org/10.1021/es049584l, 2005.

Chang, R.-W., Slowik, J., Shantz, N., Vlasenko, A., Liggio, J., Sjostedt, S., Leaitch, W., and Abbatt, J.: The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation, Atmos.Chem.Phys., 10, 5047-5064, https://doi.org/10.5194/acp-10-5047-2010, 2010.

Chebbi, A. and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, Atmos. Environ., 30, 4233-4249, https://doi.org/10.1016/1352-2310(96)00102-1, 1996.

Chen, J., Lee, W.-C., Itoh, M., and Kuwata, M.: A significant portion of water-soluble organic matter in fresh biomass burning particles does not contribute to hygroscopic growth: an application of polarity segregation by 1-Octanol–water partitioning method, Environ. Sci. Technol., 53, 10034-10042, https://doi.org/10.1021/acs.est.9b01696, 2019.

Cheng, Y., Wiedensohler, A., Eichler, H., Heintzenberg, J., Tesche, M., Ansmann, A., Wendisch, M., Su, H., Althausen, D., and Herrmann, H.: Relative humidity dependence of aerosol optical properties and direct radiative forcing in the surface boundary layer at Xinken in Pearl River Delta of China: An observation based numerical study, Atmos. Environ., 42, 6373-6397, https://doi.org/10.1016/j.atmosenv.2008.04.009, 2008.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H+− NH4+− Na+− SO42-− NO3-− Cl-− H2O at 298.15 K, J. Phys. Chem. A, 102, 2155-2171, https://doi.org/10.1021/jp973043j, 1998.

Darr, J. P., Gottuso, S., Alfarra, M., Birge, D., Ferris, K., Woods, D., Morales, P., Grove, M., Mitts, W. K., and Mendoza-Lopez, E.: The Hydropathy Scale as a Gauge of Hygroscopicity in Sub-Micron Sodium Chloride-Amino Acid Aerosols, J. Phys. Chem. A, 122, 8062-8070, https://doi.org/10.1021/acs.jpca.8b07119, 2018.

Deng, Y., Kagami, S., Ogawa, S., Kawana, K., Nakayama, T., Kubodera, R., Adachi, K., Hussein, T., Miyazaki, Y., and Mochida, M.: Hygroscopicity of Organic Aerosols and Their Contributions to CCN Concentrations Over a Midlatitude Forest in Japan, J.Geophy.Res.Atmos., 123, 9703-9723, https://doi.org/10.1029/2017JD027292, 2018.

Duplissy, J., Gysel, M., Sjogren, S., Meyer, N., Good, N., Kammermann, L., Michaud, V., Weigel, R., Martins dos Santos, S., and Gruening, C.: Intercomparison study of six HTDMAs: results and recommendations, Atmos. Meas. Tech, 2, 363-378, https://doi.org/10.5194/amt-2-363-2009, 2009.

Estillore, A. D., Morris, H. S., Or, V. W., Lee, H. D., Alves, M. R., Marciano, M. A., Laskina, O., Qin, Z., Tivanski, A. V., and Grassian, V. H.: Linking hygroscopicity and the surface microstructure of model inorganic salts, simple and complex carbohydrates, and authentic sea spray aerosol particles, PCCP, 19, 21101-21111, DOI:10.1039/C7CP04051B, 2017.

Fredenslund, A., Jones, R. L., and Prausnitz, J. M.: Group-contribution estimation of activity coefficients in nonideal liquid mixtures, AlChE J., 21, 1086-1099, https://doi.org/10.1002/aic.690210607, 1975.

Frosch, M., Zardini, A. A., Platt, S., Müller, L., Reinnig, M.-C., Hoffmann, T., and Bilde, M.: Thermodynamic properties and cloud droplet activation of a series of oxo-acids, Atmospheric Chemistry & Physics Discussions, 10, https://doi.org/10.5194/acp-10-5873-2010, 2010.

Giebl, H., Berner, A., Reischl, G., Puxbaum, H., Kasper-Giebl, A., and Hitzenberger, R.: CCN activation of oxalic and malonic acid test aerosols with the University of Vienna cloud condensation nuclei counter, J. Aerosol Sci, 33, 1623-1634, https://doi.org/10.1016/S0021-8502(02)00115-5, 2002.

Hansen, H. K., Rasmussen, P., Fredenslund, A., Schiller, M., and Gmehling, J.: Vapor-liquid equilibria by UNIFAC group contribution. 5. Revision and extension, Industrial & Engineering Chemistry Research, 30, 2352-2355, https://doi.org/10.1021/ie00058a017, 1991.

Hartz, K. E. H., Tischuk, J. E., Chan, M. N., Chan, C. K., Donahue, N. M., and Pandis, S. N.: Cloud condensation nuclei activation of limited solubility organic aerosol, Atmos. Environ., 40, 605-617, https://doi.org/10.1016/j.atmosenv.2005.09.076, 2006.

Hodas, N., Zuend, A., Mui, W., Flagan, R., and Seinfeld, J.: Influence of particle-phase state on the hygroscopic behavior of mixed organic-inorganic aerosols, Atmos.Chem.Phys., 15, 5027-5045, https://doi.org/10.5194/acp-15-5027-2015, 2015.

Hong, J., Kim, J., Nieminen, T., Duplissy, J., Ehn, M., Äijälä, M., Hao, L., Nie, W., Sarnela, N., and Prisle, N.: Relating the hygroscopic properties of submicron aerosol to both gas-and particle-phase chemical composition in a boreal forest environment, Atmos.Chem.Phys., 15, 11999-12009, https://doi.org/10.5194/acp-15-11999-2015, 2015.

Hong, J., Xu, H., Tan, H., Yin, C., Hao, L., Li, F., Cai, M., Deng, X., Wang, N., and Su, H.: Mixing state and particle hygroscopicity of organic-dominated aerosols over the Pearl River Delta region in China, Atmos.Chem.Phys., 18, 14079-14094, https://doi.org/10.5194/acp-18-14079-2018, 2018.

Jimenez, J. L., Canagaratna, M., Donahue, N., Prevot, A., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., and Ng, N.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525-1529, DOI: 10.1126/science.1180353, 2009.

Jing, B., Tong, S., Liu, Q., Li, K., Wang, W., Zhang, Y., and Ge, M.: Hygroscopic behavior of multicomponent organic aerosols and their internal mixtures with ammonium sulfate, Atmos.Chem.Phys., 16, 4101-4118, https://doi.org/10.5194/acp-16-4101-2016, 2016.

Kier, L. B.: Quantitation of solvent polarity based on molecular structure, J. Pharm. Sci., 70, 930-933, https://doi.org/10.1002/jps.2600700825, 1981.

Koehler, K., Kreidenweis, S., DeMott, P., Prenni, A., Carrico, C., Ervens, B., and Feingold, G.: Water activity and activation diameters from hygroscopicity data-Part II: Application to organic species, Atmos.Chem.Phys., 6, 795-809, https://doi.org/10.5194/acp-6-795-2006, 2006.

Kuang, Y., Xu, W., Tao, J., Ma, N., Zhao, C., and Shao, M.: A Review on Laboratory Studies and Field Measurements of Atmospheric Organic Aerosol Hygroscopicity and Its Parameterization Based on Oxidation Levels, Curr. Pollut. Rep., 6, 410-424, https://doi.org/10.1007/s40726-020-00164-2, 2020.

Kundu, S., Kawamura, K., Andreae, T., Hoffer, A., and Andreae, M.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, Atmos.Chem.Phys., 10, 2209-2225, https://doi.org/10.5194/acp-10-2209-2010, 2010.

Kuwata, M., Shao, W., Lebouteiller, R., and Martin, S.: Classifying organic materials by oxygen-to-carbon elemental ratio to predict the activation regime of Cloud Condensation Nuclei (CCN), Atmos.Chem.Phys., 13, https://doi.org/10.5194/acp-13-5309-2013, 2013.

Lambe, A., Onasch, T., Massoli, P., Croasdale, D., Wright, J., Ahern, A., Williams, L., Worsnop, D., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), Atmos.Chem.Phys., 11, https://doi.org/10.5194/acp-11-8913-2011, 2011.

Lei, T., Zuend, A., Wang, W., Zhang, Y., and Ge, M.: Hygroscopicity of organic compounds from biomass burning and their influence on the water uptake of mixed organic ammonium sulfate aerosols, Atmos. Chem. Phys, 14, 11165-11183, https://doi.org/10.5194/acp-14-11165-2014, 2014.

Lei, T., Zuend, A., Cheng, Y., Su, H., Wang, W., and Ge, M.: Hygroscopicity of organic surrogate compounds from biomass burning and their effect on the efflorescence of ammonium sulfate in mixed aerosol particles, Atmos.Chem.Phys., 18, 1045, https://doi.org/10.5194/acp-18-1045-2018, 2018.

Li, J., Liu, Z., Gao, W., Tang, G., Hu, B., Ma, Z., and Wang, Y.: Insight into the formation and evolution of secondary organic aerosol in the megacity of Beijing, China, Atmos. Environ., 220, 117070, https://doi.org/10.1016/j.atmosenv.2019.117070, 2020.

Luo, Q., Hong, J., Xu, H., Han, S., Tan, H., Wang, Q., Tao, J., Ma, N., Cheng, Y., and Su, H.: Hygroscopicity of amino acids and their effect on the water uptake of ammonium sulfate in the mixed aerosol particles, Sci. Total Environ., 139318, https://doi.org/10.1016/j.scitotenv.2020.139318, 2020.

Marcolli, C. and Peter, T.: Water activity in polyol/water systems: new UNIFAC parameterization, 5, 1545–1555, https://doi.org/10.5194/acp-5-1545-2005, 2005.

Marsh, A., Miles, R. E., Rovelli, G., Cowling, A. G., Nandy, L., Dutcher, C. S., and Reid, J. P.: Influence of organic compound functionality on aerosol hygroscopicity: dicarboxylic acids, alkyl-substituents, sugars and amino acids, Atmos.Chem.Phys., 17, 5583, https://doi.org/10.5194/acp-17-5583-2017, 2017.

Martău, G. A., Coman, V., and Vodnar, D. C.: Recent advances in the biotechnological production of erythritol and mannitol, Crit. Rev. Biotechnol., 1-15, https://doi.org/10.1080/07388551.2020.1751057, 2020.

Massoli, P., Lambe, A., Ahern, A., Williams, L., Ehn, M., Mikkilä, J., Canagaratna, M., Brune, W., Onasch, T., and Jayne, J.: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles, Geophys. Res. Lett., 37, https://doi.org/10.1029/2010GL045258, 2010.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., and Lohmann, U.: The effect of physical and chemical aerosol properties on warm cloud droplet activation, Atmos.Chem.Phys., 6, 2593-2649, https://doi.org/10.5194/acp-6-2593-2006, 2006.

Mei, F., Hayes, P. L., Ortega, A., Taylor, J. W., Allan, J. D., Gilman, J., Kuster, W., de Gouw, J., Jimenez, J. L., and Wang, J.: Droplet activation properties of organic aerosols observed at an urban site during CalNex-LA, J.Geophy.Res.Atmos., 118, 2903-2917, https://doi.org/10.1002/jgrd.50285, 2013.

Mikhailov, E., Vlasenko, S., Niessner, R., and Pöschl, U.: Interaction of aerosol particles composed of protein and saltswith water vapor: hygroscopic growth and microstructural rearrangement, Atmos. Chem. Phys., 4, 323–350, https://doi.org/10.5194/acp-4-323-2004, 2004.

Mikhailov, E., Vlasenko, S., Martin, S., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos.Chem.Phys., 9, 9491–9522, https://doi.org/10.5194/acp-9-9491-2009, 2009.

Mochida, M., Kawabata, A., Kawamura, K., Hatsushika, H., and Yamazaki, K.: Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, J.Geophy.Res.Atmos., 108, https://doi.org/10.1029/2002JD002355, 2003.

Mochida, M. and Kawamura, K.: Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles, J. Geophys. Res.-Atmos., 109, D21202, https://doi.org/10.1029/2004jd004962, 2004.

Nakao, S., Suda, S., Camp, M., Petters, M., and Kreidenweis, S.: Droplet activation of wet particles: development of the Wet CCN approach, Atmos. Meas. Tech., 7, 2227-2241, https://doi.org/10.5194/amt-7-2227-2014, 2014.

Nakao, S.: Why would apparent κ linearly change with O/C? Assessing the role of volatility, solubility, and surface activity of organic aerosols, Aerosol Sci. Technol., 51, 1377-1388, https://doi.org/10.1080/02786826.2017.1352082, 2017.

Ng, N., Canagaratna, M., Zhang, Q., Jimenez, J., Tian, J., Ulbrich, I., Kroll, J., Docherty, K., Chhabra, P., and Bahreini, R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos.Chem.Phys., 10, 4625-4641, https://doi.org/10.5194/acp-10-4625-2010, 2010.

Ohrem, H. L., Schornick, E., Kalivoda, A., and Ognibene, R.: Why is mannitol becoming more and more popular as a pharmaceutical excipient in solid dosage forms?, Pharm. Dev. Technol., 19, 257-262, https://doi.org/10.3109/10837450.2013.775154, 2014.

Ohm, P. B., Asato, C., Wexler, A. S., and Dutcher, C. S.: Isotherm-Based Thermodynamic Model for Electrolyte and Nonelectrolyte Solutions Incorporating Long-and Short-Range Electrostatic Interactions, J. Phys. Chem. A, 119, 3244-3252, https://doi.org/10.1021/jp512646k, 2015.

Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, Environ. Sci. Technol., 35, 4495-4501, https://doi.org/10.1021/es0107531, 2001.

Petters, M. and Kreidenweis, S.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, https://doi.org/10.5194/acp-7-1961-2007, 2007.

Petters, M., Kreidenweis, S., Prenni, A., Sullivan, R., Carrico, C., Koehler, K. A., and Ziemann, P.: Role of molecular size in cloud droplet activation, Geophys. Res. Lett., 36, https://doi.org/10.1029/2009GL040131, 2009.

Petters, S. S., Pagonis, D., Claflin, M. S., Levin, E. J., Petters, M. D., Ziemann, P. J., and Kreidenweis, S. M.: Hygroscopicity of organic compounds as a function of carbon chain length and carboxyl, hydroperoxy, and carbonyl functional groups, J. Phys. Chem. A, 121, 5164-5174, https://doi.org/10.1021/acs.jpca.7b04114, 2017.

Piens, D. S., Kelly, S. T., Harder, T. H., Petters, M. D., O'Brien, R. E., Wang, B., Teske, K., Dowell, P., Laskin, A., and Gilles, M. K.: Measuring mass-based hygroscopicity of atmospheric particles through in situ imaging, Environ. Sci. Technol., 50, 5172-5180, https://doi.org/10.1021/acs.est.6b00793, 2016.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., DeMott, P. J., and Ziemann, P. J.: Cloud droplet activation of secondary organic aerosol, J.Geophy.Res.Atmos., 112, https://doi.org/10.1029/2006JD007963, 2007.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y.: The effects of low molecular weight dicarboxylic acids on cloud formation, J. Phys. Chem. A, 105, 11240-11248, https://doi.org/10.1021/jp012427d, 2001.

Randall, D. A., Wood, R. A., Bony, S., Colman, R., Fichefet, T., Fyfe, J., Kattsov, V., Pitman, A., Shukla, J., and Srinivasan, J.: Climate models and their evaluation, in: Climate change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the IPCC (FAR), Cambridge University Press, 589-662, 2007.

Rickards, A. M., Miles, R. E., Davies, J. F., Marshall, F. H., and Reid, J. P.: Measurements of the sensitivity of aerosol hygroscopicity and the κ parameter to the O/C ratio, J. Phys. Chem. A, 117, 14120-14131, https://doi.org/10.1021/jp407991n, 2013.

Rosenørn, T., Kiss, G., and Bilde, M.: Cloud droplet activation of saccharides and levoglucosan particles, Atmos. Environ., 40, 1794-1802, https://doi.org/10.1016/j.atmosenv.2005.11.024, 2006.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons, Inc., New York, 2016.

Su, H., Rose, D., Cheng, Y., Gunthe, S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M., and Pöschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol particle mixing state with regard to hygroscopic growth and CCN activation, Atmos.Chem.Phys., 10, 7489-7503, https://doi.org/10.5194/acp-10-7489-2010, 2010.

Suda, S. R. and Petters, M. D.: Accurate determination of aerosol activity coefficients at relative humidities up to 99% using the hygroscopicity tandem differential mobility analyzer technique, Aerosol Sci. Technol., 47, 991-1000, https://doi.org/10.1080/02786826.2013.807906, 2013.

Suda, S. R., Petters, M., Matsunaga, A., Sullivan, R., Ziemann, P., and Kreidenweis, S.: Hygroscopicity frequency distributions of secondary organic aerosols, J.Geophy.Res.Atmos., 117, https://doi.org/10.1029/2011JD016823, 2012.

Suda, S. R., Petters, M. D., Yeh, G. K., Strollo, C., Matsunaga, A., Faulhaber, A., Ziemann, P. J., Prenni, A. J., Carrico, C. M., and Sullivan, R. C.: Influence of functional groups on organic aerosol cloud condensation nucleus activity, Environ. Sci. Technol., 48, 10182-10190, https://doi.org/10.1021/es502147y, 2014.

Swietlicki, E., Hansson, H. C., Hämeri, K., Svenningsson, B., Massling, A., McFiggans, G., McMurry, P. H., Petäjä, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments – a review, Tellus B, 60, 432–469, https://doi.org/10.1111/j.1600-0889.2008.00350.x, 2008.

Tan, H. B., Xu, H. B., Wan, Q. L., Li, F., Deng, X. J., Chan, P. W., Xia, D., and Yin, Y.: Design and Application of an Unattended Multifunctional H-TDMA System, Journal of Atmospheric and Oceanic Technology, 30, 1136-1148, 10.1175/Jtech-D-12-00129.1, https://doi.org/10.1175/JTECH-D-12-00129.1, 2013.

Tang, M., Chan, C. K., Li, Y. J., Su, H., Ma, Q., Wu, Z., Zhang, G., Wang, Z., Ge, M., and Hu, M.: A review of experimental techniques for aerosol hygroscopicity studies, Atmos.Chem.Phys., 19, 12631-12686, https://doi.org/10.5194/acp-19-12631-2019, 2019.

Topping, D., Barley, M., Bane, M. K., Higham, N., Aumont, B., Dingle, N., and McFiggans, G.: UManSysProp v1. 0: an online and open-source facility for molecular property prediction and atmospheric aerosol calculations, Geoscientific Model Development, 9, 899-914, https://doi.org/10.5194/gmd-9-899-2016, 2016.

Wang, J., Shilling, J. E., Liu, J., Zelenyuk, A., Bell, D. M., Petters, M. D., Thalman, R., Mei, F., Zaveri, R. A., and Zheng, G.: Cloud droplet activation of secondary organic aerosol is mainly controlled by molecular weight, not water solubility, Atmos.Chem.Phys., 19, 941-954, https://doi.org/10.5194/acp-19-941-2019, 2019.

Wang, Z., Jing, B., Shi, X., Tong, S., Wang, W., and Ge, M.: Importance of water-soluble organic acid on the hygroscopicity of nitrate, Atmos. Environ., 190, 65-73, https://doi.org/10.1016/j.atmosenv.2018.07.010, 2018.

Wang, Z., Su, H., Wang, X., Ma, N., Wiedensohler, A., Pöschl, U., and Cheng, Y.: Scanning supersaturation condensation particle counter applied as a nano-CCN counter for size-resolved analysis of the hygroscopicity and chemical composition of nanoparticles, Atmospheric Measurement Techniques, 8, 2161-2172, https://doi.org/10.5194/amt-8-2161-2015, 2015.

Wexler, A. S.: Atmospheric aerosol models for systems including the ions H+, NH4+, Na+, SO42−, NO3−, Cl−, Br−, and H2O, J. Geophys. Res., 107, https://doi.org/10.1029/2001JD000451, 2002.

Wise, M. E., Surratt, J. D., Curtis, D. B., Shilling, J. E., and Tolbert, M. A.: Hygroscopic growth of ammonium sulfate/dicarboxylic acids, J.Geophy.Res.Atmos., 108, https://doi.org/10.1029/2003JD003775, 2003.

Wu, Z., Nowak, A., Poulain, L., Herrmann, H., and Wiedensohler, A.: Hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their influence on the water uptake of ammonium sulfate, Atmos.Chem.Phys., 11, 12617-12626, https://doi.org/10.5194/acp-11-12617-2011, 2011.

Wu, Z., Zheng, J., Shang, D., Du, Z., Wu, Y., Zeng, L., Wiedensohler, A., and Hu, M.: Particle hygroscopicity and its link to chemical composition in the urban atmosphere of Beijing, China, during summertime, Atmos.Chem.Phys., 16, 1123-1138, https://doi.org/10.5194/acp-16-1123-2016, 2016.

Wu, Z., Poulain, L., Henning, S., Dieckmann, K., Birmili, W., Merkel, M., Pinxteren, D. v., Spindler, G., Müller, K., and Stratmann, F.: Relating particle hygroscopicity and CCN activity to chemical composition during the HCCT-2010 field campaign, Atmos.Chem.Phys., 13, 7983-7996, https://doi.org/10.5194/acp-13-7983-2013, 2013.

Xu, J., Shi, J., Zhang, Q., Ge, X., Canonaco, F., Prévôt, A. S., Vonwiller, M., Szidat, S., Ge, J., and Ma, J.: Wintertime organic and inorganic aerosols in Lanzhou, China: sources, processes, and comparison with the results during summer, Atmos.Chem.Phys., 16, 14937-14957, https://doi.org/10.5194/acp-16-14937-2016, 2016.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, Atmos.Chem.Phys., 15, 7307-7336, https://doi.org/10.5194/acp-15-7307-2015, 2015.

Zhang, Q., Jimenez, J. L., Canagaratna, M., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M., Takami, A., Middlebrook, A., and Sun, Y.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, https://doi.org/10.1029/2007GL029979, 2007.

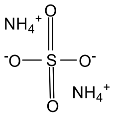
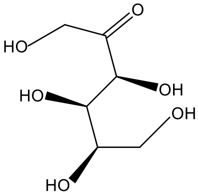
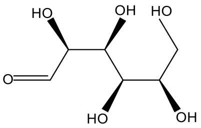
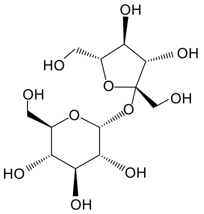
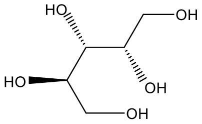
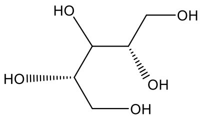
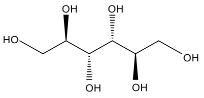
Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.: Formation of urban fine particulate matter, Chem. Rev., 115, 3803-3855, https://doi.org/10.1021/acs.chemrev.5b00067, 2015.

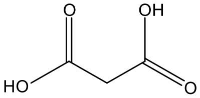
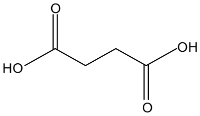
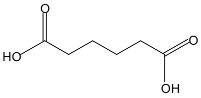
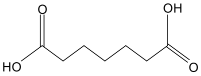
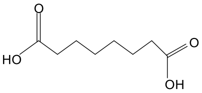
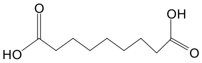
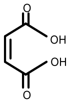
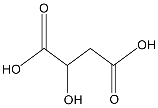
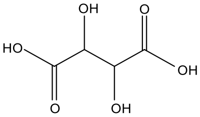
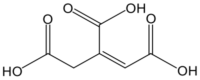
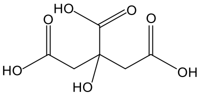
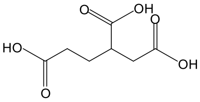
Zheng, G., Duan, F., Su, H., Ma, Y., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., and Chang, D.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmos.Chem.Phys., 15, 2969-2983, https://doi.org/10.5194/acp-15-2969-2015, 2015.

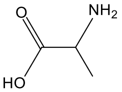
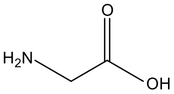
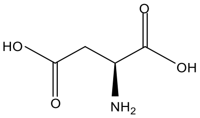
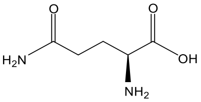
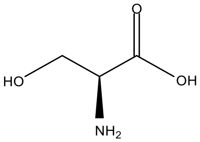
Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients, Atmos.Chem.Phys., 8, 4559-4593, https://doi.org/10.5194/acp-8-4559-2008, 2008.

Zuend, A., Marcolli, C., Booth, A., Lienhard, D. M., Soonsin, V., Krieger, U., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, Atmos.Chem.Phys., 11, 9155-9206, https://doi.org/10.5194/acp-11-9155-2011, 2011.

Table 1. Substances and their relevant properties investigated in this study.

Compounds	Molecular structure	Chemical formula	Molar weight (g mol^{-1})	Density (g cm^{-3})	O/C	Solubility (g ml^{-1})	Supplier, purity
Ammonium sulfate		$(NH_4)_2SO_4$	132.14^a	1.77^a	-	0.77^a	Macklin, 99.99%
Sugars							
D(-)-fructose		$C_6H_{12}O_6$	180.16^a	1.59^a	1	3.75^a	Sigma Aldrich, ≥99%
D(+)-mannose		$C_6H_{12}O_6$	180.16^a	1.54^a	1	2.48^a	Sigma Aldrich, ≥99%
Sucrose		$C_{12}H_{22}O_{11}$	342.30^a	1.58^a	0.9	2.1^b	Sigma Aldrich, 99%
Sugar alcohols							
Xylitol		$C_5H_{12}O_5$	152.15^a	1.52^a	1	0.642^b	Sigma Aldrich, ≥99%
L-(-)-arabitol		$C_5H_{12}O_5$	152.15^a	1.15^a	1	0.664^d	Sigma Aldrich, ≥98%
D-mannitol		$C_6H_{14}O_6$	182.17^a	1.52^a	1	0.216^b	Sigma Aldrich, ≥99.0%

Carboxylic acids							
Malonic acid		$C_3H_4O_4$	104.06^{a}	1.62^{a}	1.33	0.763^{b}	Sigma Aldrich, 98%
Succinic acid		$C_4H_6O_4$	118.09^{a}	1.19^{a}	1	0.0832^{b}	Sigma Aldrich, ≥99.0%
Adipic acid		$C_6H_{10}O_4$	146.14^{a}	1.36^{a}	0.67	0.03^{b}	Sigma Aldrich, 99%
Pimelic acid		$C_7H_{12}O_4$	160.17^{a}	1.33^{a}	0.57	0.05^{b}	Yuanye Bio-Technology, 98%
Suberic acid		$C_8H_{14}O_4$	174.19^{a}	1.30^{a}	0.5	0.0006^{a}	Yuanye Bio-Technology, 99%
Azelaic acid		$C_9H_{16}O_4$	188.22^{a}	1.03^{a}	0.44	0.0024^{a}	Yuanye Bio-Technology, 98%
Maleic acid		$C_4H_4O_4$	116.07^{a}	1.59^{a}	1	0.79^{a}	Aladding, ≥99.0%
DL-malic acid		$C_4H_6O_5$	134.09^{a}	1.61^{a}	1.25	0.592^{b}	Sigma Aldrich, ≥99%
Tartaric acid		$C_4H_6O_6$	150.09^{a}	1.79^{b}	1.5	1.43^{e}	CATO, 99.7%
cis-Aconitic acid		$C_6H_6O_6$	174.11^{a}	1.66^{a}	1	0.4^{d}	Sigma Aldrich, ≥98%
Citric acid		$C_6H_8O_7$	192.12^{a}	1.54^{a}	1.17	0.383^{b}	Sigma Aldrich, ≥99.5%
Butane-1,2,4-tricarboxylic acid		$C_7H_{10}O_6$	190.15^{a}	1.48^{a}	0.86	0.3897^{c}	Bidepharm, 97%
Amino acids							

DL-alanine		$C_3H_7NO_2$	89.09[a]	1.42[a]	0.67	0.164[b]	Macklin, 99%
Glycine		$C_2H_5NO_2$	75.07[a]	1.59[a]	1	0.25[a]	Sigma Aldrich, ≥99.0%
L-aspartic		$C_4H_7NO_4$	133.10[a]	1.66[a]	1	0.005[a]	Sigma Aldrich, ≥99%
L-glutamine		$C_5H_{10}N_2O_3$	146.14[a]	1.47[a]	0.6	0.0413[b]	Sigma Aldrich, ≥99.5%
L-serine		$C_3H_7NO_3$	105.09[a]	1.60[a]	1	0.425[b]	Sigma Aldrich, ≥99%

[a] https://www.chemicalbook.com/ [b] https://pubchem.ncbi.nlm.nih.gov/ [c] https://www.chemspider.com/

[d] https://hmdb.ca/ [e] Peng et al. (2001)

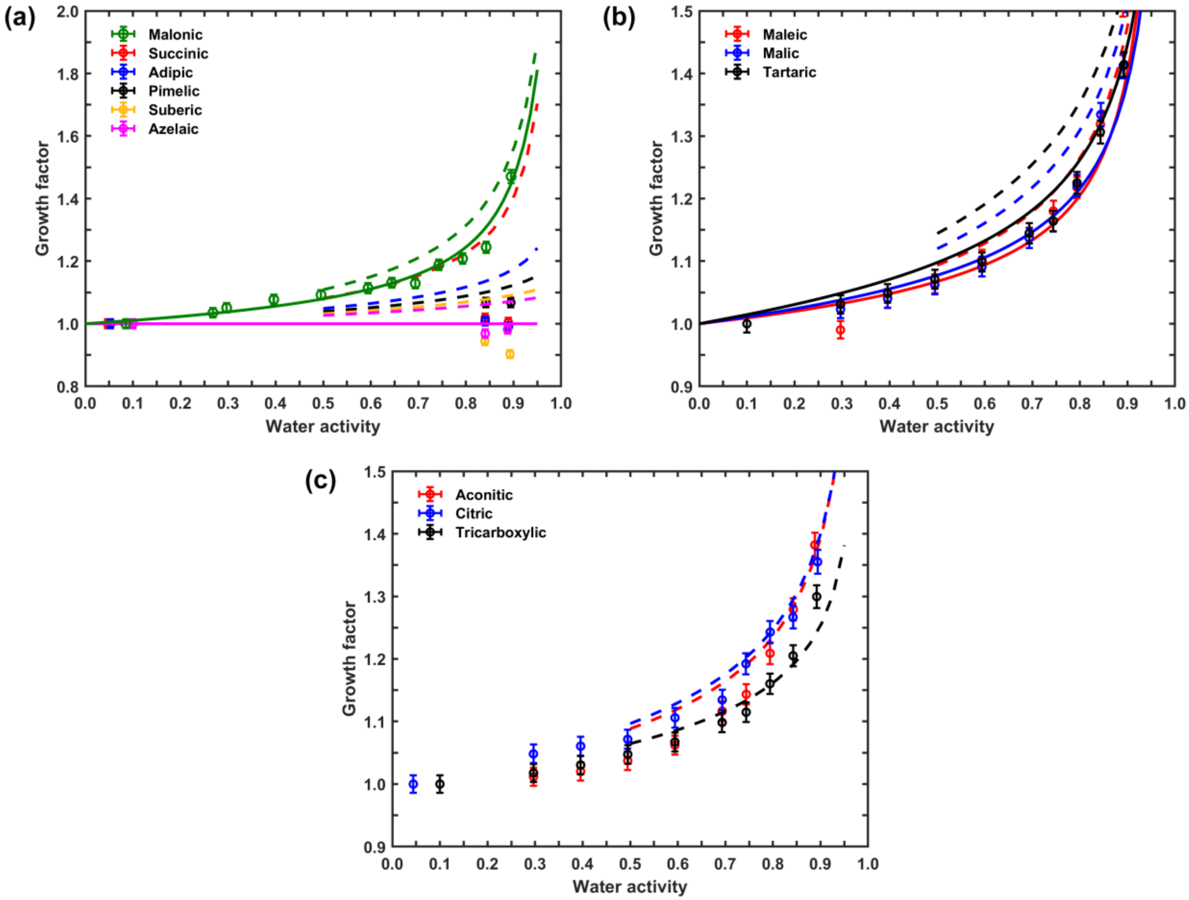


Figure 1: Hygroscopic growth curves of straight-chain dicarboxylic acids (a), dicarboxylic acids with substitutions (b) and tricarboxylic acids (c) particles (200 nm). Points represent the measurement data; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines show the UManSysProp calculated predictions.

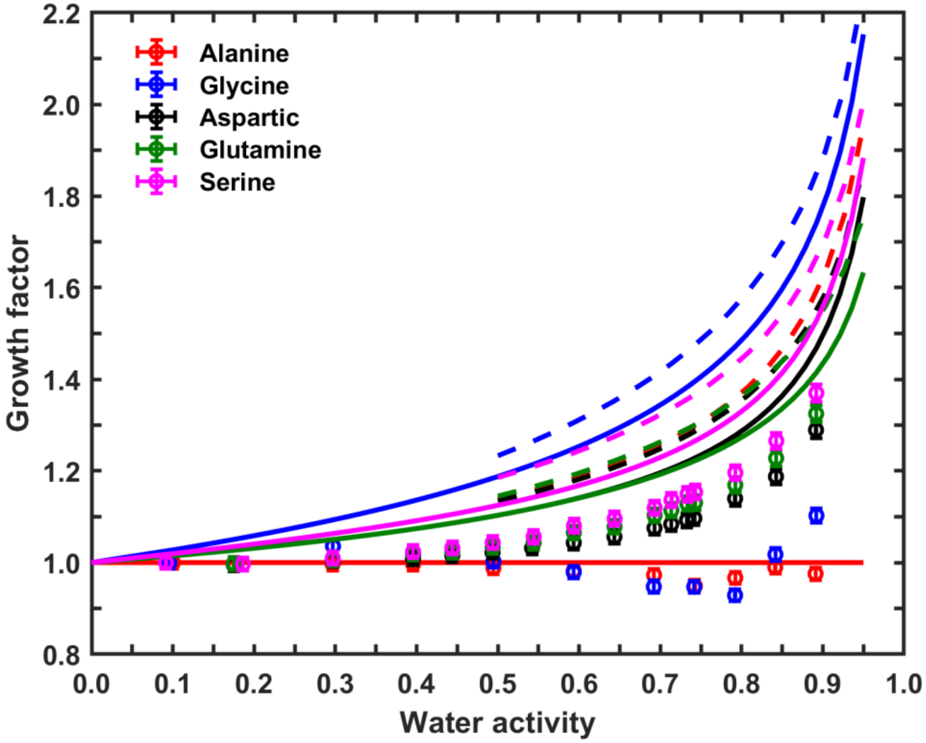


Figure 2. Hygroscopic growth factors of amino acids. Points represent the measurement values; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines represent the UManSysProp predictions.

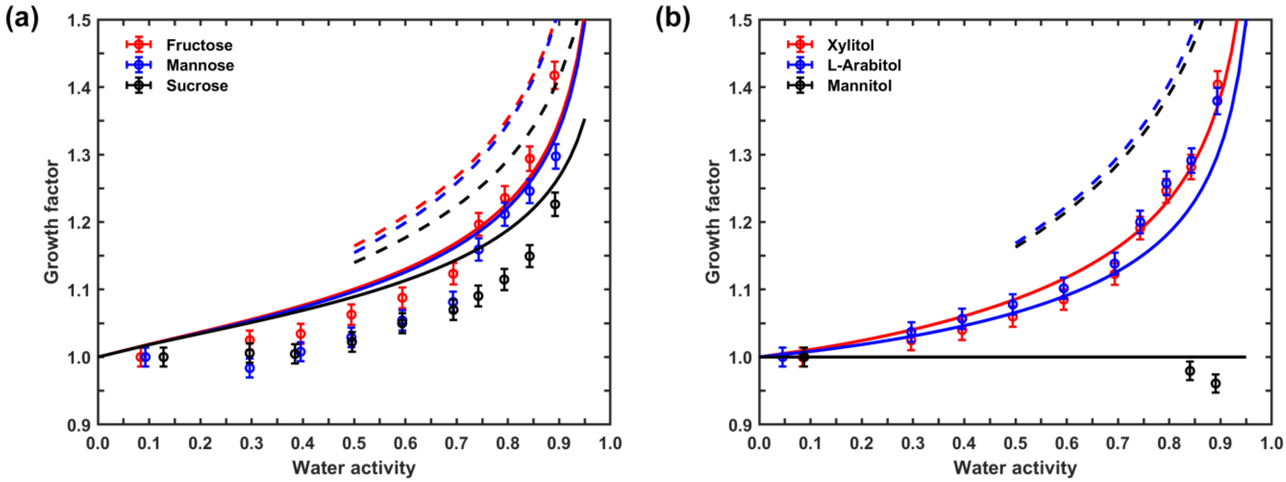


Figure 3. Hygroscopic growth curves of sugars (a) and alcohols (b). Points represent the measurement values; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines represent the UManSysProp calculated predictions.

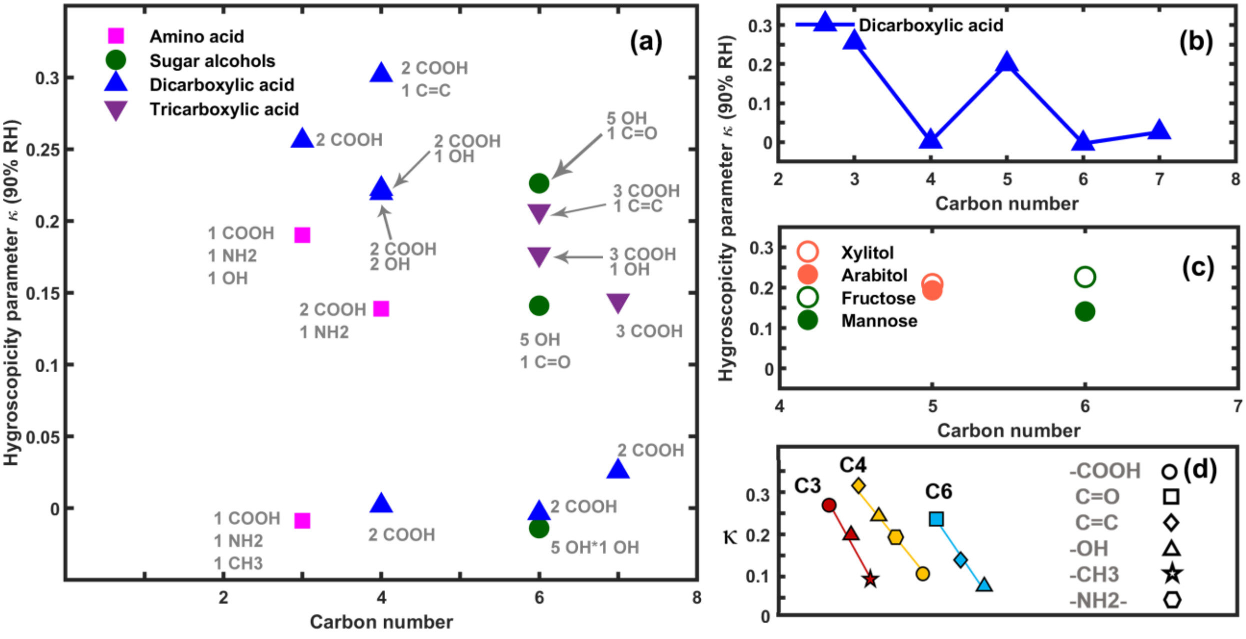


Figure 4. Hygroscopicity of organics as a function of carbon number (a); hygroscopicity of dicarboxylic acids vs carbon number (b); hygroscopicity of isomers (c); organic hygroscopicity as a function of their functionality with the same carbon number (d).

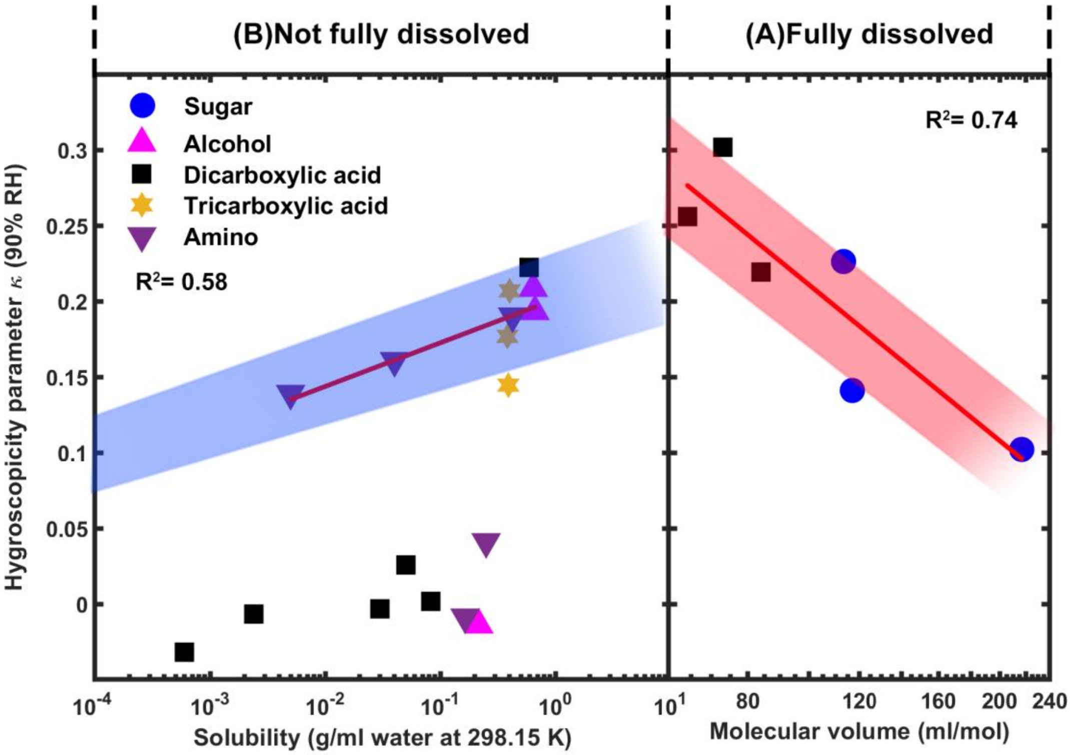


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Figure 5. Hygroscopicity of organic compounds as a function of molecular volume (A) and solubility (B).

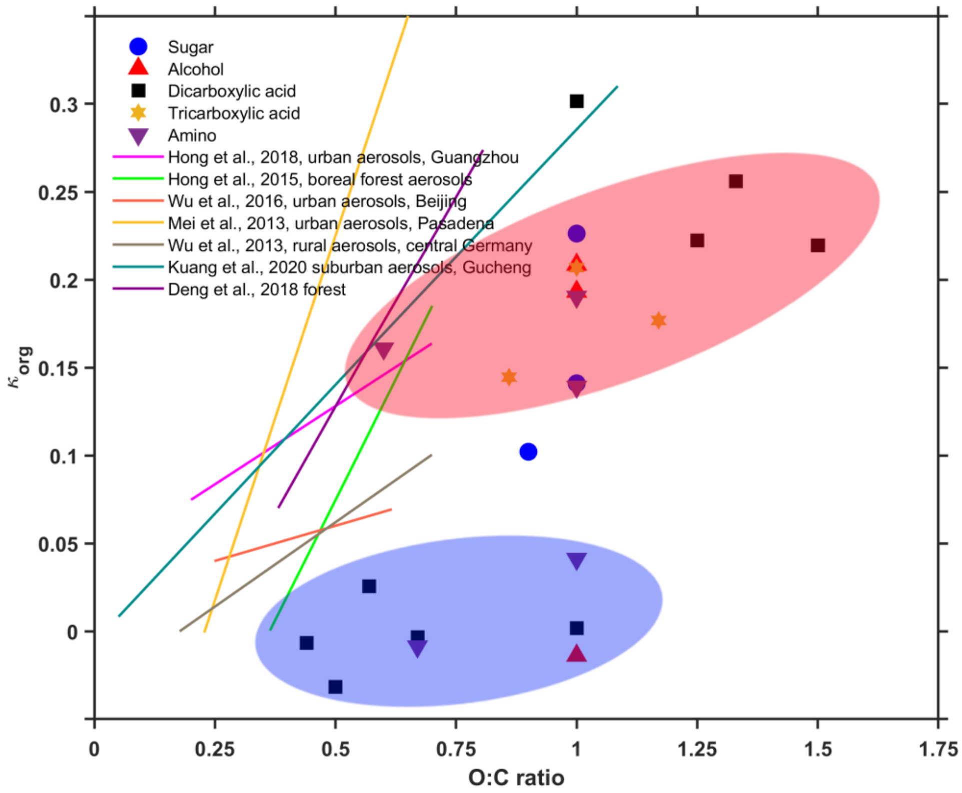

Figure 6. Correlation between O:C ratio and κ_{org}, and comparison with previous literature results. Blue and red shades represent the fitting of results of non-hygroscopic and more hygroscopic organics, respectively.