



## RESEARCH LETTER

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## Key Points:

- CCN activity (hygroscopicity parameter  $\kappa$ ) of SOA decreased with particle size
- The degree of oxidation of SOA decreased with particle size
- Neglecting size-dependent  $\kappa$  can significantly affect predicted CCN concentration

## Supporting Information:

- Texts S1–S4, Figures S1–S4, and Tables S1–S9
- Data Set S1
- Data Set S2

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**Abstract** Secondary organic aerosol components (SOA) contribute significantly to the activation of cloud condensation nuclei (CCN) in the atmosphere. The CCN activity of internally mixed submicron SOA particles is often parameterized assuming a size-independent single-hygroscopicity parameter  $\kappa$ . In the experiments done in a large atmospheric reactor (SAPHIR, Simulation of Atmospheric PHotochemistry In a large Reaction chamber, Jülich), we consistently observed size-dependent  $\kappa$  and particle composition for SOA from different precursors in the size range of 50 nm–200 nm. Smaller particles had higher  $\kappa$  and a higher degree of oxidation, although all particles were formed from the same reaction mixture. Since decreasing volatility and increasing hygroscopicity often covary with the degree of oxidation, the size dependence of composition and hence of CCN activity can be understood by enrichment of higher oxygenated, low-volatility hygroscopic compounds in smaller particles. Neglecting the size dependence of  $\kappa$  can lead to significant bias in the prediction of the activated fraction of particles during cloud formation.

## 1. Introduction

Secondary organic aerosol (SOA), formed by gas-to-particle conversion, is an important class of aerosols which impacts air quality and climate change [Hallquist et al., 2009; Jimenez et al., 2009; Kanakidou et al., 2005; von Schneidmesser et al., 2015; Zhang et al., 2011]. A significant fraction (20–90%) of atmospheric aerosol in the submicrometer size range consists of organic components, mainly of secondary origin [Jimenez et al., 2009]. SOA can absorb or scatter light [Laskin et al., 2015; Moise et al., 2015] and acts as cloud condensation nuclei (CCN) [Farmer et al., 2015]. The latter has been demonstrated by several laboratory studies for various biogenic and anthropogenic precursors [Alfarra et al., 2013; Asa-Awuku et al., 2009; Duplissy et al., 2008; Engelhart et al., 2008, 2011; Frosch et al., 2011; Hartz et al., 2006; Juranyi et al., 2009; King et al., 2009; Kreidenweis et al., 2006; Lambe et al., 2011a, 2011b; Massoli et al., 2010; Petters et al., 2009; Prenni et al., 2007; VanReken et al., 2005; Wex et al., 2009]. Therefore, SOA can affect climate by modifying the Earth's radiative budget and influencing cloud properties [Intergovernmental Panel on Climate Change, 2013].

The CCN activation of aerosol particles depends on their size (diameter) and their chemical composition [Andreae and Rosenfeld, 2008; Farmer et al., 2015]. For a given composition, larger particles more readily activate at a given supersaturation. Particles larger than 200 nm normally act as CCN at common atmospheric supersaturation conditions (0.1–1%) regardless of the chemical composition [McFiggans et al., 2006; Quinn et al., 2008; Wallace and Hobbs, 2006]. For particles smaller than 200 nm, chemical composition determines whether particles of a given size act as CCN at a given supersaturation.

In order to parameterize the relationship between the dry particle diameter and CCN activity, a  $\kappa$ -Köhler theory with single hygroscopicity parameter  $\kappa$  was proposed by Petters and Kreidenweis [2007], which is useful when comparing the CCN activity of different compounds and can be conveniently incorporated in the model to predict the CCN concentration (cf. supporting information (SI) Text S4 for detailed equations of  $\kappa$ -Köhler theory). For particles with fixed chemical composition,  $\kappa$  is constant.

In the ambient atmosphere the chemical composition of particles often depends on particle size, which leads to size-dependent  $\kappa$ . Size dependence can arise from different sources (external mixing) or from different

fractions of various components such as sulfate, nitrate, chloride, and organics [Gunthe *et al.*, 2009, 2011; Levin *et al.*, 2014; Mei *et al.*, 2013; Wu *et al.*, 2013; Zábory *et al.*, 2015].

SOA itself may also have a size-dependent chemical composition and CCN activity, whereby the composition can vary gradually due to various processes in the SOA formation. For example, the Kelvin effect can result in size-dependent composition via the partitioning of compounds of different volatility between gas and particle phase [Winkler *et al.*, 2012]. Heterogeneous reaction [Kroll and Seinfeld, 2008] and irreversible uptake of low-volatility compounds [Ehn *et al.*, 2014; Riipinen *et al.*, 2011] may also affect the size dependence of composition due to the varying surface to volume ratio of particles at different sizes. However, a single hygroscopicity parameter  $\kappa$  and thus the CCN activity of SOA particles are typically used to represent the entire SOA population at all sizes.  $\kappa$  of laboratory-generated SOA is approximately 0.1 with a range of 0.01–0.2 depending the specific experimental conditions [Alfarra *et al.*, 2013; Duplissy *et al.*, 2008; Engelhart *et al.*, 2011; Juranyi *et al.*, 2009; Lambe *et al.*, 2011a; Massoli *et al.*, 2010; Pajunoja *et al.*, 2015; Petters and Kreidenweis, 2007; Prenni *et al.*, 2007; Tang *et al.*, 2012; Wex *et al.*, 2009, and references therein]. Here we present the first extended study of the size-dependent CCN activity ( $\kappa$ ) of SOA in relation to chemical composition. This size dependence has seldom been explicitly discussed in the literature and not been investigated in combination with the analysis of the size-resolved particle chemical composition, to the best of our knowledge, although many studies have conducted similar studies on the CCN activity of SOA.

We report on CCN activity of SOA particles generated from various common biogenic volatile organic compound (VOC) precursors (mainly terpenes) and anthropogenic VOC precursors (aromatics) in a large photochemical simulation reactor (SAPHIR, Simulation of Atmospheric PHotochemistry In a large Reaction chamber) under natural solar light conditions and from direct plant emissions in the Jülich Plant Atmosphere Chamber (JPAC). The size-dependent CCN activity is linked to the size-dependent chemical composition which is represented by the SOA degree of oxidation, determined by the fraction of the  $\text{CO}_2^+$  fragment in total organics ( $f_{44}$ ) [Aiken *et al.*, 2007, 2008; Heald *et al.*, 2010; Ng *et al.*, 2010].

## 2. Experimental

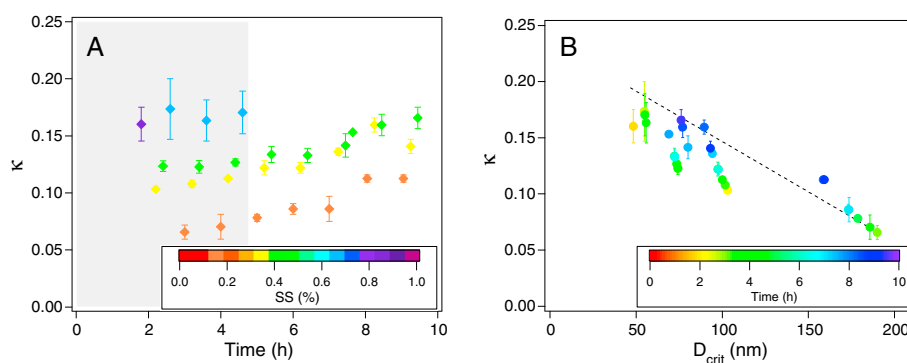
### 2.1. Experiment Setup and Instrumentation

The experiments were performed in the atmospheric simulation chamber SAPHIR, a 270 m<sup>3</sup> double-wall Teflon chamber of cylindrical shape at the Forschungszentrum Jülich, Germany (surface to volume ratio: 0.88 m<sup>-1</sup>). The chamber uses natural sunlight as light source. The details of the chamber are provided in previous studies [Bohn *et al.*, 2005; Rohrer *et al.*, 2005] and described in the SI (Text S1).

Various gas phase species (VOC, NO<sub>x</sub>, O<sub>3</sub>, and OH radical) and particle phase species and properties (size distribution, number concentration, and chemical composition) as well as chamber physical conditions were measured. The instrumentation details related to this study are described in previous papers [Zhao *et al.*, 2015a, 2015b].

Here we only briefly mention the particle measurements. The number size distribution was characterized using a scanning mobility particle sizer (SMPS). Additionally, the total number concentration was measured using a condensation particle counter (CPC). The composition of particles was characterized by a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). For measurement details and data processing procedure we refer to Zhao *et al.* [2015a]). From the AMS data,  $f_{44}$  and  $f_{43}$ , the fraction of organics signal at  $m/z$  44 and  $m/z$  43 to the total organics were derived. The fraction  $f_{44}$  is a proxy for O/C, i.e., the degree of oxidation of SOA, which is widely used [Ng *et al.*, 2010]. Moreover,  $f_{44}$  is an indicator of carboxylic oxidation products, while  $f_{43}$  is an indicator of carbonylic oxidation products.

The CCN activation was measured by scanning the size of the particles and determining the condensation nuclei (CN) and CCN in parallel as described previously ("Scanning Mobility CCN Analysis" [Buchholz, 2010; Zhao *et al.*, 2010, 2015b]). Particles with diameters ( $D_p$ ) between 10 nm and 500 nm were studied. From the CCN data, the critical diameters ( $D_{\text{crit}}$ ) at various supersaturations (SS) were determined. The SS was calibrated using the theoretical SS versus  $D_{\text{crit}}$  data set of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles. The theoretical values by Rose *et al.* [2008] (OS1 data set, cf. Table S2) were used. The details of CCN measurement were further described in the SI (Text S2). According to the method in Petters and Kreidenweis [2007],  $\kappa$  was calculated.



**Figure 1.** (a) CCN activity ( $\kappa$ ) of SOA at different supersaturations (SS) from ozonolysis and subsequent photooxidation of  $\alpha$ -pinene (experiment #1). Reaction started at time zero when ozone was added. The shaded area corresponds to the dark period. The calculated  $\kappa$  were different for different supersaturations, corresponding to different critical dry diameter ( $D_{crit}$ ), implying thus that the particle composition was size dependent. (b)  $\kappa$  as function of critical dry diameter. The color indicates the time since the beginning of the reaction. The smaller is  $D_{crit}$ ; the larger is the  $\kappa$  in the same period. The dash line is only for guiding the eyes. Note the lower SS (and narrower  $D_{crit}$  range) in the later period of the experiment because at higher SS values the particles grew to large sizes at which almost all particles activated at high SS.

## 2.2. Experiment Procedure

The experiment procedures for SOA studies in SAPHIR have been described in detail before [Emanuelsson et al., 2013; Flores et al., 2014; Zhao et al., 2015a]. Various VOC and their mixtures including biogenic and anthropogenic VOC such as  $\alpha$ -pinene, limonene, a mixture of  $\alpha$ -pinene/limonene (1:1, molar ratio), toluene, xylene, and mixtures of  $\alpha$ -pinene/limonene (1:1, molar ratio) with toluene or xylene were applied as SOA precursors. The experiments are summarized in Table S1. In a typical experiment, the VOC was added to the chamber and then the roof was open to induce the photooxidation and SOA formation. Experiments #1, 2, and 3 contained only biogenic VOC and experiments #4 and 5 contained only anthropogenic VOC. Experiments #6 and 7 contain the mixture of biogenic and anthropogenic VOC. In experiment #1, SOA was formed by the photooxidation and ozonolysis. In all other experiments, SOA was formed by photooxidation. In addition, in the experiment #3, SOA was formed from direct boreal tree emission in JPAC. The details of the JPAC chamber have been reported in previous studies [Mentel et al., 2009].

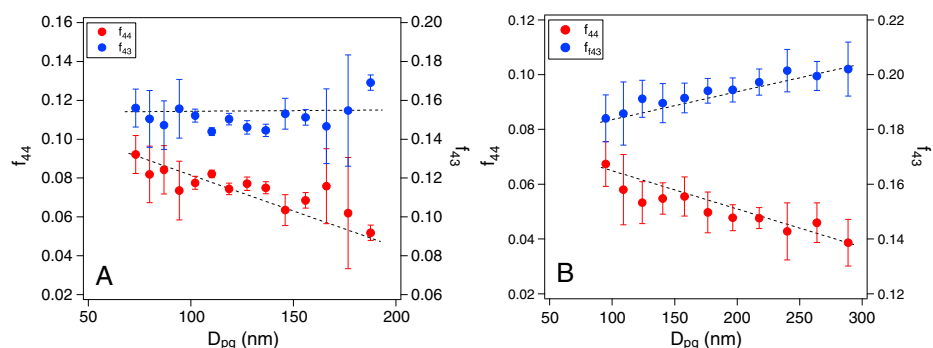
## 3. Results and Discussion

### 3.1. Dependence of the CCN Activity and Composition of SOA on Particle Size

Figure 1 shows the CCN activity of SOA formed by  $\alpha$ -pinene photooxidation (experiment #1), parameterized as hygroscopicity parameter  $\kappa$ .  $\kappa$  at a given time increased with increasing supersaturation (Figure 1a). Accordingly,  $\kappa$  decreased with increasing  $D_{crit}$  (Figure 1b) since  $D_{crit}$  corresponds to SS (also cf. Figure S1). At the same time,  $\kappa$  evolved in the experiment—generally increasing with chemical aging. Though, the  $\kappa$  value at 0.17% SS at 10 h was still lower than the value of  $\kappa$  at 0.67% SS at 2.6 h. The  $\kappa$  of SOA from  $\alpha$ -pinene in this study (0.07–0.17) is generally consistent with the  $\kappa$  values reported in the previous studies [Alfarra et al., 2013; Duplissy et al., 2008; Frosch et al., 2011; Juranyi et al., 2009; Lambe et al., 2011a; Massoli et al., 2010; Prenni et al., 2007; Wex et al., 2009] (also see Table S4).

The size dependence of  $\kappa$  is reflected in the composition of particles from  $\alpha$ -pinene photooxidation as can be seen from  $f_{44}$  and  $f_{43}$  as a function of size (Figure 2a) measured by the AMS operating in the pToF (particle time of flight) mode. The  $f_{44}$  decreased with increasing particle diameter in the range of 70–200 nm (geometric diameter derived from vacuum aerodynamic diameter using the density estimated from AMS and SMPS data [DeCarlo et al., 2004]), while  $f_{43}$  was invariant or slightly increased with particle size for larger particles. A 4 h average in the period with highest aerosol mass concentration ( $\sim 40 \mu\text{g m}^{-3}$ ) was used to derive the size-resolved  $f_{44}$  due to the low signal in the pToF mode.

Similar dependence of  $\kappa$  (and composition) on particle size was found for other SOA systems from various precursors such as boreal tree VOC emissions, a monoterpene mixture with  $\alpha$ -pinene/limonene (1:1, molar ratio), toluene, and a mixture of  $\alpha$ -pinene, limonene, and toluene (cf. Figure S2a–S2d). The size dependence of the



**Figure 2.**  $f_{44}$  and  $f_{43}$  of SOA from (a)  $\alpha$ -pinene photooxidation and (b) monoterpene ( $\alpha$ -pinene/limonene = 1, molar ratio) photooxidation as a function of particle size (geometric diameter ( $D_{pg}$ ), derived from vacuum aerodynamic diameter ( $D_{va}$ ) divided by particle density).  $f_{44}$  decreased with particle size, while  $f_{43}$  was largely invariant or increased with particle size. In Figure 2a,  $f_{44}$  is a 4 h average at a period with the highest mass concentration ( $\sim 40 \mu\text{g m}^{-3}$ ), and in Figure 2b,  $f_{44}$  is a 1 h average with the highest mass concentration ( $\sim 200 \mu\text{g m}^{-3}$ ). The dash lines are only for guiding the eyes.

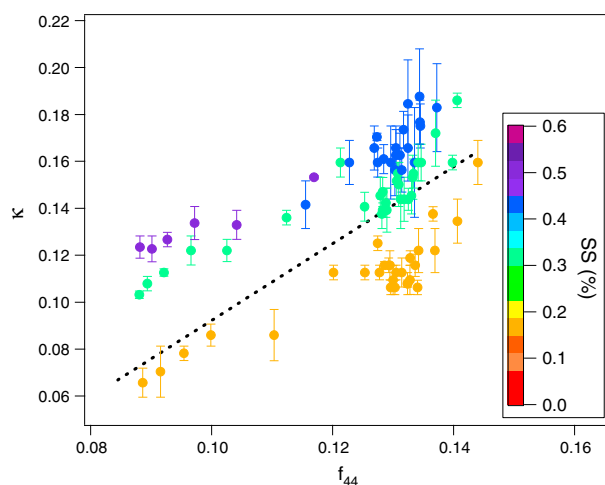
degree of oxidation was distinct for SOA from equal molar  $\alpha$ -pinene/limonene mixture oxidation with high particle loading (peak concentration  $\sim 200 \mu\text{g m}^{-3}$ , experiment #2) as shown in Figure 2b. Here  $f_{44}$  also showed a clear decrease with increasing particle size, while  $f_{43}$  showed a clear increase with increasing particle size. Similar dependence of  $f_{44}$  and  $f_{43}$  on particle size was observed for SOA from other reaction systems with high particle loadings such as SOA from photooxidation of the monoterpene and xylene mixture (Figure S3). Note that the size-resolved  $f_{44}$  and  $f_{43}$  was too noisy to get a reliable result in some experiments when the particle loading was low; therefore, high particle loadings were needed.

Smaller particles exhibited higher CCN activity and  $f_{44}$ . Higher  $f_{44}$  indicates that the organic components in the small particles had an overall higher degree of oxidation. An increase of  $f_{44}$  is typically the result of photochemical oxidation, which leads to the formation of more functionalized compounds with polar groups such as hydroxyl, carbonyl, carboxylic acid, and hydroperoxide group [Kroll and Seinfeld, 2008; Zhao *et al.*, 2015a], which increases  $\kappa$  [Duplissy *et al.*, 2008; Suda *et al.*, 2014; Topping *et al.*, 2005]. Oxygenated compounds with polar functional groups such as organic acids and carbonyl compounds were found in the filter samples of the SOA studied here (see also Table 3 in Emanuelsson *et al.* [2013]). And it is often found that  $\kappa$  correlates with the degree of oxidation ( $f_{44}$  or O/C [Alfarra *et al.*, 2013; Lambe *et al.*, 2011a; Massoli *et al.*, 2010]), although we showed that this relation strictly holds only within a single reaction system [Zhao *et al.*, 2015b]. Here we found that  $\kappa$  increased with increasing  $f_{44}$  of the whole SOA particles (Figure 3). Therefore, the higher  $\kappa$  of the smaller particles are in line with their higher  $f_{44}$ . Both findings suggest that smaller SOA particles contained overall more oxygenated compounds. Note that  $f_{44}$  or O/C is only a general measure of composition, and specific differences in the chemical composition on molecular level such as different functional groups may not be reflected in  $f_{44}$  or O/C. In other words, aerosols with the same  $f_{44}$  or O/C can still have a different molecular composition and thus different hygroscopicity [Suda *et al.*, 2014].

While different experimental systems show similar dependence of  $\kappa$  with size, the exact dependence of  $\kappa$  on size may be affected by specific VOC species and their concentration, and experimental conditions (cf. Figure S2). The dependence of  $\kappa$  with size is not necessarily linear although for simplicity we used a linear line to indicate a decreasing trend in Figure 1b. Such dependence of  $\kappa$  on size may also change dynamically as particles age since the exact effect of the aging on particles of different sizes may not be the same and particle size distribution often shifts in aging thus shifting the size dependence of  $\kappa$ .

### 3.2. Processes Causing Size-Dependent Chemical Composition and CCN Activity ( $\kappa$ )

The size dependence of particle chemical composition and  $\kappa$  observed here can be caused by various processes. First, it can be caused by the Kelvin effect. It is expected that in the photooxidation of VOC studied here, the chemical aging happened primarily in the gas phase [Donahue *et al.*, 2012] and the products partitioned between the particle phase and gas phase through condensation and evaporation. Due to the Kelvin effect, less oxygenated compounds with higher volatility are relatively depleted in smaller particles, while more oxygenated compounds with lower volatility are relatively enriched in the smaller particles. Therefore, the relative amount of more



**Figure 3.**  $\kappa$  of SOA from  $\alpha$ -pinene photooxidation as a function of  $f_{44}$  derived from AMS measurement.  $\kappa$  generally increased with  $f_{44}$  of the SOA. The dash line is for guiding the eyes.

oxygenated compounds with low volatility to less oxygenated compounds with high volatility and thus  $f_{44}$  in smaller particles should be enhanced (see Text S3).

Moreover, products of the different generations may contribute to the size-dependent chemical composition. The condensational flux of the low-volatility compounds is proportional to the surface area, and the smaller particles have a higher surface to volume ratio compared to the larger particles [D'Andrea *et al.*, 2013; Riipinen *et al.*, 2011; Zhang *et al.*, 2012]. Therefore, smaller particles incorporate over time a higher fraction of later generation products, which usually have higher degree of oxidation and higher  $f_{44}$ .

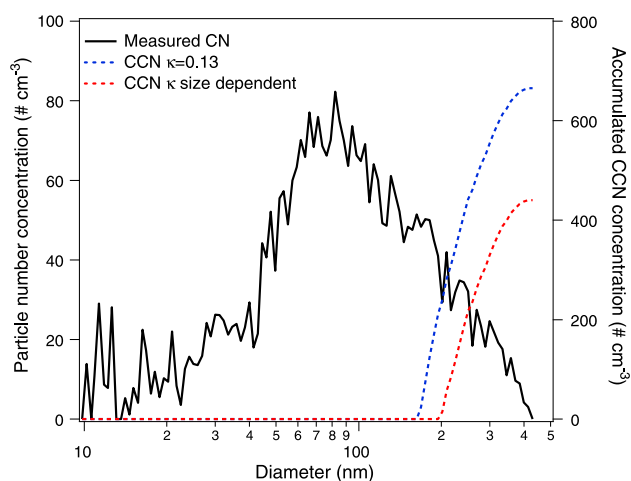
In addition, the heterogeneous oxidation of compounds on the particle surface or in the liquid phase driven by uptake of oxidants such as OH, HO<sub>2</sub>, or H<sub>2</sub>O<sub>2</sub> may also contribute to the size-dependent chemical composition [Kroll and Seinfeld, 2008]. Such a mechanism can result in the relative enrichment of the more oxygenated compounds in the smaller particles because of their higher surface to volume ratio.

All these processes suggest that smaller particles should contain relatively higher fraction of more oxygenated hygroscopic products, leading to higher CCN activity, even in homogeneous gas phase reaction systems.

The dependence of SOA composition on particle size has been observed in previous studies. Winkler *et al.* [2012] found a size-dependent chemical composition for the SOA from  $\alpha$ -pinene ozonolysis generated in a flow tube. They showed that 40 nm particles contained more carbonyl compounds while 10 and 20 nm particles contained more carboxylic acid compounds, in line with our study. The size dependence of  $\kappa$  for SOA can be traced in some previous studies for SOA from  $\alpha$ -pinene and  $\beta$ -caryophyllene [Frosch *et al.*, 2013, 2011; Tritscher *et al.*, 2011], although this dependence was not explicitly discussed. For example, Tritscher *et al.* [2011] found in some experiments that the  $\kappa$  values derived from hygroscopic growth measurements decreased with particle size for SOA from  $\alpha$ -pinene ozonolysis and subsequent photooxidation, consistent with the trend found in this study. Alfarra *et al.* [2013] showed that different particle size classes have different growth factors at 90% relative humidity for SOA from  $\alpha$ -pinene and myrcene photooxidation. Frosch *et al.* [2011] found that  $\kappa$  is lower for the largest particles for the SOA from  $\alpha$ -pinene ozonolysis and subsequent photochemical aging, which agrees with this study. However, this phenomenon was interpreted as being related to the slight dependence of  $\kappa$  on water activity, in general, and the dependence of water activity at activation on dry diameter [Frosch *et al.*, 2011].

In contrast, some previous studies reported different dependence or no dependence of  $\kappa$  on SS [Petters *et al.*, 2009; Prenni *et al.*, 2007; VanReken *et al.*, 2005]. The different findings in these studies are probably related to different experimental and oxidation conditions. In the studies by VanReken *et al.* [2005], Petters *et al.* [2009], and Prenni *et al.* [2007], SOA was formed from ozonolysis, while in the studies by us and Frosch *et al.* [2011] SOA was formed from photooxidation (include some ozonolysis). Ozonolysis and photooxidation can produce SOA of different composition and, e.g., different solubility. While the Kelvin effect affects particles formed by both ozonolysis and photooxidation, heterogeneous oxidation and the effects of higher generation products only occur for photooxidation involving OH radicals. The variety of experimental conditions applied mentioned above may lead to a variety of detailed size-dependent SOA composition, which makes the direct comparison of  $\kappa$  difficult. For example, if the SOA components have the limited solubility, this can cause an apparent decrease of  $\kappa$  with increasing SS (decreasing  $D_{crit}$ ) [Kreidenweis *et al.*, 2006; Petters *et al.*, 2009] even though  $\kappa$  increases with decreasing size. Moreover, in field studies the size-dependent composition and CCN activity in the sense described above can be masked by external mixing and is thus difficult to detect.





**Figure 4.** Modeled CCN concentration at 0.15% SS using constant  $\kappa$  and size-dependent  $\kappa$  for a typical ambient aerosol size distribution. The left axis shows the particle number concentration, and the right axis shows the modeled accumulated CCN concentration. Using size-dependent  $\kappa$  decreased the CCN concentration by approximately 50% here compared with a calculation that assumes a constant  $\kappa$  of 0.13. A linear dependence of  $\kappa$  between 0.18 and 0.07 on particle diameter was assumed in the range from 55 nm to 190 nm as obtained in the  $\alpha$ -pinene oxidation experiment (cf. Figure 1). The activation fraction was set 0, 0.5, and 1, respectively, if  $D_{\text{crit}}$  was below, within, and above a size bin. The aerosol size distribution (CN) was measured by a SMPS on board a Zeppelin airship in a rural area around San Pietro de Capofiume during the PEGASOS (Pan-European Gas-Aerosol-Climate Interaction Study) 2012 field campaign.

Other processes may also contribute to the dependence of  $\kappa$  on the supersaturation and thus on particle size as observed here. Deviation from ideality depends on the solute concentration, thus on the supersaturation, i.e., particle size as discussed by Frosch *et al.* [2013] and Juranyi *et al.* [2009]. If the surface tension would depend on the concentration of the solute thus on supersaturation, it could affect such dependence as  $\kappa$  was calculated here assuming the surface tension of water ( $0.072 \text{ N m}^{-1}$ ). However, the surface tension effect (Kelvin term) caused by surface active organics can be inherently counteracted by the decreased concentration of soluble molecules (Raoult term) in the bulk solution due to a significant partitioning of surface active organics into the surface layer [Prisle *et al.*, 2008; Sorjamaa *et al.*, 2004]. Because of such counteracting effects, it is plausible to derive  $\kappa$  using the surface tension of water and surface tension is unlikely to lead to the size-dependent  $\kappa$  as observed here, as shown by the studies investi-

gating the effects of surfactants on the CCN activation based on experimental and model analysis [Prisle *et al.*, 2008; Sorjamaa *et al.*, 2004].

The evaporation of organics inside the CCN column, resulting in shrinking of aerosol particles at high temperature difference (higher SS), could also cause different  $\kappa$  at different supersaturations [Asa-Awuku *et al.*, 2009; Tang *et al.*, 2014]. However, this would cause a lower  $\kappa$  at higher supersaturation due to more efficient evaporation at higher temperature used at higher supersaturation, which is opposite to the finding in this study.

Another process that may affect the size dependence of  $\kappa$  is the cocondensation of organic vapors under supersaturation conditions [Topping and McFiggans, 2012; Topping *et al.*, 2013]. However, this would also result in a lower  $\kappa$  at smaller size (higher supersaturation) due to the smaller droplet surface and volume as well as higher temperature at higher supersaturation.

#### 4. Conclusion and Implications

We investigated the size-dependent CCN activity of SOA from various precursors including both the biogenic and anthropogenic VOC and related it to size-dependent chemical composition. The CCN activity in a size range of 50 nm–200 nm, parameterized as  $\kappa$ , depended on particle size with higher  $\kappa$  at smaller particle sizes. This indicates that the smaller particles contained higher fraction of hygroscopic compounds. AMS analysis showed that the degree of oxidation decreased with increasing particle size. This suggests that smaller particles exhibited higher degree of oxidation and contained either higher oxygenated compounds or a larger fraction of oxygenated compounds. Both scenarios can explain the higher hygroscopicity of the small particles. The size-dependent chemical composition may result from multiple mechanisms, e.g., components on smaller particles had higher saturation vapor pressure due to the higher curvature (Kelvin effect), more effective heterogeneous oxidation driven by uptake of gas phase oxidants, and larger fraction of “aged” oxidation products. We cannot fully exclude that the inherent change of  $\kappa$  with solute concentration and dependence of surface tension on solute concentration may have also contributed to the observations.

In this study SOA is mainly formed by photooxidation at OH concentrations close to ambient (OH concentration: several  $10^6$  molecules  $\text{cm}^{-3}$ ) and relatively low VOC (several to several tens of parts per billion) and  $\text{O}_3$  concentrations (0–200 ppb). And the SAPHIR chamber has the minimal walls' effects due to the low surface to volume ratio. Therefore, this study represents daytime photooxidation under conditions close to ambient. Comparison of this study with other studies indicated that experimental and oxidation conditions may have significant effects on the particle chemical composition and its properties. Applying such conditions is important in order to better simulate the specific ambient processes and SOA formation.

Chemical composition is especially important for the size classes with  $D_p \approx D_{\text{crit}}$  for a given supersaturation. Size-dependent  $\kappa$  shifts the activation diameter, thus affecting the number of potential CCN compared to the common assumption of a constant  $\kappa$  over the entire size distribution. As an example, we used the size-dependent  $\kappa$  of SOA from  $\alpha$ -pinene oxidation (Figure 1) and applied it to a typical size distribution measured in a rural area of Europe during the Pan-European Gas-Aerosol-Climate Interaction Study (PEGASOS) 2012 campaign, assuming that all the particles were organic. Here approximately a 50% change in the CCN number concentration was obtained compared to the case of constant  $\kappa$  through all sizes (cf. Figure 4 for details). Our study clearly shows that the dependence of SOA chemical composition and  $\kappa$  on size should be considered to better model the CCN concentration of organic aerosol, especially for environments where the organic aerosol is the dominant aerosol component or externally mixed with other aerosols. Neglecting the dependence of  $\kappa$  on particle size may lead to significant biases in predicting the CCN concentration and thus the effect of aerosol on radiative forcing and climate. In the ambient atmosphere, the quantitative influence of the size dependence of  $\kappa$  on the CCN number concentration is affected by the SS, the aerosol size distribution, the  $\kappa$  and its dependence on particle size used, and the mixing state with other species. For example, if organic components are internally mixed with small amount of very hygroscopic inorganic compounds such as  $(\text{NH}_4)_2\text{SO}_4$ , the difference between the CCN number concentration for a constant  $\kappa$  case and for a size-dependent  $\kappa$  case becomes smaller ( $\sim 20\%$  at 10% of  $(\text{NH}_4)_2\text{SO}_4$ ). Moreover, other physicochemical properties of SOA are likely to also depend on the particle size based on the size-observed dependent chemical composition here and are worthwhile to be studied.

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